



Nanomaterials: Applications, waste-handling, environmental toxicities, and future challenges – A review

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ABSTRACT

Currently, nanotechnology is referred to be one of the attractive research sectors in several countries because of its vast potential and commercial impact. Nanotechnology includes the investigation, development, fabrication, and processing of structures and materials on a nanoscale in various fields of science, health care, agriculture, technology, and industries. As such, it has provided a steady restructuring of related technologies. However, the irregularities and uncertainties in dimensions and chemical compositions, makes the viability of such materials questionable. Concerns have been inclined about the transport, destiny, and transformation of nanomaterials discharged into the environment. A critical analysis of the present phase of knowledge concerning the exposure and effects of nanomaterials has been discussed in-depth. In this review, different nanomaterials along with their applications have also been reviewed, that include graphene-based nanomaterials, carbon nanotubes, and their composites, nanoclay composites, nanostructured thin films, metal-organic frameworks, conducting polymers and their composites, MXenes, chalcogenide nanocrystals, and quantum dots. Besides, a few of the ground-breaking applications of nanomaterials for different sectors like human health, processes, photochemical process, energy conversion and energy storage, separation and purification processes, optoelectronics, etc. are discussed in detail with their chemistry. Moreover, the unique characteristics and applications of nanomaterials, they inherently introduce challenges for their applications and large-scale production. Acknowledgment of the potential benefits and unknown dangers of nanomaterials is critically analyzed and discussed in the manuscript.

1. Introduction

The introduction of nanotechnology has revolutionized the impact of natural sciences and engineering. Nanotechnology deals in the development and application of materials of sizes less than 100 nm, which we call nanomaterials. The difference between nanomaterials and non-nanomaterials is the size i.e., ≤ 100 nm in 1D are referred to as a nanomaterial and > 100 nm in all dimensions are non-nanomaterials. Besides, nanomaterial cannot be seen by naked eyes, whereas non-nanomaterials are visible through a simple microscope. In contrast to

non-nanomaterials, nanomaterials display a higher surface/volume ratio which allows good performance and applies them to be used in various applications such as Nanosensors, nano-sorbents, and fuel cells. Furthermore, nanomaterials have shown higher adsorption capacity in both gas and liquid phases [1]. Nanomaterials due to their size, quantum effect, and extended surface are of versatile use. Other properties like physical, chemical, morphological, mechanical, thermal, optical, magnetic, and conductivity come through the selection, doping, and composition of different materials. Scientists and researchers have exploited the inherent, modified, and added characteristics of these

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nanomaterials to several fields of science, engineering, and technology. Some of the major technology sectors which are going through and shall benefit from the wonderful impact of nanomaterials are energy, medicine, environmental science, information technology, homeland security, food safety, and transportation [2].

These nanomaterials are synthesized through methods, depending upon the end-user property demand. Synthesis of nanomaterials has two major approaches, one is top-down, in which the size of larger molecules makes smaller to nanoscale and the other is a bottom-up approach, in which small molecules or atoms are combined to produce nanomaterials. These approaches involve several synthesis methods and four major categories like chemical, physical, mechanical, and biological. Generally, the top-down approach involves methods like high-energy ball milling, severe plastic deformation, etching, mechanical alloying, lithography, reactive milling, and micromachining methods. Whereas, bottom-up includes molecular self-assembly, sol-gel, electron (or ion) beams, metal-organic chemical vapor deposition, vacuum arc deposition, inert gas condensation, molecular beam epitaxy, electrodeposition, physical/chemical vapor deposition, and ultrasonic dispersion [3].

The subsection of this technology under most investigation include graphene-based nanomaterials, metal-organic frameworks, carbon nanotubes, and their composites, nanoclay composites, nanostructured thin films, conducting polymers and their composites, MXenes, chalcogenide nanocrystals, and quantum dots [4–6]. Graphene and its derivatives like reduced graphene oxide (rGO), graphene oxide (GO) consist of graphene nanosheets (GNS), few-layer-graphene (FLG), and ultrathin graphite come under the family of graphene. Graphene-based nanomaterials and composites may include any member of the graphene family. It is often functionalized with different atoms and molecules to get the desired characteristics for end-user applications. Some of the common functional groups are amine, nucleic acids, and proteins, metals, etc. [7]. CNTs stand for Carbon Nanotubes, are produced by carbon atoms with sizes in nanometer. The CNTs fundamentally come in three variations: Singular-walled CNTs (SWCNTs) and double-walled CNTs (DWCNTs) and multi-walled CNTs (MWCNTs). Single-walled carbon nanotubes (SWCNTs) are sliced off pieces of carbon atoms of a 2-D hexagonal lattice to form a hollow cylindrical shape [8]. Nanoclays are layered mineral silicates. Some of the common nanoclays are montmorillonite, kaolinite, bentonite, hectorite, halloysite, nacrite, antigorite, beidellite, illite, taeniolite, saponite, lizardite, talc, octosilicate, magadite, kenyaite, brucite, berlinite, etc. [9]. These have a phyllosilicate or sheet structure having a thickness of around 1 nm and come with weaker physical forces, for instance, interactions of van der Waal forces [9]. A nanostructured thin film is a layer of material whose thickness is in the nanometer. These films can be prepared from different materials and composites like CNTs, graphene-based materials, semiconducting metals and alloys, oxides, and several other combinations depending upon the end-user applications [10,11]. Metal-organic frameworks (MOFs) are much stronger as compared to other bonding like π - π stacking because they are porous materials that are synthesized through bridging of metal-ligand coordinate as well as highly crystalline material [12]. Conductive polymers are organic polymers which are also called intrinsically conducting polymers (ICPs). These materials can conduct electricity. MXenes are nitrides, carbides and carbonates are two-dimensional (2D) transition metals, which can be obtained by quaternary layered carbides, or ternary or nitrides chemical delamination [13]. Chalcogenide nanocrystals are semiconducting metal compounds, incorporated with group elements from II–VI and IV–VI. These compounds display band gap energies from near-infrared to visible and into ultraviolet regions [14]. Quantum dots (QDs) are nanosize semiconductor particles with optical and electronic properties involving quantum mechanics. These materials can be of silicon, cadmium sulfide, cadmium selenide, indium arsenide, carbon, graphene, etc. or in general made up of element groups from III to V or II to VI [15]. Among others, graphene and carbon based QDs are widely researched. Apart from diverse characteristics and applications, nanomaterials come with some

serious challenges like application limitations, desired property control, toxicities, environmental concerns, bulk material production, and their waste management recycling [16–19].

Apart from considerable progress in nanomaterials, data in terms of the possible effects of nanomaterials on human health and the environment is yet insufficient. Since nanomaterials typically are not visible after released into the environment, they may cause different kinds of environmental issues if a satisfactory remediation strategy is not planned [20]. The use of nanomaterials in different fields requires several concerns such as un-known ecological effects, fouling properties, regeneration, inadequate detection limits, environmental soundness and deposition, and high costs [21]. In this review, we focus on the adverse effects of nanomaterials on both human health and the environment. Also, provide an in-depth review of the different nanomaterials, particularly in terms of their fabrication approaches, and real-life applications. Furthermore, their current status and future challenges are also discussed, for instance, toxicities, and waste and recycling management.

2. Synthesis and characterization

Nanomaterials are synthesized through various methods such as vacuum deposition and vacuum vaporization, solution synthesis, chemical vapor deposition as well as chemical vapor condensation, gas condensation, combustion synthesis, physical vapor deposition, mechanical attrition, self-propagating high-temperature synthesis, chemical precipitation, sol-gel techniques, and electrodeposition, etc. [22–24]. In the vapor-phase synthesis of nanomaterials, the vapor phase mixture is thermodynamically unstable to that of the solid material to be prepared. This may also be called chemical supersaturation, where to produce condensed phase, thermodynamics favors the vapor phase to react chemically. On sufficient levels of supersaturation, condensation may allow particles to form nucleates [25]. The vapor deposition method is subdivided into chemical as well as physical vapor deposition techniques, which has further subcategories. chemical vapor deposition includes evaporation, condensation, chemical reaction, coalescence, deposition, coagulation, postprocessing takes place, whereas physical vapor deposition consists of sublimation, condensation, coalescence, postprocessing, coagulation, deposition, etc. [26]. Chemical vapor deposition also includes plasma-enhanced electron cyclotron resonance chemical vapor deposition, plasma assistant chemical vapor deposition, and chemical vapor deposition. Whereas, the deposition of physical vapor is subcategorized into vacuum arc deposition, ion beam deposition, magnetron sputtering Ion beam sputtering, pulsed laser deposition, electron beam deposition, and filtered arc deposition [27]. The formation of a colloidal suspension or a sol takes place in the sol-gel process through precursors reactions of the polymerization as well as hydrolysis, where the formation of transition from the liquid sol into a solid gel phase caused by the loss of solvent as well as complete polymerization [28,29]. Electrodeposition is favorable for nanomaterials produced for conduction purposes in catalysis and electrochemical reactions, where conducting nanomaterials are deposited on electrode surfaces [30]. In solution combustion, synthesis of nanomaterials in homogeneous solutions of different oxidizers and fuels takes place leading to the formation of nanomaterials [23].

Nano-metals and their synthesized composites are characterized by using Atomic Force Microscopy (AFM), X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Cyclic voltammetry (CV), Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS), Raman Spectroscopy, Ultraviolet–Visible Spectroscopy (UV–vis), High-Resolution TEM (HRTEM), Fourier-Transform Infrared Spectroscopy (FTIR), Electrochemical Impedance Spectroscopy for physical, chemical, morphological and electrochemical properties [31–33]. For the characterization of materials, Raman Spectroscopy is used as a non-destructive tool. The tool helps in determining the quality of synthesized materials in terms of structural

footprints leading to the identification of molecules. In the working principle, incident light from a sample is inelastically scattered and by the energy of its characteristic molecular vibrations, shifted in frequency [34]. Different versions of Raman spectroscopy have been used for several synthesized nanomaterials for size, shape, surface of the material, chemical properties, mechanical properties, optical properties [35, 36]. For graphene nanomaterials, Raman helps determine the number and quality of layers. Raman generates peaks at carbon atoms, in which D and G bands are more commonly disused, where first indicates the curved graphene nanosheets defects and disordered structures of turbostratic and later shows the photons propagating along with the graphitic structures [33]. TEM, HRTEM, SEM, and FESEM are popular electron microscopy tools for determining morphological characteristics of materials. Similarly, their applications are widely available for the characterization of nanomaterials. The electron microscope working principle is based on the application of energetic electrons as the source, which is focused on electromagnetic lenses [37]. 3D electron microscopy techniques have also been used for quantitative and qualitative measurements [38]. The optical transparency of nanomaterials is characterized by UV-vis by measuring the transmittance characteristics of the specimen [39]. XRD examines the atomic arrangement, crystallinity, imperfections, crystallite size, and material structure in other aspects [40]. FTIR confirms the linkages and functionalities of different materials. The thermal behavior of nanomaterials is investigated by using Thermogravimetric Analysis (TGA). Cyclic voltammetry and EIS deals with the electrochemical or conductive behavior of materials. Various characterization techniques are exhibited in Fig. 1.

Apart from the above-mentioned approaches for the synthesis of nanomaterials, there is a variety of other fabrication approaches also exist and employed. However, the essential thing to take into account in nanomaterial synthesis is to explore the optimum conditions to enhance the quantity and reproducibility. Table 1 has provided an overview of the different synthesis approaches for nanomaterials.

3. Graphene and its composites

Graphene consists of carbon atoms in a hexagonal array. Nanotechnology has diversified its applications and worth in the market due to its favorable electronic, thermal, optical, mechanical, morphological, transport, antimicrobial, fire, and heat retardation characteristics [75–81]. Broadly, graphene and its composites are produced through two major approaches, top-down and bottom-up methods. The top-down method includes cutting down the bigger carbon tree layer into smaller ones leading to graphene development. Hummers' method is one of the most commonly used methods which is top-down [82,83]. Whereas in the bottom-up method, the specific precursors cyclo-dehydrogenation, as well as surface-assisted polymerization, are used to produce graphene nanoribbons [84]. More specifically, graphene is synthesized through liquid-phase exfoliation, ball-milling exfoliation, mechanical exfoliation, thermal exfoliation, thermal decomposition on SiC and other substrates, graphene oxide (GO) chemical reduction, chemical vapor deposition (CVD), unzipping carbon nanotubes (CNTs), solvothermal synthesis, plasma-enhanced chemical vapor deposition (PECVD), electrochemical synthesis, calcination, irradiation of highly charged ions, epitaxial growth, etc. [32,40]. Nanoparticles are grown on graphene, reduced graphene oxide (rGO), and graphene oxide sheets or their derivatives to synthesize graphene nanoparticle composites. These are synthesized by attaching pre-made nanoparticles to the graphene surface or growing the nanoparticles on the graphene surface [85]. Among others, CVD has gained more reputation and familiarity in the synthesis of graphene and its composite nanomaterials [86].

Given a wide range of properties, graphene and its composites have gained applications in several sectors like energy storage, catalysis, medical and biomedical, sports, environment, drug delivery and tissue engineering, biosensors, strain sensors and nanomedicine, antibacterial applications, optical and optoelectronic applications, etc. [87–90]. Cheng et al. [91] reported that functional graphene nanomaterials (FGNs) can be used for drug/gene delivery, bio-imaging, phototherapy, interfacial bio-interactions, adsorption and concentration of nutrition

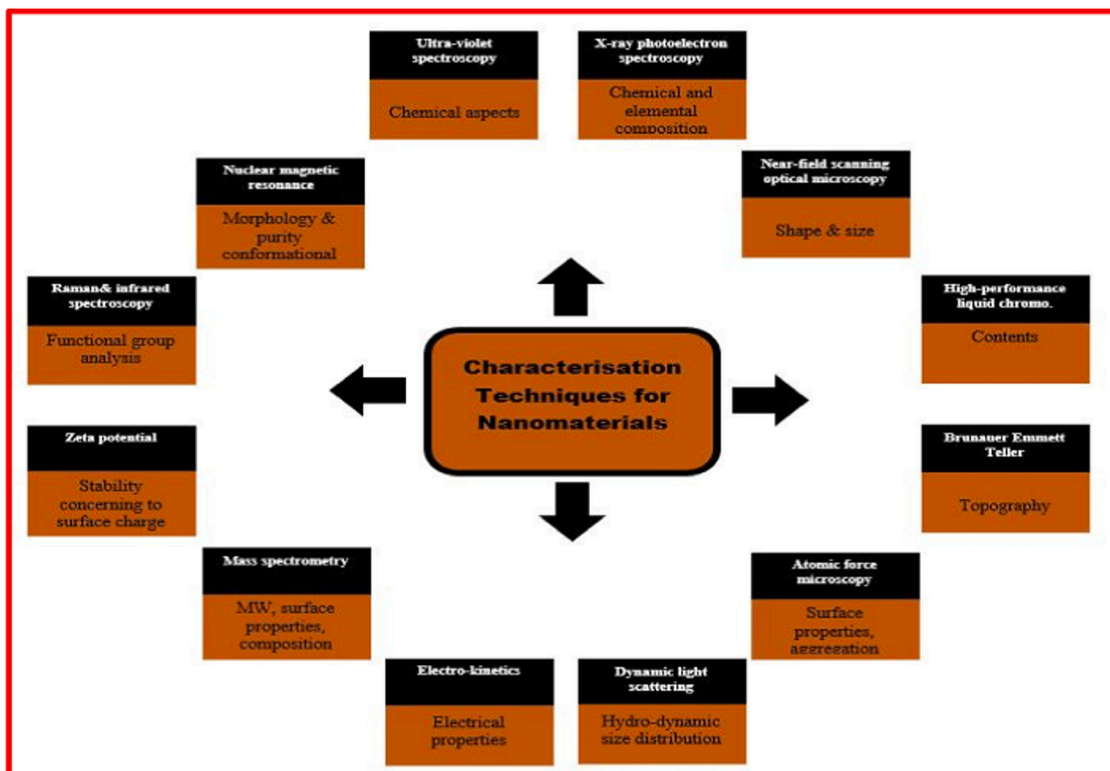


Fig. 1. Few of the known characterization techniques for nanomaterials.

Table 1

Various approaches for the synthesis of nanocomposites.

| Synthesis approach | Description | Advantages | Disadvantages | References |
|---------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| Mechanical milling | <ul style="list-style-type: none"> It was initially explored by John Benjamin and co-associates in 1960 at the International Nickel company. Also known as mechanical alloying, as it has the potential to produce a fine product in powdered form. Different kinds of mills have been developed for various objects such as attritor mills, tumbler mills, and vibratory mills | <ul style="list-style-type: none"> Potential to attain fine powder, range from 2 to 20 nm Appropriate approach for milling toxic materials. Suitable for continuous operation Initial cost is relatively low Wide-spectrum applications | <ul style="list-style-type: none"> Requires high consumption of energy to operate Display low efficiency Operate at strong vibration and noise Shape of nanomaterial produced is irregular | [41–43] |
| Physical vapor deposition | <ul style="list-style-type: none"> It defines as a variety of vacuum deposition techniques which can be employed to fabricate thin films and coatings The approach involves the following steps i.e. deposited material is converted into a vapor, the vapor is transferred to low pressure from its origin to the substrate, the vapor experiences condensation on the substrate to develop a thin film The primary categories of PVD are evaporation and sputtering | <ul style="list-style-type: none"> Eco-friendly approach Display good durability and strength Relatively safe approach in contrast to chemical vapor deposition | <ul style="list-style-type: none"> Operate at high temperature and vacuum Cooling system is must | [44,45] |
| Co-precipitation | <ul style="list-style-type: none"> One of the quoted approach in literature Mostly recommended for the fabrication of oxide, fluoride, and oxy-fluoride-based nanophosphorous The approach refers to attain a uniform composition via precipitation reaction. | <ul style="list-style-type: none"> Size and composition of the particle can be conveniently controlled Operate at low temperature Fast and simple preparation Different possibilities to enhance the surface | <ul style="list-style-type: none"> Not a time-saving approach Contaminants also precipitated with the product Not suitable for reactants with different precipitation rates Batch to batch reproducibility issues Do not have the capability to un-charged species | [46–48] |
| Inert gas condensation | <ul style="list-style-type: none"> This approach involves the vaporization of inorganic and metal materials through a vaporizing source in the existence of inert gas surrounding led via rapid condensation of the vaporized atoms of inorganic or metal material on a cold surface to produce nanoparticles Mostly employed for metallic nanocomposites and nanoparticles The approach consists of evaporation, sputtering or ablating Magnetron-sputtering, thermal-evaporation, and pulsed-laser-ablation are a few of the techniques that fall under this approach | <ul style="list-style-type: none"> Well-known and simplest approach Particle size can be maintained | <ul style="list-style-type: none"> Limited to lab-scale only Time-consuming approach Not a suitable approach for industrial applications | [49,50] |
| Microemulsion | <ul style="list-style-type: none"> The approach was explored 20 years ago for the fabrication of nanomaterials Generally, the microemulsion system is composed of polar (water), non-polar (oil) phase, and a surfactant. | <ul style="list-style-type: none"> Convenient approach Operate at room temperature Higher thermodynamic stability i.e. prolonged life Higher degree of particle size and composition can be maintained Develop nano-meter size particles with limited agglomeration | <ul style="list-style-type: none"> Required high content of surfactant and/or co-surfactant In terms of microemulsion stability, depends on various external factors such as pH and temperature Low solubilizing capacity for constituents with a high melting point | [51,52] |
| Hydrothermal | <ul style="list-style-type: none"> The approach is defined as an artificial route to fabricate nanomaterials The approach was introduced by Schafhautl in 1845 The fabrication of nanomaterials can occur in a broad temperature range i.e. room to extremely high temperature The use and application of microemulsion are substantial in both chemical and biological sectors, due to its extraordinary properties | <ul style="list-style-type: none"> Most of the material developed is soluble in proper solvent via heating and pressuring Size, shape, and crystallinity of the product can be easily maintained Substances with high vapor pressure and low melting point and that tend to go pyrolysis can be attained | <ul style="list-style-type: none"> Required costly autoclave Safety concerns during the reaction process Impossibility of detecting the reaction process | [53–55] |
| Sol-gel | <ul style="list-style-type: none"> It is known as the wet chemical approach, which uses chemical solution or colloidal particles to develop an integrated network i.e. gel The approach is useful for the production of functional materials such as photo-catalyst, metal nanoparticles, and superconductors | <ul style="list-style-type: none"> Initial materials are in the molecular phase, whereas, the prepared products are homogenous High purity product can be attained Different size of particles can be developed, conveniently Synthesis can be performed at low temperature Potential to prepare multi-component materials Manageable degree of porosity | <ul style="list-style-type: none"> Prolonged reaction time Organic solvent can be noxious to the human body | [56–58] |
| Sputtering | | | <ul style="list-style-type: none"> Lower sputtering rates | [59,60] |

(continued on next page)

Table 1 (continued)

| Synthesis approach | Description | Advantages | Disadvantages | References |
|---------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| | <ul style="list-style-type: none"> The approach is also referred to as sputtering deposition. In this approach, atoms in a solid-state are discharged and pass into the gas medium via bombardment with energetic ions, particularly noble gas ions. Direct current sputtering, radio frequency sputtering, and magnetron are a few of the known types of sputtering used for the development of nanomaterials | <ul style="list-style-type: none"> Versatile approach can be employed for all material types Properties of the product can be adjustable Permit the deposition of films holding a similar composition as the target source | <ul style="list-style-type: none"> Sputtering targets are usually costly To avoid poisoning the sputtering target, the gas composition should be controlled carefully | |
| Ultra-sound | <ul style="list-style-type: none"> The approach is already in the research field offering a controlling tool for developing nanomaterials. In past, the approach was mainly used in the medical and food sector for the emulsification and homogenization of biological substances | <ul style="list-style-type: none"> Prepared at ambient condition Ultra-sound reaction rate is high Time-saving approach Rapid and convenient approach Different shape and size of nanoparticles can be developed | <ul style="list-style-type: none"> Not suitable for heat-sensitive materials Known as an energy-intensive approach Difficult to scale-up Higher energy consumption | [61–63] |
| Electric arc deposition | <ul style="list-style-type: none"> In this approach, an electric arc is developed when extremely high electric field strength over normally non-conductive materials, for instance, gas, causes an electric breakdown of the material, which inclines the conductivity in the medium The method was initially used for CNT production by Iijima in 1991 | <ul style="list-style-type: none"> Simple in terms of apparatus building Low contaminants and high throughput Economical High yield Potential to be employed for various materials such as composites, nanoparticles, and microcrystals Eco-friendly | <ul style="list-style-type: none"> Use of noble gases and low pressure Mostly recommended for microparticles formation | [64,65] |
| Laser ablation | <ul style="list-style-type: none"> Since the 1980s, this approach has been widely used for the development of a range of nanomaterials The approach is also referred to as photo-ablation The development of nanomaterials through this approach can be performed either in liquid, or gas | <ul style="list-style-type: none"> Relatively more efficient due to the distribution and formation of plasma plume occurs in the liquid surrounding, as liquid display high thermal conductivity than gas Highly recommended for medical and food-related applications No use of noxious chemicals High purity product produced Single-stage process Potential to maintain the particle size and film porosity High purity | <ul style="list-style-type: none"> Low yield, therefore, restricted for industrial applications Need high energy laser to operate Not a cost-saving approach Ablation efficiency declines with long ablation time | [66–68] |
| Flame spray pyrolysis | <ul style="list-style-type: none"> Also named flame-assisted spray pyrolysis Referred to as thermal spray process which develops quality coating using heat to melt materials that are generally in ceramic, wire or powder form The fabrication of nanomaterials using flame spray pyrolysis is a fresher, but previously well-organized process in regards to product diversity. Vapor assisted flame spray pyrolysis, and flame aerosol spray pyrolysis are the types of flame spray pyrolysis | <ul style="list-style-type: none"> Potential to be employed for various materials Final product of high purity Capability to grow epitaxial films Deposit materials which are difficult to evaporate Suitable for scale-up production | <ul style="list-style-type: none"> Limited to laboratory Several health and safety issues are concerned The approach uses high exothermic liquid precursors; therefore, the flame temperature reaches up to 2800 K. | [69–71] |
| Chemical vapor deposition | <ul style="list-style-type: none"> It is suggested as the most appropriate approach for the development of nanomaterials The approach was introduced in the 19th century by J.M. Blocher The approach is employed in various formats such as low-pressure chemical vapor deposition, laser chemical vapor deposition, metal-organic chemical vapor deposition, photochemical vapor deposition, and ultra-high chemical vapor deposition. The approach comprises of two stages i.e. transportation of gas-medium materials into the chamber, and gas-medium reaction, and deposition of the product (nanomaterial) on the substrate. | | <ul style="list-style-type: none"> Operate at higher temperature i.e. 300–900°C Tough to mask surface Size is dependent on the chamber capacity Approach is not simple and convenient Use of corrosive and toxic gases | [72–74] |

factors, cell colonization, improving cellular signaling, and biological performance. For example, bovine albumin is adsorbed on GO for proteins, or through hydrogen bonding, π - π stacking, and hydrophobic interaction, blood protein is adsorbed on rGO to improve the compatibility of cell and to reduce the interaction of cell membrane [92,93]. Graphene, its derivatives, and composites have been used for several purposes in energy conversion as well as energy storage. Graphene Nanomaterials have demonstrated superior electrochemical performances. Their results for lithium-ion batteries, metal-air as well as metal-sulfur batteries, and electrochemical capacitors have proved to be superior performance [94]. Graphene-based aerogels synthesized from biomass have been found to provide sustainable energy with higher power density than conventional sources, which not only serve the

energy purpose but also can mitigate environmental pollution [95]. Due to its high carrier mobility, Nano-optoelectronic devices greatly improve the performance on the use of graphene and by combining the graphene with other nanomaterials as well as changing the shape of a graphene structure, photoelectric response in conventional semiconductor optoelectronic devices can be improved [96]. Nanomaterials based on 3D hierarchical porous graphene (hpG) have shown higher porosities, favorable mass/electron transport, exceptional energy conversion storage characteristics, and versatile functionalization [97]. Due to interconnected porosity as well as high surface areas, 3D hpGs can be doped through heteroatoms which can provide high-performance graphene layers, guest components, and porous scaffolds [98]. Different application ranges of graphene-based nanomaterials and their composites are

depicted in Fig. 2.

4. Carbon nanotubes and their composites

Thin-walled carbon nanotubes are one of the hallmarks discovery and development of nanoscience [105]. These materials are also considered “Buckytubes” because of their similarity with the fullerene family. They are carbon molecules, dominantly framed in a cylindrical shape. Their morphological properties and the shape itself make them revolutionary synthetic materials in many applications such as optics, sensors, and nanoelectronics. CNTs show incredible material strength and stability as well as unique thermal stability, high electric conductance, and mechanical properties [106]. Carbon-carbon sp^2 hybridization exhibit various unique structures. A widely known example is Graphite. But unlike that, carbon molecules can also form closed and open cages with honeycomb structure. Graphene is derived from carbon which is a 2D single layer of graphite in the family of nanomaterials. Because of the sp^2 hybridization, Graphene has stronger material properties than diamonds. When C-atoms form graphite, they undergo sp^2 hybridization. One S-orbital and two P-orbitals combine at 120° . This bond is called the sigma bond [107]. Sigma (σ) bond binds the atoms in the plane, which is a strong covalent bond, contributing to the CNT's high mechanical strength. The remaining π -orbital remains perpendicular to σ -bonds plain. These orbitals contribute to the interlayer interaction within the tubular structure, resulting in π -bonds [108]. This interlayer interaction is considerably weaker and contains less energy than the sigma bonds. Carbon nanotubes have a fullerene-like structure and having graphene sheets that contain sp^2 hybridization of each carbon atom [109]. Because of a very high weight-to-structural strength ratio, CNTs are produced in thin layers of graphene, as if they are cast on

a round cylinder, which is why their final form is cylindrical with seamless carbon bonds interconnected with each other in a repetitive hexagonal lattice. This is also what provides them an aspect ratio greater than 1000 [107].

The CNTs fundamentally come in three variations: Singular-walled CNT, Double as well as Multi-walled CNT. SWCNTs (Single-walled carbon nanotubes) are sliced off pieces of carbon atoms of a 2-D hexagonal lattice to form a hollow cylindrical shape. In the terminology of the concept of “Bravais Lattice”, periodic boundary limitations are applied over the entire major axis i.e., the length of this vector to produce a lattice with helical symmetry of continuously bonded carbon atoms without any disjoint or break in structure [108]. DWCNTs (Double-walled carbon nanotubes) are also of the group of 1-D materials of the carbon family. This class of material has a unique shape of one cylinder being nested into another of a larger diameter. It is this difference in diameters that produces different degrees of interlayer interactions between the two tubes. A significant advantage of this shape is the flexibility it allows in modifying the outer layer without changing the properties of the inner layer. It also contributes to unique material properties not found in the single-walled members. Additionally, DWCNTs enable a combination of solubility and functionality [110]. Although their morphology is like that of SWCNTs, they are more chemical resistant, which makes them a perfect material for grafting. MWCNTs (Multi-walled carbon nanotubes) consist of more than two layers of graphene attached as well as rolled over itself. Depending on the number of graphene tubes, their typical diameters range from 2 nm to 50 nm. The approximate average distance between the various layers is around 0.34 nm [106]. From the structural construction point of view, the MWCNTs are described with 2 different models. One model is named Russian Doll and the other is the Parchment model [111].

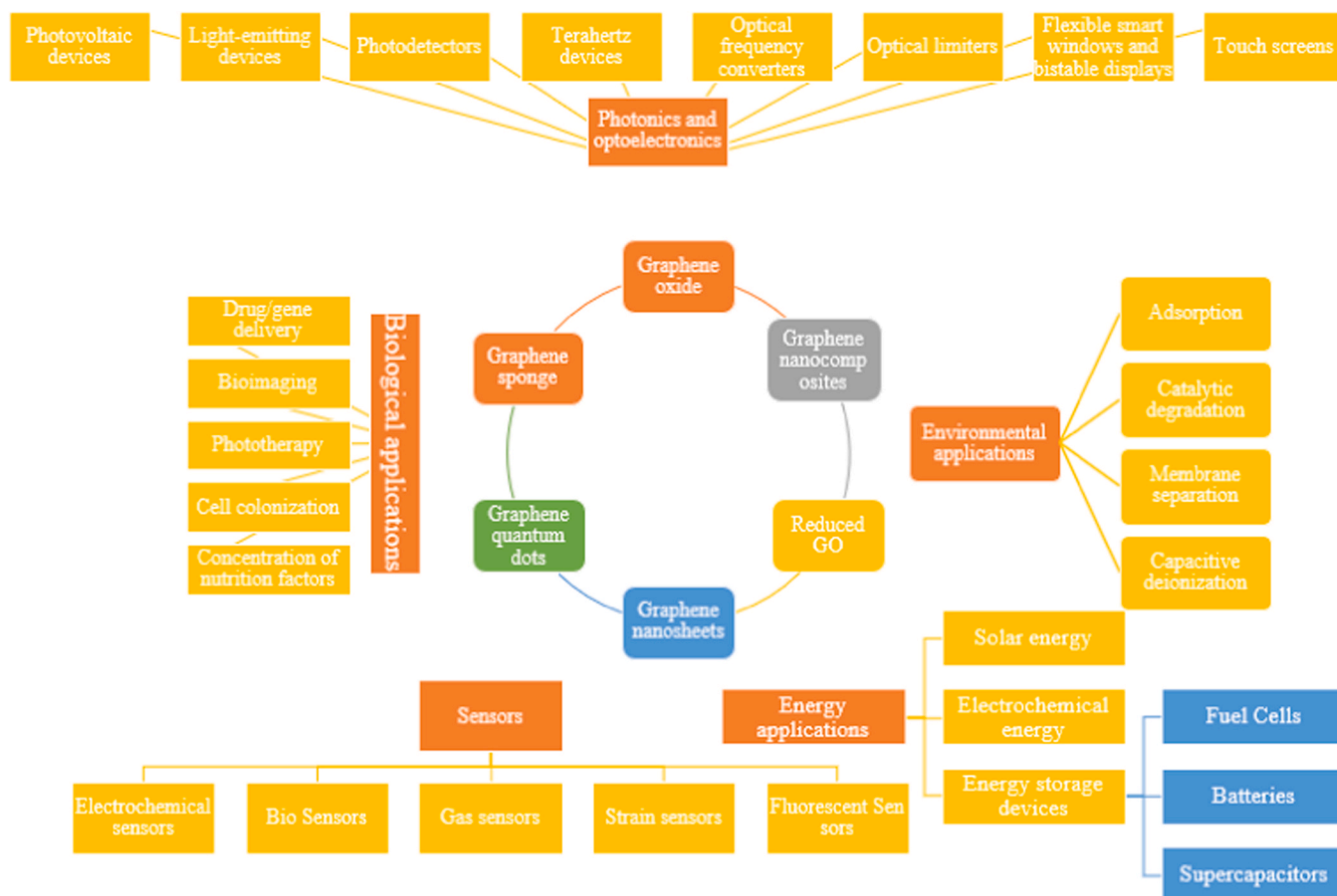


Fig. 2. Various applications of graphene-based nanomaterials [99–104].

The carbon nanotube state-of-the-art synthesis depends on various high-end techniques and new methods are continuously being developed. Some of the established CNT synthesis methods are laser ablation, electrolysis, arch discharge, hydrothermal, sonochemical, template, and chemical vapor deposition method. CVD further includes plasma-enhanced, injection assisted, thermal, radiofrequency, microwave, laser-assisted, hot filament, aerogel assisted, water-assisted, alcoholic, oxygen assisted, liquid pyrolysis, high-pressure Co (HiPco), Co-Mo catalysis (CoMoCat), and solid pyrolysis [112]. One of the strongest and stiffest material properties yet discovered exhibit in Carbon nanotubes, in terms of elastic modulus as well as tensile strength [113]. This strength comes from the covalent sp^2 bonds, which are formed between the carbon atoms individually. Nanotubes exhibit a property known as ballistic conduction which introduces remarkable thermal conductivity, but also has good insulators in lateral direction to the tubular axis [114].

Carbon nanotubes are usually small in size with a high aspect ratio, light in weight, and have good conducting characteristics as well as good tensile strength, which enables them to be applied to several fields of science, engineering, and technology like nanotechnology, nanomedicine, capacitors, actuators, membranes, transistors, drug delivery, sensors, etc. [106]. In the nanostructured anode materials, CNTs serve as the backbone which is known as components of effective buffering. They also lessen the structural integrity deterioration which leads to substantial change in volume linked with the discharging as well as the charging process. Due to conductive characteristics, CNTs can offer enhanced electronic transport in nanostructured anodes [115]. This makes them viable for catalysis and energy storage applications [116]. These have been used in supercapacitors, ultracapacitors, and electrochemical capacitors. Processing of CNTs into flexible, highly electrically conductive, and strong fabric enables them to be served as electrodes in multifunctional electric double-layer capacitors (EDLCs) to be served in weight-sensitive devices, equipment, and machinery in the aerospace industry or military [117]. CNTs have found several applications in human healthcare like cancer diagnosis and treatment, carriers for peptides, proteins, and genes, delivery devices for antigens and adjuvants, point-of-care devices, photoacoustic imaging, nanoprobe sensing applications, photothermal ablation therapy, enzyme biosensors, DNA biosensors, cancer biosensors, antimicrobial treatment, bone scaffolding, protein separation, etc. [118]. Separation sciences also utilize vast properties of CNTs and have been used for analytical procedures like solid-phase extraction and microextraction of sorbents in membranes water treatment (removal of heavy metals, organic and inorganic pollutants, dyes, color, etc.) and gas separation [119–122]. CNTs can also be used in flexible and high-temperature electronics, optoelectronics, thermo-electrics, single-carbon-nanotube field-effect transistors (CNT-FETs), polymer-fullerene bulk-heterojunction (BHJ) solar cells, etc. [123–125]. Carbon nanotubes have also been tested for automobile applications [126]. It is not possible to highlight the different applications of CNTs in different combinations and composites in a brief write up. However, a detailed list of different CNTs and their composites for some of the selected applications is provided in Table 2.

5. Nanoclay composites and polymers

As the advancement in different aspects of nanotechnology in various fields of sciences and even in environmental protection increases, the basic principles of the technology are being applied to remediate problems that were once thought to be inevitable. As the demand for increased strength in polymers grows, it has become imperative to reinforce the basic polymer structure with non-polymeric molecules. In this aspect, several types of natural and synthetic clay are a case in point. Nano-sized fillers such as carbon black and nano-oxides are, while prospective candidates for this role, stringent regulations of quality control and environment make some of them unsustainable to be upscaled, because of the lack of precision in synthesis or non-degradability of the final product. Following this line, natural clay

particles of nanometer scales are studied to be used in the crystalline or amorphous structures in the polymer composite [208]. Clays can be divided into several subtypes such as illite, halloysite, kaolinite, etc, and owing to the low environmental impact as well as their easy availability, they are under extensive research for incorporation as reinforcing materials in polymer structures. Fundamentally, nano-clays are mineral silicate nanoparticles with structural units of layers, and by stacking these layers able to form complex crystallites [209]. According to the method of interlacing of the clay particles in the polymer structure, nanoclay composites can be divided into following types on this basis: intercalated composites and exfoliated nanocomposites. Intercalated composites are polymer chains penetrated in the layers of clay, resulting in an ordered multiple-layered structure with alternating inorganic – polymer layers, designed at specific intervals, all within size range of a few hundred nanometers. Whereas exfoliated nanoclay composites are synthesized through larger and extensive penetration of polymer solution within the crystal lattice of mineral clay. The mineral clay is dispersed randomly which allows for greater interaction between the inorganic (mineral) and polymer particles [210]. Furthermore, they are also categorized as organo-clays and Pillared layered clay. In the clay layers, when the loosely bonded inorganic cation is replaced by an organic one, the resulting mineral is referred to as “Organo-clay”. Due to the replacement of most inorganic cations, the material, in bulk, becomes organophilic. It enhances its reactivity with specific organic reagents during the processing of nanoclay synthesis. Whereas, in Pillared layered clay, charged balancing cations are gradually replaced with polymeric hydroxyl cations. It is accomplished by tearing apart the thin layer of clays with modified nano-sized pillars of organic cations [211].

Although the basic principles of nanoclays synthesis appear to be lucid, there are glaring challenges in its actual synthesis. The two main problems are compatibility of chemicals between the filler particles at the molecular scale and polymer matrix, and uniform and polymer-solvent homogenous dispersion within the matrix. These are the parameters that ultimately govern the bulk properties the material will attain for eg. elasticity, tensile and compressional strength, temperature stability and shape memory abilities, etc. The three major synthesis methods for nanoclay-polymer composites are solution blending method, melt blending method, and In-situ Polymerization. The solution blending method is a solvent-based technique in which the prepolymer, a polymer is dissolved in a solvent such as toluene, chloroform, or water. When the clay is dissolved in this solution, the polymer chains gradually replace the solvent within the nanolayers of the clay material, thus forming clay-polymer layers at distinct distances [212]. After the replacement is complete and the interlayer solvent is completely removed, the intercalated sheets reassemble, forming a composite. In solution blending, the driving force of intercalation is the entropy which is gained from the solvent molecules' desorption. This process is comprised of three fundamental steps i.e. composite casting, clay dispersion in a polymer solution, solvent's gradual, and controlled replacement. Constant energy input in the form of agitation and stirring is required in this technique through mechanical means for uniform dispersion of clay. For this purpose, research is underway on techniques using resonance, vibration, and even ultrasonication. Although solution blending is a thorough and viable technique in terms of uniform dispersion of nanoclay, the method has drawbacks because the intercalation is specific for certain polymer-clay combinations. Moreover, the technique requires large quantities of organic solvents which prohibits them to be considered an environmentally friendly option [213]. In the melt blending method, a fixed number of intercalated nanoparticles are melted along with desired polymers at temperatures above the polymers' softening point. In the presence of inert gas, this process is carried out. Three essential elements in the melt-blending method are: for the functionalized macromolecules, an enthalpy-based driving force, a sufficient time for the center-stacked layers diffusion process, and for the macromolecular Gaussian coil a relatively large interlayer spacing. This technique is further divided based on whether mid-process mixing is

Table 2

Selected applications of different CNTs and their composites.

| Field of study | Specific research area | CNT based materials used | Ref. |
|-----------------------------|-----------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------|
| Separation and purification | Adsorption of heavy metals | MWCNTs, Acidified MWCNTs, Oxidized CNTs, HNO ₃ -modified CNTs, Nitrogen-doped magnetic CNTs, Magnetic-functionalized MWCNTs, MnO ₂ /CNTs, MWCNTs/Fe ₃ O ₄ modified with 3-amino propyltriethoxysilane (APTS), SWCNTs, SWCNTs-COOH, Raw CNTs, Pristine CNTs, Ionic liquid-functionalized oxi-MWCNTs, As-grown CNTs, H ₂ O ₂ oxidized CNTs, Alumina-decorated MWCNTs, Multiwall carbon nanotube-zirconia nanohybrid (MWCNT-ZrO ₂), Iron oxide coated multiwall carbon nanotubes, Phenolic hydroxyl functional group P-MWCN, Carboxylic functional group COOH-MWCNT, Sulfur-containing MWCNTs (S-MWCNTs), MnO ₂ -coated carbon nanotubes, Chitosan/poly(vinyl) alcohol thin adsorptive membranes modified amino-functionalized MWCNTs, MWCNTs purified with sodium hypochlorite, | [119,127–129] |
| | Adsorption of organic and inorganic pollutants | SWCNTs, MWCNTs, MWCNT15, S-MWCNT-2040, L-MWCNT-2040, L-MWCNT-60100, polycarbonate/carboxyl-functionalized multiwalled carbon nanotubes (PC/cMWCNTs), oxidized multi-walled carbon nanotubes (MWCNTs), metal-organic framework ZIF-8/magnetic multi-walled carbon nanotubes (M-M-ZIF-8), carbon nanotubes/graphene hybrid aerogel, f-MWNTs, CNTs/activated carbon fiber, Magnetic MWCNTs, Calcium alginate/MWCNTs, Chitosan/Fe ₂ O ₃ /MWCNTs, G-CNTs, Chitosan/Fe ₂ O ₃ /MWCNTs, MWCNT 8, MWCNT 30, MWCNT 50, MWCNT 10, MWCNT 20, MWCNT 40, MWCNT 60, MWCNT 100, K-SWCNT, Graphitized CNT | [130–138] |
| | Gas adsorption | Raw CNTs, Li doped MWNT, K doped MWNT, 3-aminopropyl-triethoxysilane (APTS) modified CNTs, tetraethylenepentamine (TEPA) impregnated industrial-grade multiwalled carbon nanotubes (IG-MWCNTs), boron carbon nanotubes (B2CNTs), polyaspartamide (PAA)-MWNTs | [139–143] |
| | Analytical separation | SWCNTs, Pd-doped-SWCNTs, COOH-MWCNTs, CNTs, CONH ₂ -MWCNTs; PEG/MWCNTs, COO (CH ₂) ₆ OH-MWCNTs, COO(CH ₂) ₁₀ OH-MWCNT, COCl-SWCNTs, NH ₂ -R-MWCNTs, SiO ₂ -MWCNTs, NH ₂ -SWCNTs, PS-DVB-MWCNTs, Poly (GMA-EDMA-MWCNTs), BMA/COOH-MWCNTs, MMA/COOH-MWCNTs, MES/COOH-MWCNTs, Carboxylated-SWCNT, Br-MWCNTs, o-CNTs/silica gel, CTAC/carboxyl MWCNTs, NBHAE-MWCNTs, 5-(4-dimethylaminobenzyliden)-rhodanine-MWCNTs, N-phenyl-1,2-hydrazinedicarbothioamide MWCNTs, PIDA-MWCNTs, Ga3+-imprinted MWCNTs, TAA-MWCNTs, (dimethylaminobenzyliden)- rhodanine-MWCNTs, MWCNTs/PVA cryogels, Melamine MIP-MWCNTs, Fullerene C ₆₀ , c-MWCNTs, | [144–148] |
| | Membrane separation | Aligned SWNTs, CNTs (forward osmosis), MWCNT-COOH/polyvinylidene fluoride, Polyaniline polymer/SWCNT for capacitive deionization electrodes, 0.1% MWCNT/polyamide polymer, Polyethersulfone/0.045% MWCNT, MWCNT/polyethyleneimine-poly (amide-imide) hollow fiber forward osmosis, MWCNT/aromatic polyamide (PA) (15 mg MW-CNT/g PA), MWCNT/carbonized nanofibrous membranes, Zwitterion functionalized CNT/polyamide nanocomposite membrane, CNT-Bucky-papers/vacuum filtration in 99.8% pure propane-2-ol, Polyvinylchloride/MWCNT-co-copper nanolayer composite nanoparticles, Vertically aligned-CNT (VA-CNT), CNT-film synthesized on the macroporous surface of α -alumina support by chemical vapor deposition (CVD) of cyclohexanol and ferrocene, Honeycomb-CNT membrane (HC-CNT), Carbon nanotube immobilized membrane (CNIM), CNTs/chitosan, chitosan membrane modified by carboxylated MWCNTs, MWCNT-NH ₂ /PEG, Chitosan/PVA/MWCNT | [149–152] |
| Energy | Energy Storage devices (batteries, supercapacitors, fuel cells) | CNT-Ni-Si, scaffolds for carbon nanohorns (CNHs), MWCNT arrays, Vertically aligned CNTs, as-grown pillar CNTs, Fe ₂ O ₃ -SWCNT, V ₂ O ₅ -SWNTs, CNTs-Ni foam, As-grown N-doped CNTs, ordered mesoporous carbon (OMC)/Ni/CNTs, carbon nanotubes oxide, nanotube- polyaniline (CNT-PANI), Manganese oxide/CNT, Nanostructured Fe ₃ O ₄ /SWCNT, Fe ₃ O ₄ -aligned CNTs, Fe ₂ O ₃ /SWCNT, Fe-O ₃ NP/CNTs composite films, LiCoO ₂ /MWCNT, LiNi _{0.7} Co 0.3O ₂ (LNC)/MWCNT, LiFePO ₄ (LFP)/MWCNT, LiMn ₂ O ₄ (LMO)/MWCNT, polyethyleneimine (PEI)/CNTs, unzipped multi-walled carbon nanotubes (UCNTs) film, Sn-SnO ₂ /CNTs, polypyrrole/CNTs, carboxylated multiwalled carbon nanotubes/carbon nanofibers (CNTs/CNFs), N-CNTs/rGO, organic nanocrystalline (ONC)/MWCNT, Ti ₃ C ₂ Tx MXene/CNT | [115,153–163] |
| | Electrochemical Energy | Fe-Ag/TiO ₂ , CNTs/Graphene based hybrids (GHs), MnO ₂ /CNTs/GO, MnO ₂ /CNTs/GHs, Mn ₂ O ₃ /CNTs/GHs, NiO/CNTs/GrF, MoO ₃ /CNTs/GrF, MoS _x /CNTs/PGr, FeS/CNTs, FeF ₂ /CNTs, CoO/N-CNTs, ZnO (CZO)/CNT, Fe ₂ O ₃ /CNT, SnO ₂ /graphited carbon nanotubes (gCNTs), CNTs/rGO, MWCNT-p, MWCNT-c and MWCNT-a/COOH-NH ₂ , Fe/Fe ₃ C/M-CNTs, Pt/SWNTs, polypyrrole/CNTs, poly(1-vinyl-3-octylimidazole hexafluoride phosphorus)/MWCNTs | [164–171] |
| | Solar Energy | SWNT/pyrene, SWNT/sodium poly (styrene-4-sulfonate) (PSS ⁿ⁻), poly(diallyl dimethylammonium) chloride (PDDA ⁿ⁺)/SWNT, poly(3,4-ethylenedioxythiophene) (PEDOT)/CNTs, partially unzipped multiwalled carbon nanotubes (PUMWNTs), CNT nanofluids, MWCNT/3OT/n-Si, DWCNT/3OT/n-Si, DSSCs/MWCNTs/TiO ₂ , MWCNTs/TiO ₂ , MWCNT/PEDOT:PSS, TiO ₂ /Al ₂ O ₃ /NiO-SWNTs, NiCo ₂ O ₄ -MCNTs, CNT:Si/Cr/Au, Ti/Pt, Ag, CNTs incorporated TiO ₂ nanorods (CTNRs), MMWCNTs-CeO ₂ | [172–180] |
| | Mechanical energy storage | SWCNTs, MWCNTs, MWCNT on graphite, Bundle of SWCNTs, Ultralong carbon nanotubes, Carbon Nanotube Springs | [181–184] |
| | Biomedical | SWNTs, MWCNTs, acid-oxidized SWCNTs, Oxidized ultrashort SWCNTs, Amine-terminated CNTs, SWCNT-PL-PEG, SWCNT-PEG-drug, SWCNT-PEG-cisplatin/doxorubicin, Streptavidin-CNT-protein conjugates, DNA-encased MWCNTs, Fluorescent-CNT- fluorescein isothiocyanate (FITC)/biotin conjugates, cationic functionalized (fCNTs), Pristine single walled carbon nanotubes (pSWCNTs), SWCNT- Paclitaxel (PTX), SWCNTs- Doxorubicin, MWNT-COOH, CNT-(Fe)/hydroxyapatite composite, TiO ₂ -Au embedded on MWCNTs, pH-responsive polyethyleneimine-betaine functionalized CNT, CNT-dendrimer system, Injectable and thermosensitive chitosan-CNT hybrid hydrogel, Antibody-conjugated CNTs, Boron nitride nanotubes, and CNTs, Hydroxyapatite-MWCNT composite filled by iron, PEG-functionalized CNTs/gelatin-chitosan nanocomposite, Hyperbranched polyglycerol modified CNTs, Copper nanoparticles synthesized on the surface of CNTs, Starch/MWCNT-glucose nanocomposites | [185–188] |
| | Disease diagnostic | SWNTs, MWCNTs, SWCNT-PEG-mAb ($\alpha_v\beta_3$), hexamethylenediamine (HMDA)-SWCNTs; cetyltrimethylammonium bromide (PDPA) chloride-SWCNTs, CNTs/Gadolinium(III) salts, sodium iodide, iodine, nitroxide radicals, Bismuth [189] salts, ferromagnetic material, SWCNTs | [185,186,188, 190–194] |

(continued on next page)

Table 2 (continued)

| Field of study | Specific research area | CNT based materials used | Ref. |
|----------------|--------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| | Antibacterial and antifungal | conjugated with ArgGly-Asp (RGD) peptide, carboxyl functionalized SWCNTs modified with the copolymer poly(para-phenylene) (PPP) containing polystyrene (PSt) and poly(ϵ -caprolactone) (PCL), folic acid, etc. polydopamine-encapsulated gadolinium-loaded CNTs | [190,195–200] |
| | Tissue engineering and artificial implants | SWCNTs, DWCNTs, MWCNTs, Pristine MWCNTs, MWCNTs-lysine, MWCNTs-arginine, aminosilicohydrazide cross-linked chitosan-MWCNTs, aminohydrazide cross-linked chitosan-MWCNTs, pyrazole derivatives-MWCNTs, trimellitic anhydride isothiocyanate-cross linked chitosan hydrogels-MWCNTs, Porphyrin appended SWCNTs | [201–207] |
| | | SWCNTs, MWCNTs, Carboxylated SWCNTs, Oxidized CNTs, polymer/collagen (poly-L-lactide; PLA or poly-D, L-lactide-co-glycolide PLGA)- SWCNTs, G-CNT coated hydroxyapatite polyetheretherketone (HAP/PEEK), cellulose acetate (CA)-CNT-GO, nanofibers of poly(ϵ -caprolactone) (PCL)-MWCNTs, polyethylene glylated CNTs (PEG-CNTs), poly (3-hydroxybutyrate) (PHB)-chitosan (Cs)-MWNTs, C/COOH-SWCNTs nanocomposite films, Tricomponent scaffold with an oxidized fMWCNT alginate HAP, | |

required or not. During static melt blending, a vacuum is maintained at a temperature of around 50 °C. On the other hand, in the presence of an inert gas, continuous mixing in a batch or continuous reactor is performed in the dynamic melt blending. Melt blending provides better control and extent of mixing of nanoclay within the polymer matrix, and it is compatible with standard polymer processing procedures such as injection molding, extrusion, etc. Furthermore, due to the absence of any organic solvent, it reduces the environmental impact significantly [214]. In the polymer matrix, in-situ polymerization provides better nanoparticles dispersion, through which the problems of aggregation and composite deformation can be avoided, which are common in the methods. This technique also bypasses the thermodynamic requirements that come in conjunction with the previous method. Because of greater precision and control, this method also allows for tuning of matrix designs within the nanoclay-polymer structure, and thus provides a wider range of properties in terms of elastic modulus, thermal stability, and performance strength [215]. The synthesis of the clay-polymer composite was first reported by Ozkose et al. [216] using a poly/nanoclay combination. In their study, a ring-opening polymerization method was employed, which initiated the delamination of clay layers in the polymer matrix, resulting in a composite formation. The results exhibited mixed exfoliated/intercalated layers and improved thermal stability compared to pure poly(2-ethyl-2-oxazoline). Recent studies focused on the performance enhancement of the final yield shows that needle-shaped clay particles provide better mechanical properties and higher molar mass (thus larger composite structures) compared to other counterparts. Detailed methods of in-situ polymerization can be found in literature.

The precise control of the interaction between the clay particles and polymer matrix allows for the synthesis of native tissue as a replacement in biomedical applications. This field is gaining prominence as the science of biomedical engineering becomes more developed. Polymer-clay nanocomposites appear as suitable prospects for this job because of their thermal stability and controlled reactivity with the body cells. The cell scaffolding also allows for the easy transport of nutrients inside and out of the composite structure, while keeping the overall scaffold intact due to its shape memory abilities [217]. As the world moves towards a sustainable future, the usage bio and naturally degradable materials is being reinforced through international environmental regulations. While biopolymers provide a substitution for petroleum-based polymers, issues of fragmentation and loss of mechanical properties over time hinder their large-scale applications. On the other hand, nanoclay composites face almost none of the issues faced by the biopolymers [218]. The use of nanoclay with some commonly used polymers such as PVC and PLA are found to increase their rate of degradation. The use of clays as beauty products is ancient. Several modern synthetic skincare products make use of the properties of clays like adsorption capacity, high internal surface area and high cation exchange capacity. Improving from this application, extensive research is being conducted on the use of nanoclay composites as efficient Drug Delivery Systems. Their ability for rapid ion exchange makes their use as viable drug enhancers to relieve severe pain. While physically inducing fire retardants work by

reducing the flame temperature and acting as a blanket to reduce the oxygen intake, chemical fire retardants are mostly comprised of polymeric chains that rupture and create a cascade of ionization and deionization reactions, resulting in dripping of the remnants on the fire directly, reducing the flame rapidly. Halogen-based FRs are widely popular for their cost-effectiveness and functionality, but stringent environmental regulations and continuous increment in the types of synthetic materials, and thus the fire generated from them, halogen-based FRs are reaching their limits. To replace them, nanoclay-polymer composites are considered a suitable candidate because of the presence of mineral (just as in normal sand used for fire reduction) and polymer matrix that breaks down and envelopes the fire, cutting off the oxygen supply rapidly. Various applications of nanoclay composites and their polymers are shown in Fig. 3.

6. Nano-structured thin films

Since the discovery of nano-carbon tubes, in-depth research in its different facets is being conducted. The application of 1-D nanotubes has especially restarted to gain attention after the works on the advancement of renewable technologies like solar fuel cells and optoelectronic devices and in purification processes as membranes. Thin films can be prepared from different materials and composites like MOFs, graphene, metal oxides, diamond-like carbon, piezoelectric and ferroelectric,

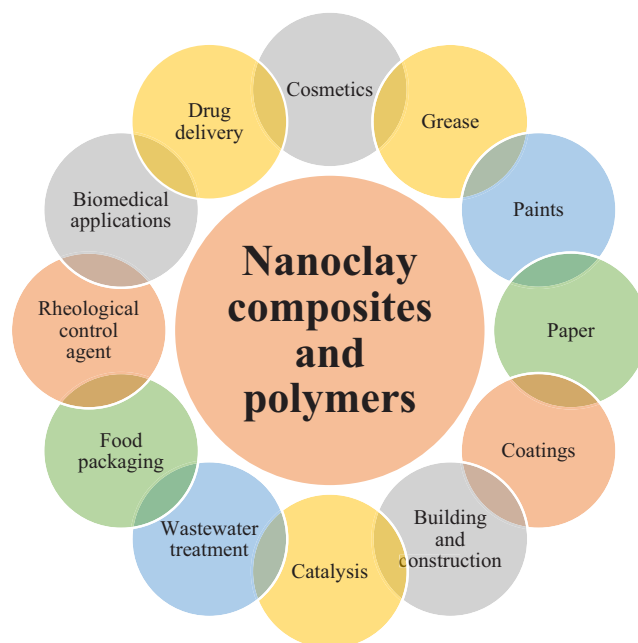


Fig. 3. Various applications of nanoclay composites and their polymers [219–223].

nanocellulose thin films, and several other combinations depending upon the end-user applications [10,11]. The choice of substrate and the active layers are the two most important aspects of this technology. It is the activity of the substrate layer that determines the activity and response of nanoparticles to be deposited on them. Therefore, it is essential to find alternative synthetic materials for the substrate layer. Polyethylenephthalate substrates generally have better thermal and mechanical properties and stability against solvent treatment than amorphous films, such as polycarbonate, and poly, due to their bi-axially oriented semi-crystalline structure [224]. Once the nanoparticles have been deposited on the selected substrate layer, these thin films comprised of the polymer substrate can be coated on the rest of the active layers and buffer material within the cell by mechanical techniques such as knife-coating, slot die coating, screen printing, and spray coating. These are synthesized through methods like CVD, chemical bath deposition, sol-gel, layer-by-layer synthesis, one-pot method, Successive ionic layer adsorption and reaction (SILAR), evaporating the hydrothermally synthesized nanoparticles, reactive laser pulsed as a deposition method (RPLD), etc. [225–228].

Polymer substrate-based solar cells (PSCs) are also known as “Organic Photovoltaic Cells” because of their use of organic substrate for the deposition of thin films comprised of metallic nanoparticles to produce photoelectric current. Most layers of the organic solar cells can be prepared through standard procedures in a solution and can be deposited using a low-cost casting method that offers a significant advantage to the PSCs compared to other inorganic solar cells. A PSC works in a simplistic way photon is absorbed by the acceptor or a donor which transfers the electrons to the lowest unoccupied molecular orbital, leaving behind holes in the highest occupied orbital. This transfer produces excited electron-hole pairs. The excited pair diffuse to the interface of donor and acceptor and separate into free charge carriers that can be transported to respective anode and cathode, thus generating electricity [229]. Nanostructured thin films have been investigated for several applications like separation processes, energy storage devices, sensors and actuators, surface abrasion resistance, gas sensing, antimicrobial application, micro-electro-mechanical systems (MEMSs) [230–234]. A list of different nanostructured thin films is provided in Table 3 with some of the selected applications.

7. Metal-organic frameworks

Metal-organic frameworks (MOFs) are porous and highly crystalline materials synthesized through metal-ligand coordinate bridging, which is stronger than other weak bonding such as π - π stacking [12]. Due to porosity, a high degree of crystallinity, and coordinate bonding, MOFs exhibit dynamic properties [263–265]. These are organic-inorganic crystalline and porous materials that consist of a regular single or multi-dimensional structure of positively charged metal ions surrounded by organic molecules. The organic molecules are bounded by the metal ions, acting as nodes between them. Together they form a repetitive cage-like structure, whose main feature is its large internal surface area, up to 7000 m²/g [266]. The crystalline materials are comprised of two fundamental building blocks or secondary building units (SBUs) i.e metal containing SBUs and organic SBUs. The metal-containing SBUs, which could be a metal ion or a cluster, act as nodes that are connected through organic linkers [267]. Therefore, MOFs are also referred to as Porous Coordination Polymers. The specialized branch of chemistry that deals with the molecular synthesis and property modification of the metal-organic frameworks is “Reticular Chemistry”. Coordination polymers comprise the basic building blocks of MOFs. These are a group of compounds with larger structures formed by metal ions and organic and/or inorganic ligands with coordination bonds. They can form multiple frameworks comprised of single or double or three-dimensional networks. Late transition metals are the key to this framework design, and the understanding of this process has been enhanced with the advent of single-crystal X-ray crystallography. The synthesis of MOFs is

Table 3

Various types of nanostructured thin films and their applications.

| Thin-film type | Applications | Ref. |
|--------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| MOF thin films | Photovoltaics, CO ₂ reduction, energy storage, water splitting, electronic devices, fabrication of membranes, sensing and micro-pattern devices, adsorption, organic field-effect transistors, optical applications, catalysis, sensors | [235–238] |
| Graphene-based thin films | Supercapacitors, flexible transparent circuits, electromagnetic interference shielding, photocatalysis, electrothermal applications, surface-enhanced Raman scattering, and metamaterial applications | [239–242] |
| Metal oxide thin films | Dielectric, transparent-conductors, photocatalytic applications, memristive devices, galvanic corrosion protection, sensors, transistors, solar cells, optoelectronics, flexible electronics | [243–248] |
| Diamond-like carbon thin films | Infrared optical, mechanical, electronic, and biomedical applications, coating application on silicon solar cells, microfluidic devices, optoelectronics | [249–252] |
| Piezoelectric thin films | Micro-electromechanical system switches and resonators, film-type speakers, flying objects, flexible displays, soft haptic devices, actuators for millimeter-scale robotics, droplet ejectors, medical imaging transducers, and energy harvesters for wireless sensors, structural health monitoring, ultrasonic transducers, acoustic sensors, lab-on-chip applications | [253–256] |
| Ferroelectric thin films | Memory applications, micro-sensors, actuators, MEMs, magnetic sensors, current sensors, energy harvesters, magnetoelectric based electronic components, microwave electronic components, microdevices with pyroelectric and piezoelectric | [257–259] |
| Nanocellulose thin films | Coatings, plies, packaging, transparent and conductive paper, composite reinforcing, biomedical, actuators | [260–262] |

analogous to other crystallization processes. The only difference arises due to the action of a polymer-solvent instead of a polar one. In this setting, the polymer structure retains its form like a hollow cage even after the removal of the guest solvent, which could be refilled with other compounds. Because of this, MOFs are under intensive research for the storage of gases as well as catalysis. The study of MOFs developed from the study of zeolite. Except for the use of preformed ligands, MOFs and zeolites are produced almost exclusively by hydrothermal or solvo-thermal techniques, where crystals are slowly grown from a prepared solution. In contrast to zeolites, the organic ligands in MOFs remain intact during the production step [268]. In Zeolite synthesis, ions called “Templates” are deployed to influence the structural growth of the inorganic framework. On the other hand, in MOFs, secondary building units are used to template the framework in conjunction with an organic ligand. Due to this specialized difference and requirement of increase precision and functionality, reticular chemistry of MOFs has emerged as a powerful tool for producing porous materials and precisely designing their interior to address the world’s energy and environmental problems [269]. The post-synthetic exchange of organic linkers and metal ions is an expanding area of the field and opens up possibilities for more complex structures, enhanced functionality, and better system control [270]. MOFs are a variety of advanced micro-porous coordination materials that have a high surface area, permanent porosity, and a precisely controlled inorganic-organic structure. These characteristics make it possible to use MOFs as potential sorbents for many important applications; especially analytical chemistry [271]. MOFs are also suitable candidates for adsorption and separation applications over other crystalline porous solids such as zeolitic materials [272]. MOFs are a suitable group of materials for hydrogen energy production because of

their characteristics [273]. As molecular hydrogen is a very stable compound, with two electrons, the method of its adsorption is a physical one, and not a chemical one. Also, the weak dispersion forces make it viable to use at ambient temperatures [274].

MOFs have received major applications in two sectors i.e. the separation processes, and catalysis. In the separation process, MOFs have been used for the removal of gaseous and liquid contaminants through adsorption and membrane processes. Whereas catalysis, mainly focuses on photocatalysis, electrocatalysis, hydrogenation, Knoevenagel condensation, aldol condensation, Michael addition, Henry reaction, transesterification, cycloaddition, one-pot cascade reactions, etc. [275]. Nano-sized MOFs are also considered efficient drug delivery materials as their properties can be modified chemically. Several MOFs have been prepared to have hydrophilic pores that can carry either positive or negative charges, which easily encapsulate drugs having the opposite charge for the MOFs. MOFs can also incorporate in their lattice bio-molecules and bioactive metals, which is a convenient aspect for their usage for imaging [276]. The antibacterial action of 4,4'-bipyrazolyl-based silver(I) coordination polymers embedded in polyethylene disks have been researched extensively in various literature. Complete reduction of three bacterial strains has been reported to be achieved in 24 h, the reduction of *Staphylococcus aureus* reaching ca 90% in only 2 h [276]. Many MOFs have a great affinity for CO₂; their porosity and structure flexibility make them prospective catalysts for the formation of organic carbonates by CO₂ and epoxides through cycloaddition reactions [276]. Major applications of metallic organic framework nanomaterials are displayed in Fig. 4.

8. Conducting polymers and their composites

The conductive polymer composites provide several advantages including low density, redox properties, ease of shaping, unique morphologies, corrosion resistance, and a wide range of electrical conductivities [280,281]. Due to these extraordinary characteristics of conductive polymer composites, they have many applications as electric devices, drug delivery, chemosensory, and actuators, etc. [282,283]. The conducting polymers are also being tested for applications in solar cells, which shows the potential of their application within that field [284]. Similarly, due to suitable physical and electrical characteristics, low cost, ease of manufacturing the conducting composites are being tested and used for several applications like supercapacitors, electrochromic devices, batteries, solar cells biomedical applications, and sensors [285]. Vapor grown carbon nanofibers (VGCNF)/polymers have reported as robust conductive polymers and are cost-effective compared to carbon nanotubes (CNTs), multi-walled carbon nanotubes (MWNTs), single-wall carbon nanotubes (SWNTs) [286]. This provides an option of replacement of CNTs, MWNTs, and SWNTs with VGCNF. Strong inter-fiber bonding and preparation of these fibers with polymeric resins sometimes reduce electrical conductivity and tensile strength. The π -electron backbone present in conducting polymers is responsible for unusual behavior in terms of electrical conductivity. This elongated π -conjugated arrangement in conducting polymers consists of single and double bonds that alternate throughout the polymer chain. Such organic polymers with high electrical conductive values are named 'synthetic metals' [287].

Several applications of conducting materials and composites have been discovered so far. Due to their nature of electronic and ionic conductivity, reversible doping, adjustable chemical and electrochemical

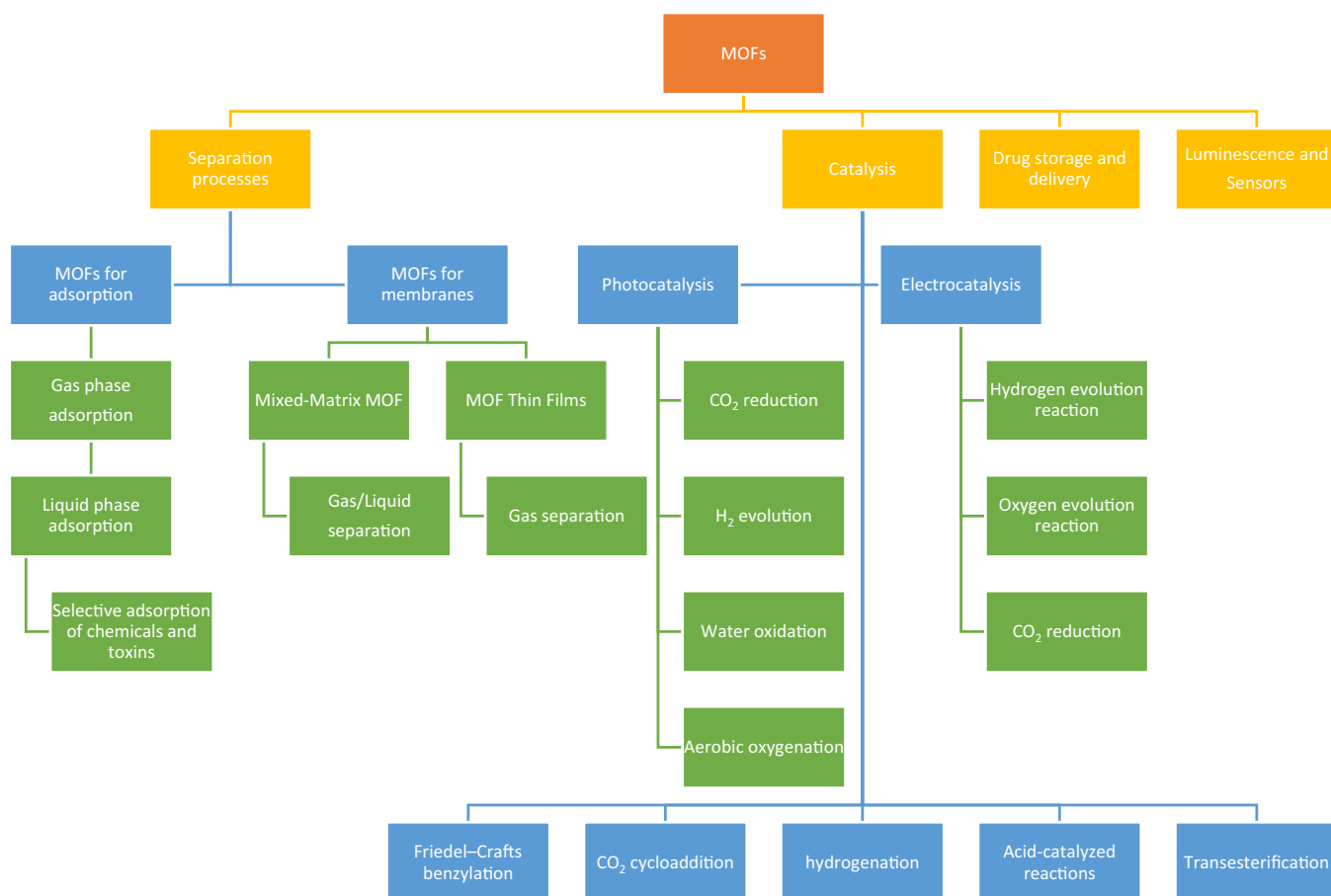


Fig. 4. Major applications of metallic organic framework nanomaterials [277–279].

characteristics, low cost, and convenient process-ability, they introduce due application in a variety of fields. Some of the well-researched areas for these materials have been batteries, light-emitting diodes (LEDs), sensors/bio-sensors, electro-optic and optical devices, membranes/films microwave and conduction-based devices, electrochromic devices, electrochemical and mechanical devices, energy storage devices, fuel cells, supercapacitors, corrosion protection, electrorheological fluids, tissue engineering, neural interfaces, actuators semiconductors, lithography, artificial muscles, catalysis, drug delivery, biomedical, analytical applications, etc. [288–290]. The solid conducting polymer electrolytes can be produced by crosslinking of mobile chains to develop networks or by the development of solid polymer electrolytes (SPEs) with supra-molecular architectures [291]. Single-ion conducting polymer electrolytes (SIPEs) prepared by lithium sulfonamide methacrylic monomer, bifunctional poly(ethylene glycol) methyl ether dimethacrylate (PEGDM) and poly(ethylene glycol) methyl ether methacrylate (PEGM) in presence of propylene carbonate (PC) shown lithium transference number approaching to unity and ionic conductivity $\sigma \approx 10^{-4} \text{ S cm}^{-1}$ at ambient temperature [292]. Ion-solvation-site connectivity plays a vital role in polymer electrolytes for high lithium-ion conductance [189]. Poly(ϵ -caprolactone) (PCL)/Succinonitrile (SN) blends integrated with n polyacrylonitrile (PAN) a skeleton with hierarchical architectures have exhibited high ionic conductivity, degree flexibility, large electrochemical windows, thermal stability, and good flame-retardance strength [293].

Core/shell particles of poly (3,4-ethylene dioxythiophene) (PEDOT) and sulfur showed great electrochemical performance when they were as used as the cathode material for Li/S battery [294]. The polyaniline/TiO₂ while used as a cathode in the rechargeable battery has shown charge-discharge properties up to 50 cycles than its conducting polymer alone [295]. Polypyrrole and polythiophenes doped with redox-active $\text{Fe}(\text{CN})_6^{4-}$ anions are reported to enhance 56–300% redox capacity [296]. Many researchers studied conducting polymers contributing in various applications such as analytical chemistry, bio-sensing devices [297], supercapacitors [298], memories [299], transistors [299], lithium ionic batteries [300], sensors [301], and actuators/artificial muscles [302]. A list of different applications of conducting polymers and their composites is presented in Fig. 5.

9. MXenes

A top-down selective etching process is usually employed to synthesize MXenes. This synthetic approach is considered stable and scalable as the batch size increases without any loss or alteration in the properties [308]. MXene is produced by etching a MAX phase by either using aqueous hydrofluoric acid (HF) or by in-situ formation of hydrofluoric acid by hydrochloric acid (HCl) and fluoride reaction [309]. Ammonium fluoride and Ammonium hydrogen bifluoride (NH_4HF_2) have also been used successfully to synthesize Ti_3C_2 from Ti_3AlC_2 , causing the selective removal of Al atoms at room temperature and O, OH, and F atoms being responsible for terminating the surface of the carbide layer [310]. Moreover, MXene is also produced in Lewis acid molten salts, such as ZnCl_2 . The MXene obtained is structurally stable as the Cl terminal can be noticed [311]. The nitride MXenes are produced by a different technique than that of carbide MXenes. The first nitride MXene reported was Ti_4N_3 . A molten eutectic fluoride salt mixture containing fluoride of potassium, sodium, and lithium is combined with MAX phase Ti_4AlN_3 at elevated temperature to produce Ti_4N_3 . A multilayered Ti_4N_3 is formed by etching out Al which can be subsequently delaminated by treating it with tetrabutylammonium hydroxide, after which the sonication technique is applied [312]. Many theoretical and experimental measurements for MXenes have been reported in terms of various properties: and their potential applications. In the presence of oxygen and moist environments, the single MXene flakes are unstable. Light exposure can also speed up the oxidation of colloidal MXene solutions. It is therefore suggested that MXene colloids be refrigerated in an oxygen-free, dark atmosphere for storage [313]. The stability also depends on the quality of single flakes of MXenes [314]. MXene films' mechanical testing was conducted instead of single-layered MXenes. A 5 μm -thick $\text{Ti}_3\text{C}_2\text{T}_x$ paper made walls of a cylinder can withstand ~ 4000 times its weight. A composite with 10% polyvinyl alcohol (PVA) in $\text{Ti}_3\text{C}_2\text{T}_x$ can make these films stronger to support $\sim 15,000$ times their weight [315]. Better and enhanced thermal, mechanical, electrochemical properties, and wear resistance were found by various MXene-polymer composites such as Polyethylene [316], polypyrrole [317] and PVA [315], etc. MXenes thin films and their composites are suggested to be used in transparent conductive coatings and optoelectronics, as Ti_3C_2 transmits $> 97\%$ of visible light

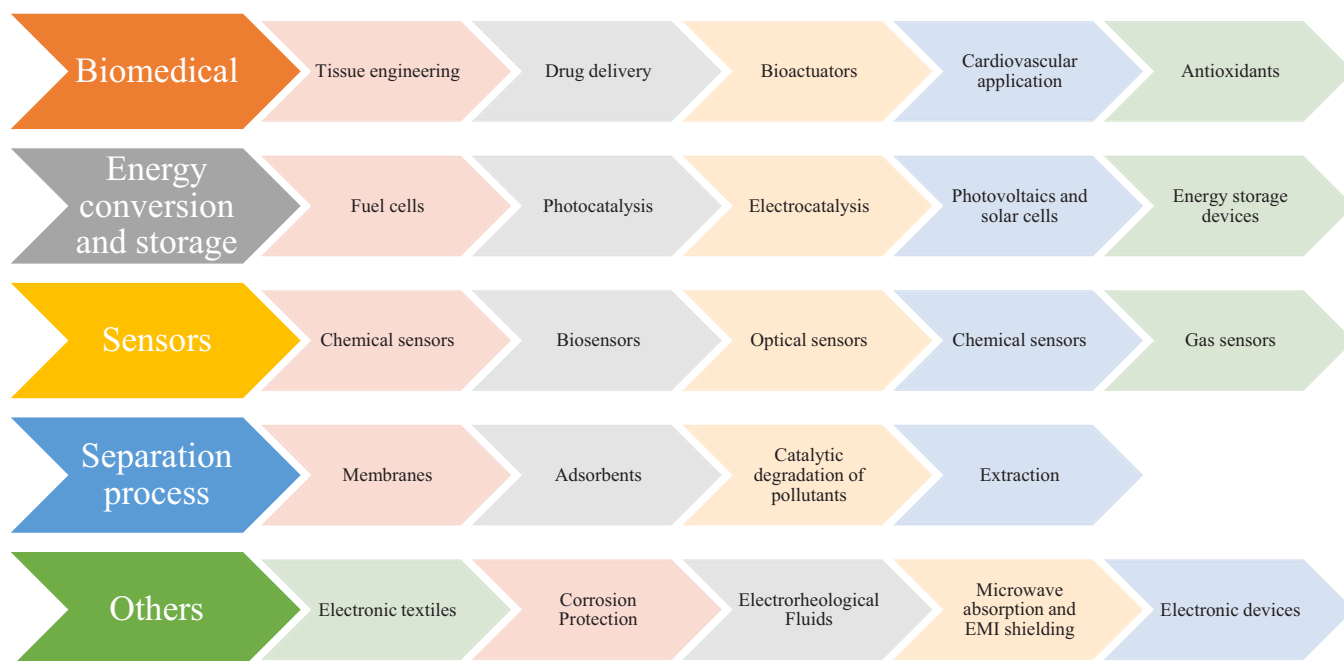


Fig. 5. Applications of conducting polymers and their composites [303–307].

per nanometer thickness [318]. The electronic properties of different MXenes vary from metallic to semiconductor, based on the type of M, X, and surface termination [319]. Also, the sample preparation technique can affect the electrical conductivity of MXenes. A large flake size and low concentration of defects yield higher conductivity [320]. For certain termination-free MXenes, ferromagnetic and antiferromagnetic properties were predicted while magnetism vanishes in the presence of surface terminations [321].

MXenes have exceptional properties for electronic and energy harvesting applications [322]. One of the studies indicated that out of almost 400 publications in 2018 on MXenes, 45% of them were on batteries and supercapacitors [323]. Some MXenes such as V_2CT_x , Nb_2CT_x , Ti_2CT_x , and $Ti_3C_2T_x$ were experimentally investigated in the application of lithium-ion batteries (LIBs). The storage capacity in terms of the highest reversible charge has been demonstrated by V_2CT_x , Nb_2CT_x in multi-layer form, while $Ti_3C_2T_x$ indicates the lowest capacity storage among the MXenes in a multi-layer form [324,325]. Additionally, every MXene can be used as anodes or cathodes in batteries as each MXene has a different active voltage window [326]. MXenes also demonstrates remarkable results for energy storage systems based on sodium Na^+ should be quickly diffused on MXene surfaces, which is desirable for rapid charging and discharging [327]. In between MXene layers, two layers of Na^+ can be inserted [328]. Furthermore, V_2CT_x MXene and Porous MXene-based paper electrodes were also reported to have high efficiency as a positive electrode material for sodium-ion storage and high volumetric capacities respectively [329,330]. In aqueous solutions, Ti_3C_2 MXene paper supercapacitor electrodes show excellent cyclability and the capability to store 300–400 F/cm³, which converts into three-fold as much energy as for activated carbon and graphene-based capacitors [331]. $Ti_3C_2T_x$ based-polyethylene, poly-vinylalcohol (PVA), and poly-diallyl dimethylammonium chloride (PDDA) composites are reported in the application of structural composites to enhance the strength, creep, hardness, and antifriction properties [317]. MXenes such as $Ti_3C_2(OH, ONa)_x F_{2-x}$, TiO_2-C or TiC and $Ti_3C_2(OH)_2$ are used to treat water for lead adsorption, toxic heavy metal adsorption, and heavy metal adsorption respectively [332–334]. $Ti_3C_2T_x$ MXene is used for water desalination by freestanding membranes for the charge- and size-selective rejection of ions and molecules. Also, $Ti_3C_2T_x$ is effective in dye adsorption, which is employed to adsorb methylene blue by multilayered MXene powder [335,336]. Various applications of MXenes are summarized in Table 4.

10. Chalcogenide nanocrystals

Chalcogenide nanocrystals are semiconducting metal compounds, incorporated with elements from groups as II–VI and IV–VI. These compounds display band gap energies from near-infrared to visible and into ultraviolet regions [14]. Nanostructured metal chalcogenides can be synthesized through Liquid Exfoliation Method, Hot-injection Method, Single-source Precursor Method, Hydrothermal Method, Solvo-thermal Method, Mixed solvent Method, Microwave Method, Sonochemical Method, Electrodeposition Method, Electrospinning method, Photochemical Method, Cation Exchange Method, Kirkendall-effect-induced Method, Template-directed Method, growth of metal chalcogenides nanostructure arrays on substrates, and these can be modified with carbon materials, noble metals, metal oxides, etc. [350]. Nanostructured chalcogenides can be used for hydrogen (H), lithium (Li), sodium (Na) storage batteries and supercapacitors, photo-electrochemical water splitting cells, electrochemical sensors, fuel cells, solar cells, coating conductive matrices, Grating fabrication, Photo-induced waveguides, fiber fabrication, fiber amplifiers and laser, optoelectronics, Optical switching, biological imaging [351–353]. When irradiated in the absence of sacrificial electron donors, metal chalcogenides may undergo photo-corrosion, which may bar rapid recombination of e^-/h^+ pairs and backward reactions. This may be minimized through metal ion doping, nonmetal ion doping, dye sensitization,

Table 4

Different specific applications of MXenes for the generalized field of study.

| Field of study | Specific applications | Ref. |
|-------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|
| Energy storage and conversion | Sodium-ion batteries, lithium-ion batteries, Non-Lithium-ion batteries, Li-S batteries, K-ion batteries supercapacitors, lithium-ion capacitors, electrochemical capacitors, hybrid capacitors, hydrogen storage, photocatalyst for direct solar energy utilization, photovoltaic devices, thermoelectric power generation | [337–342] |
| Sensors | Mechanical sensors, gas sensors, Solid-state gas adsorptive sensors, Piezoresistive wearable sensors, Photoluminescent sensors, terahertz sensors, biosensors, chemical sensors, sensors for macromolecules and cells | [343–345] |
| Electronics and Photonics | Electrical contacts, conductive fillers, Energy harvesting, ferroelectric materials, piezoelectric materials, thermoelectric materials, Optoelectronics, plasmonic | [337,343] |
| Catalysis | Electrocatalysis, photocatalysis, CO catalyst, CO ₂ reduction O ₂ evolution electrocatalyst, H ₂ generation, oxygen reduction reaction (ORR), Catalyst for NH ₃ synthesis from N ₂ , Membrane separation, toxic heavy metal Cr (vi) adsorption, Lead adsorption, Phosphate sequestration, freestanding membranes for the charge- and size-selective rejection of ions and molecules, dye adsorption, radionuclide pollutant adsorption | [339,342, 346] |
| Water purification | Membrane separation, toxic heavy metal Cr (vi) adsorption, Lead adsorption, Phosphate sequestration, freestanding membranes for the charge- and size-selective rejection of ions and molecules, dye adsorption, radionuclide pollutant adsorption | [339,347] |
| Biomedical | Antibacterial, bioimaging, biosensing, therapeutics, theranostics, nanomedicine | [348,349] |

composite semiconductors, surface defects, etc. [354]. Fig. 6 shows the applications of chalcogenide nanocrystals.

11. Quantum dots

Quantum dots (QDs) are nano-sized semiconductor particles with optical and electronic properties involving quantum mechanics. These materials can be of silicon, cadmium sulfide, cadmium selenide, indium arsenide, carbon, graphene, etc., or in general, made up of groups II to VI or III to V elements [15]. QDs are often known as artificial atoms, which



Fig. 6. Applications of chalcogenide nanocrystals [355–357].

exhibit discrete energy levels. These atoms exhibit unique luminescence electronic properties such as wide and continuous absorption spectra, narrow emission spectra, and high light stability [358].

QDs can be synthesized through top-down and bottom-up methods. Molecular beam epitaxy [169], e-beam lithography, ion implantation, and X-ray lithography are some of the Top-down processing methods. Whereas, colloidal QDs are prepared by self-assembling the solution following a chemical reduction in the Bottom-up approach [359]. In the top-down processing approach, a bulk semiconductor is thinned. For example, to get a 30 nm QD, reactive-ion etching, electron beam lithography, and/or wet chemical etching are commonly used. Bera et al. [360] reported that bottom-up approaches are mainly categorized as wet-chemical and vapor-phase methods. The wet chemical process involves microemulsion, competitive reaction chemistry, sol-gel, and hot-solution decomposition. Whereas, vapor-phase methods involve molecular beam epitaxy [169], liquid metal ion sources, sputtering, or aggregation of gaseous monomers. Murray et al [361] introduced the organometallic colloidal synthesis (OCS) for the development of QDs. The process involves high temperature using a high boiling point organic solvent like trioctylphosphine, tri-n-octyl phosphine oxide or hexadecyl amine, etc.

Quantum dots have been introduced to several applications like in energy conversion and storage, sensors, environment, optoelectronics, membrane technologies, biotechnology, chemiluminescence, catalysis, anti-cancer, drug delivery, antibacterial, disease detection and diagnosis, flexible devices, food sciences, etc. [362–366]. However, applications of QDs vary with the involvement of doping elements and scaffolds. Among others, graphene-based quantum dots (GQDs) and carbon-based quantum dots (CQDs) are vastly investigated and applied to several fields [367]. GQDs have been used in fuel cells as catalysts or catalyst supports, in dye-sensitized solar cells (DSCs) as sensitizing dyes, catalysts, or hole conductors, in light-emitting diodes (LEDs) as color converters or light emitters, in photovoltaic cells as an electron acceptor or electron donor, in lithium-ion batteries and supercapacitors as electrode materials, in bioimaging as multifunctional core-shell structured capsules [368]. Graphene quantum dots have been doped with different elements to attain the specific characteristics of specialized applications. Kaur et al. [362] reported synthesis methods and applications of Nitrogen-doped GQDs in energy, sensors, and the environment. It has been reported that GQDs have exhibited better characteristics than graphene or rGO in biological medicine due to smaller two-dimensional nanosize [369]. Molaei [365] reported that CQDs are nontoxic compared to semiconductor quantum dots and their applications can be found in bio-imaging, drug and gene delivery, optical sensors, chemiluminescence, and electro-chemiluminescence. CQDs can be made synthetically and also can be derived from natural resources like watermelon peel, hair fiber, citric acid, sweet red pepper bovine serum of albumin, PEG-200, and PVA, chitosan alginic acid, starch, lotus root, *Saccharum officinarum* juice, grass, pomelo peel, orange juice, strawberry juice, orange pericarp, cabbage, aloe, papaya, pseudo-stem of a banana plant, sweet potato, rose-heart radish etc. [370]. Apart from GQDs and CQDs, semiconducting quantum dots of CdSe/ZnS, CdSe, CdSe/CdS, ZnSe, CdSe/ZnS, ZnSe:Mn, PbSe, CdSe/CdS, CdSe/CdS/ZnCdS, CdSe/CdS/ZnCdS/ZnS, ZnSe/CdSe/ZnS, CdSe/CdS/ZnS, CdSe/SiO₂ etc. have also been synthesized, characterized and investigated for several applications [360]. A detailed list of different applications for various quantum dots is provided in Table 5.

12. Application chemistry of nanomaterials

12.1. Graphene and its composites

Understanding chemistry of materials is very important to understand their impact on specific applications. Graphene contains a single atomic sheet of conjugated sp² carbon atoms. It has a double-sided surface, which enables its every carbon atomic to react and result in a

Table 5

Applications of different quantum dots.

| Area of application | Specific application | Ref. |
|-------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|
| Energy conversion and storage | Photovoltaics, light-emitting diodes, photodetectors, thermoelectric devices, supercapacitors, rechargeable batteries, photocatalytic energy conversions, electrochemical energy conversion, electrocatalytic energy conversion, solar cells, resonance energy transfer, energy harvesting | [371–376] |
| Medical and biological applications | Bioimaging, cellular imaging, real-time molecular tracking in live cells, optical imaging, biosensing, photoluminescence sensors, electrochemiluminescence sensors, electrochemical sensors, colorimetric detection, drug/gene delivery, anticancer agents, antibacterial and antioxidant activity, application of QDs in organs like integumentary system, brain system, digestive system, pulmonary system, urinary system, cardiovascular system, musculoskeletal system, etc. photothermal and photodynamic therapy | [377–381] |
| Environmental applications | Water purification, sensing, and removal of heavy metals, organic and inorganic pollutant removal, dyes removal, gaseous pollutant adsorption, membrane separation, catalytic degradation of pollutants, disinfection of wastewater | [382–386] |
| Catalysis | Photocatalysis, electrocatalysis, photo-electrocatalysis, chemical catalysis, electrochemical catalysis, CO ₂ reduction, hydrogen evolution reaction, oxygen reduction/evolution, H ₂ O ₂ oxidation water splitting, selective hydrogenation, nitrogen reduction reaction, methanol oxidation, carbon-carbon coupling | [371, 387–395] |
| Food Science | Foodborne pathogens, protein tracking, detection of flavor compounds-vanillin sensor, determination of potassium ferrocyanide in table salt, melamine detectors, pesticide residues detection, antibiotics, and other veterinary drug residues detection, bacteria detection, vitamins, amino acids and proteins, and sugars detection | [396–398] |
| Flexible devices | Flexible memory devices, flexible electrochromic devices, flexible photodetectors, memristive devices, flexible light-emitting diodes, flexible perovskite solar cells, flexible batteries, flexible supercapacitors, flexible ultraviolet pumped white-light-emitting diodes | [371, 399–405] |

variety of reactions. Due to inherent properties when graphene is added for developing composites it results in upgradation of the properties of the material like electrical conductivity, mechanical strength, optical absorption etc. [406]. Herein, we report some of the common application chemistries of graphene-based nanomaterials. Tayebi et al. [407] reported the application of hybrid graphene nanosheets with ZnO for photocorrosion suppression and photoelectrochemical enhancement. Study reports that the developed graphene-ZnO nanorods (ZnO/GNR) showed better photocatalytic degradation of methyl orange and photocorrosion suppression compared to graphene/ZnO nanoparticles (ZnO/GNP), ZnO nanorods and ZnO nanoparticles. Firstly, this is because of crystallinity of ZnO nanorods compared to ZnO nanoparticles, secondly oxygen vacancies and defect sites trap electrons result in higher photocatalytic activity, which are higher in ZnO nanorods compared to ZnO nanoparticles. Lastly, higher aspect ratio helps in photocatalytic activity, which is higher for ZnO in GNR compared to ZnO in GNP, this is another reason which resulted in higher photocatalytic activity for ZnO/GNR compared to ZnO/GNP. Furthermore, the incorporation of graphene resulted in close contact of ZnO NR and

MO molecules adsorbed on graphene sheets due to π - π interaction, which suppressed the photocorrosion process due to consumption of photoinduced holes during photodegradation of methyl orange. A simplified reaction mechanism is exhibited in Fig. 7.

Graphene nanocomposites are well recognized for photoelectrochemical water-splitting applications. Owing to the nature of graphene oxide, it has adjustable electronic properties because of 2D carbon composition, which provides an ease in its surface modification. In graphene oxide semiconductors are deployed for water-decomposition. Four major principal methodologies are involved in photocatalysis like light-harvesting, excitation charging, separation and charge transfer and reactant surface reactions [408]. In the presence of light, photocatalysis requires a higher or equivalent energy compared to photocatalyst bandgap. The general requirement for a photocatalyst is to have a semiconductor with bandgap higher than 1.23 eV, which on the absorption of the it generates electron-hole pairs. The photocatalyst makes electronic transitions and generates pairs of e^-/h^+ under appropriate photon excitation. This is followed by separation of charges prior to the excitation of electrons from the valence band to the conduction band, which leaves holes in the valence band. The next stages involve the oxidation and reduction reactions with water, which includes electrons and holes. Oxidation involves dissociation of water molecule into H^+ , where H^+ gains an electron to produce H_2 , through reduction reaction [409,410]. Li et al. [411] synthesis of core/shell cable-like Ni_3S_2 nanowires/N-doped graphene-like carbon layers for electrocatalytic water splitting. Fig. 8 exhibits generalized reaction scheme for water splitting by using graphene-based nanocomposites.

12.2. Carbon nanotubes and their composites

Composites and nanomaterials of carbon nanotubes are widely used for several applications. One of major areas of recent applications for carbon nanotubes and their nanocomposites is hydrogen and oxygen evolution reactions [412,413]. In electrocatalytic applications, physics is more involved compared to chemistry. However, chemistry is more involved in material synthesis and their modifications. Lin et al. [414] reported oxygen plasma-activated hybrid structure of Ni-Fe Prussian blue analog (PBA) interconnected by carbon nanotubes (O-CNT/NiFe) for efficient oxygen evolution reactions. Study reports that mass ratios of CNTs to Ni-Fe PBA significantly effect on the electrocatalytic performance. In the CNTs, oxygen plasma plays the vital in activating CNTs, the oxygen plasma activated carbon nanotubes delivered higher current density and lower OER overpotential compared to untreated carbon

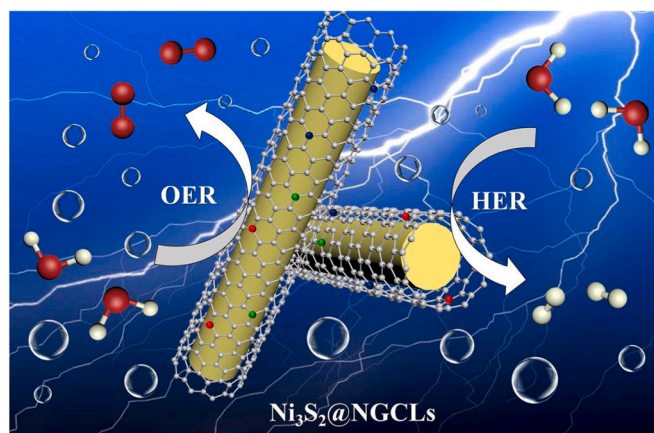


Fig. 8. Oxygen evolution reaction, hydrogen evolution reaction, and overall water splitting by using N-doped graphene based nanocomposites [411].

nanotubes. This is because oxygen plasma treatment created defects on the surface of carbon nanotubes, thus making them rough. The structures and generalized mechanism for oxygen evolution reactions by using carbon nanotubes is provided in Fig. 9 for potential Vs current

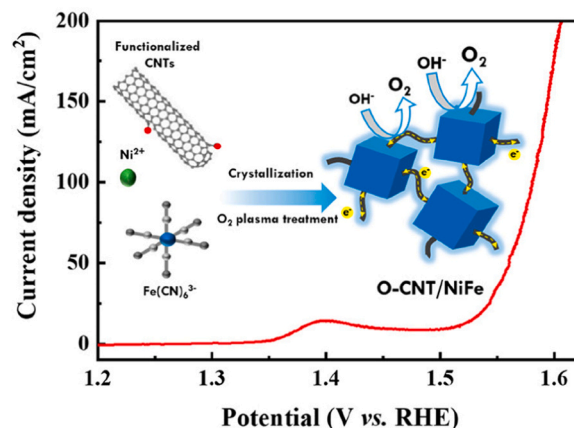


Fig. 9. Schematic Illustration of the proposed approach to synthesize O-CNT/NiFe and their application for oxygen evolution reactions [414].

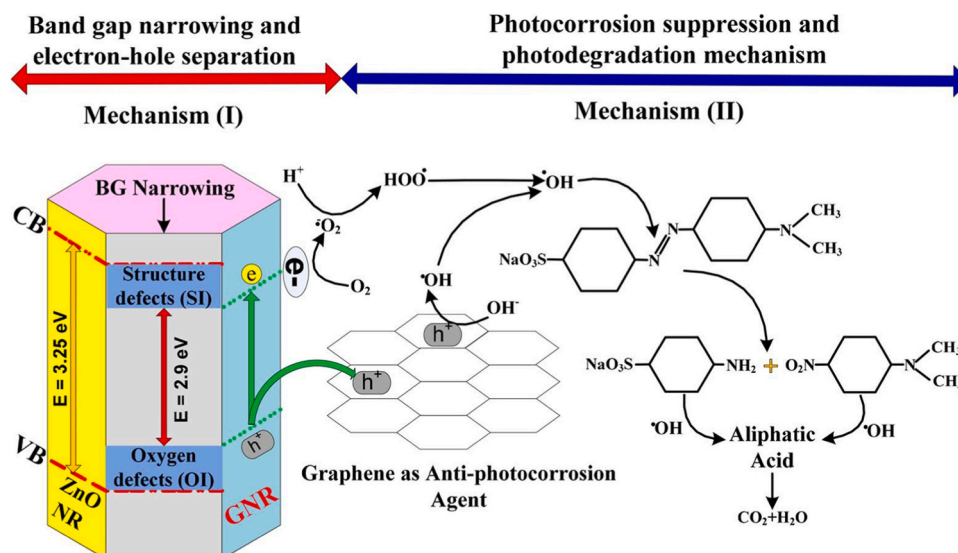
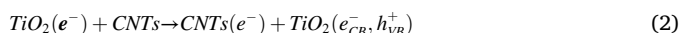


Fig. 7. Reaction mechanism for photodegradation of methyl orange and photocorrosion suppression using ZnO and graphene nanorods [407].

density.

Apart from material synthesis, chemistry dominates on various application of nanomaterials. For example, in wastewater treatment processes, such as degradation of organic pollutants, removal of dyes and even metals, catalytic processes such as electrochemical and biochemical reactions, etc. As an example, reaction mechanism for photocatalytic degradation of methylene blue dye using TiO₂ NRs/CNTs is provided as under in Eqs. (1)–(8) [415]:



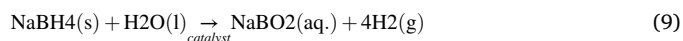
12.3. Nanoclay composites and polymers

Nanoclay composites and polymers an important class of nanomaterials, which has some attractive applications such as automotive, construction, aerospace, food packaging, textiles etc. [416]. Synthesis parameters control the physical, chemical, thermal, mechanical, and morphological characteristics of clay nanocomposites. Modification of the clay nanocomposites an important aspect, in which desired properties in the nanocomposites are obtained. The montmorillonite is hydrophilic, and the stacks of clay platelets are held together by electrostatic forces, which makes them incompatible with most organic polymer matrices. To bring the compatibility, most commonly alkylammonium ions are used. Hydroxyl groups are also used with silane compounds for modification of clay nanocomposites. However, there some applications, where application chemistry of clay nanocomposites come into play. Narayanan et al. [417] synthesized clay-graphene oxide nanocomposite catalysts for solvent free multicomponent Biginelli

reactions. Authors proposed that in first step nucleophilic addition of urea takes place to aldehyde to produce hemiaminals [N-(1-hydroxybenzyl)-urea]. In the second step, formation of N-acyliminium ion takes place rapid dehydration of hemiaminals in the presence of the composite acidic catalysts. This proceeds with π nucleophilic attack of enol tautomer of 1, 3 dicarbonyl compound to the electron deficient N-acyliminium species. This results in the formation of open chain ureide, which then is cyclized to produce corresponding Biginelli compound as shown Fig. 10.

12.4. Nano-structured thin films

Nano-structured thin films are not a type of nanomaterial, rather they are a morphological class of nanomaterials. Nano-structured thin films can be of any material for example, metals, metal organic frameworks, graphene, polymers etc. Nanostructured thin films provide outstanding surface area. Given the desired properties, some of major applications of thin films are in electronics, optics, catalysis, energy storage and harvesting, medical imaging etc. Production of H₂ is reported by using thin films of rGO-grafted with carboxymethyl chitosan and Ag nanoparticles [418]. The study reported production of hydrogen using hydrogen-storage compounds like NaBH₄. The hydrogen is proposed to be produced by the following reaction (9).



It is reported that catalyst surface adsorbs the borohydride (BH₄⁻) ions first, lead followed by the reaction of water with adsorbed BH₄⁻ ions. Transfer of H⁻ takes place from adsorbed BH₄⁻ ions to the AgNPs, which is followed by the reaction of H⁻ species with water to produce H₂ [419]. Fig. 11 provides an overview of production of hydrogen through degradation of NaBH₄ over GL/rGO-CMCHT@Ag thin film.

There are several other applications of nanostructured thin films, where chemistry plays an important role. One of the common areas of nanomaterials is wastewater treatment, which includes removal of organic contaminants, metals, and dyes. Elias et al. [420] reported Ce doping in ZnO/CNT composite thin film for visible light photo-catalysis of methylene blue. Study reported that with visible light irradiation, valence electrons move to conduction band (CB) of ZnO surface resulting charge vacancy or holes (h⁺). Under light irradiation, the carbon nanotubes act as electron acceptor and ZnO as donor. Photocatalytic efficiency enhances due to negatively charged metal and carbon

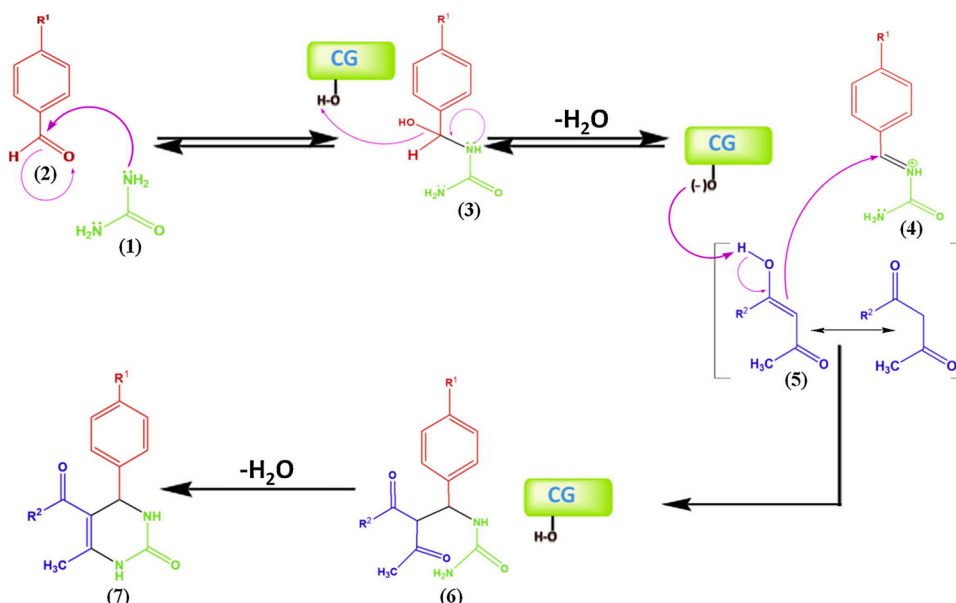


Fig. 10. Biginelli reaction over clay – GO nanocomposite [417].

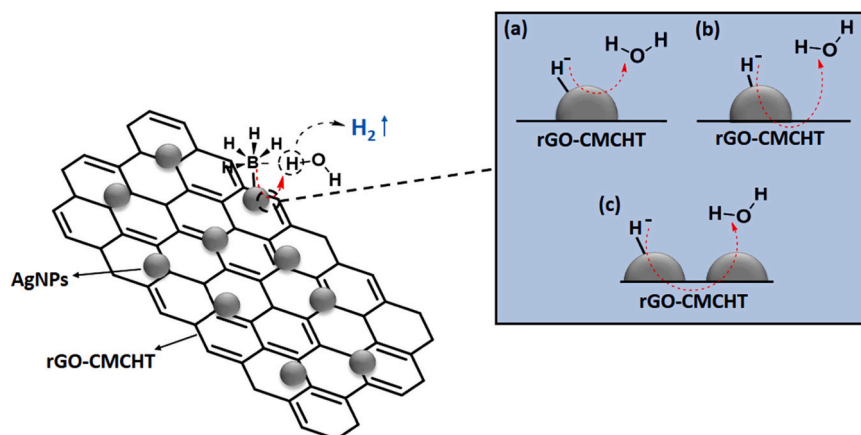


Fig. 11. Reaction pathway for hydrogen production through degradation of NaBH_4 over GL/rGO-CMCHT@Ag thin film. The mechanism involves transfer of three electrons like (a) from AgNP to the solvent molecule, (b) through graphitic structure of rGO-CMCHT to the adjacent AgNP or (c) via AgNP to another adjacent nanoparticle [418].

nanotubes by accelerating the transfer of electrons to dissolved oxygen through formation of superoxide radical ion ($\text{O}_2^{\bullet-}$), which causes oxidation of the target pollutant. Whereas the hole (h^+) oxidizes H_2O or OH^- to produce hydroxyl radical ($\bullet\text{OH}$). Fig. 12 shows the photodegradation mechanism of methylene blue using Ce-doped ZnO/CNT nanocomposite thin film.

12.5. Metal-organic frameworks

Metal-organic frameworks are a class of porous polymeric material, which consist of metal ions linked together by organic bridging ligands. The nanomaterials of MOFs have shown amazing characteristics and results for various applications like catalysis, separation processes, energy storage and harvesting, drug delivery and storage, luminance, sensors etc. Combining catalysis and separation process, MOFs have been reported as promising materials for CO_2 capture and conversion processes [421]. separation or capture processes involve CO_2 adsorption of MOF based membrane separation. The CO_2 conversion involves photo and electro chemical processes, hydrogenation and CO_2 chemical fixation using epoxides. Li et al. [422] reported successful synthesis of porous Ni(II)-organic framework with Lewis acid–base bifunctional sites for cycloaddition of CO_2 to epoxides for cyclic carbonates. Study proposed that initially Lewis acid opens the Ni sites and activates the styrene oxide by forming Ni–O adduct. Then the Br^- of the Tetrabutylammonium bromide (TBAB) attack the β -carbon atom as a

nucleophile with less sterically hindered C of epoxide resulting ring-opening reaction. In the meantime, Lewis base of amine groups activates the CO_2 molecule resulting in the formation of a carbamate salt, which is then attacked by the ring-opened epoxide as a nucleophilic. The end formation of cyclic carbonate takes place due to ring-closure, which also results the regeneration of the catalyst as shown in Fig. 13.

Among several other applications and their chemistries, one of the important reactions is asymmetric sulfoxidative cross-coupling. Sulfoxides are important building blocks for several organic compounds, asymmetric synthesis of natural products, and biologically active compounds. Ghorbani and Taherinia [423] reported synthesis of Cobalt-based peptide metal organic frameworks (Co-P-MOFs) for asymmetric sulfoxidative cross-coupling. Study reports that formation of a tetrahedral intermediate (1) takes place when hydroxide ion attacks on the poly sulfinylpiperazine. This is followed by the formation of intermediate (a) through the reaction of phenyl boronic acid with poly sulfinylpiperazine. At the end intermediate (a) reacts with intermediate (b), which leads to trans metalation and reductive elimination to produce the coupling product (c) shown in Fig. 14.

12.6. Conducting polymers and their composites

Conducting polymers and their composites are an environment-friendly and sustainable category of nanomaterials. These materials have attracted several applications such as biomedical, optics, micro-electronics, sensors, energy storage/conversion/saving devices, wastewater treatment, etc. [424]. The chemistry of photocatalytic degradation of dyes using conducting polymers is fascinating. Generally, four interactions between catalyst and the target compound take place like π – π interaction, electrostatic ionic interactions, hydrogen bonding and hydrophobic interactions. Similar like other photochemical reactions, on the irradiation of light electrons of the valence band of both MoSe_2 and PPy would be excited and transfer to the conduction band leaving behind holes. The photogenerated electrons in the conduction band of PPy could easily transfer to the conduction band of MoSe_2 in case of the MoSe_2 PPy nanocomposite, because of the potential difference between conduction band of MoSe_2 and PPy. Electrons in the conduction band of MoSe_2 may react with dissolved oxygen resulting the formation of superoxide radicals ($^{\circ}\text{O}_2^-$), leading to the oxidation of organic dye to harmless products as shown in Eqs. (10)–(18) [425].

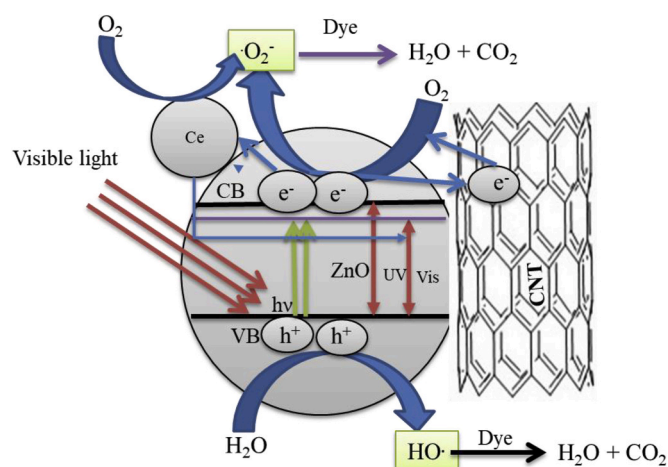
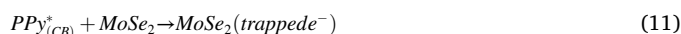
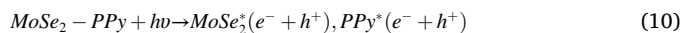


Fig. 12. Photodegradation of methylene blue under visible light by using Ce-doped ZnO/CNT nanocomposite thin film [420].

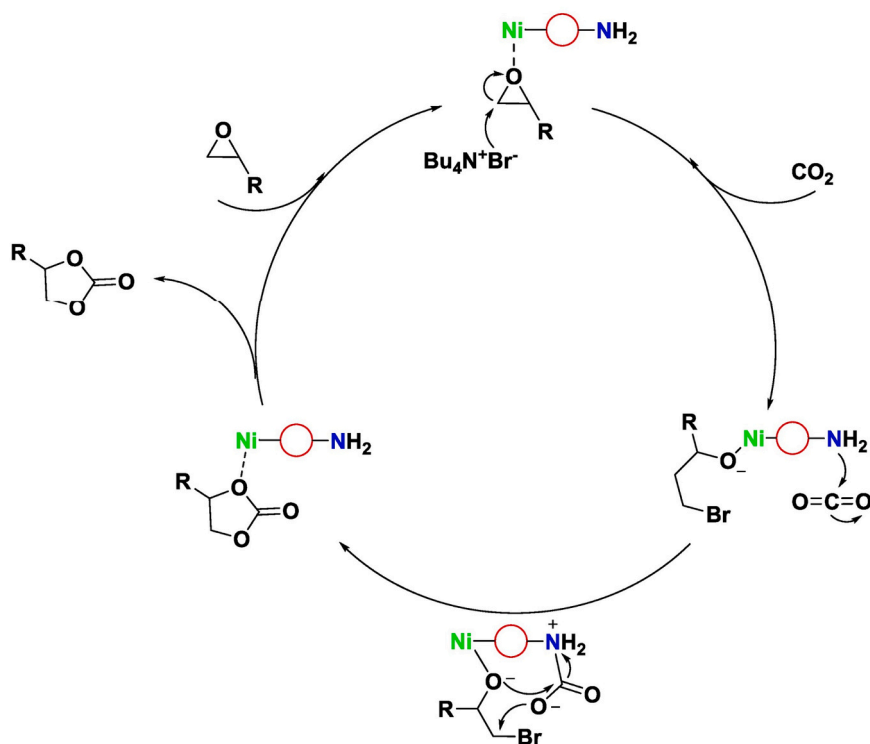


Fig. 13. Proposed reaction pathway for cycloaddition of CO₂ to cyclic carbonate catalyzed by Ni-MOF-1a/TBAB [422].

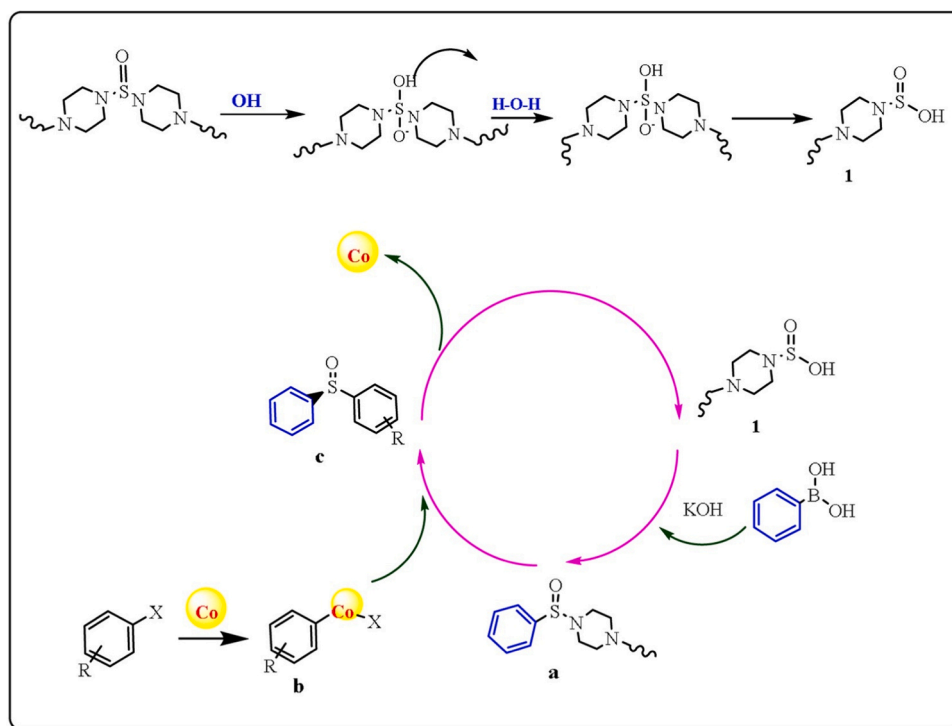


Fig. 14. Asymmetric sulfoxidative cross-coupling reaction in presence of Chiral cobalt-peptide metal-organic framework (Co-P-MOF) [423].

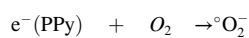
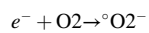
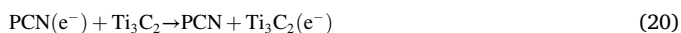
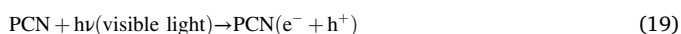




Fig. 15 provides a generalized reaction scheme for photodegradation of dyes by using MoSe₂ PPy nanocomposite.

12.7. MXenes

MXenes have exhibited attractive results for several applications, for example energy storage and conversion devices, sensors, electronics and photonics, catalysis, water purification, biomedical, separation processes etc. One of the prominent areas for the applications of MXenes is photocatalysis. Some of the major photochemical applications of MXenes involve photocatalytic hydrogen evolution, photocatalytic reduction of CO₂, photocatalytic degradation of pollutants, photocatalytic nitrogen fixation etc. Like all other photocatalytic processes, MXenes and target compound also go through light absorption resulting electron excitation, separation, and migration of photogenerated carriers, recombination of photoexcited electrons and holes and redox reactions [427]. Liu [428] reported synthesis of 2D/2D Ti₃C₂/Porous g-C₃N₄ nanolayers composite for degradation of organic pollutants with and without light. It is proposed that in the first step, electrons on the conduction band of g-C₃N₄ may be excited to the valence band in presence of light, and in the second step, the photoinduced electron may be migrated from porous g-C₃N₄ to the surface of Ti₃C₂. The electron may react with O₂ to form $\bullet\text{O}_2^-$ and may lead to the formation of $\bullet\text{OH}$ radicals. In the presence of light, the combination of h^+ , $\bullet\text{O}_2^-$, and $\bullet\text{OH}$ may decompose pollutants like phenol to CO₂ and water. The detailed reaction mechanism is provided in Eqs. (19)–(22).



Pharmaceutical wastes are the emerging pollutants which are hazardous to health and environment. Naproxen is a nonsteroidal anti-inflammatory drug whose concentration, even in parts per billion can cause significant health problems. Fayyaz et al. [429] reported development of cobalt spinel ferrite decorated Ti₃C₂Tx MXene activated

persulfate system for degradation of Naproxen. It was proposed that interactions of cobalt and iron moiety with MXene nanosheets may moderate the oxidation/reduction reactions leading to a better Naproxen degradation. The electronic migration may result in the formation of SO₄^{•-}/S₂O₈^{•-} from persulfate (PS) by thermodynamically favorable oxidation of Co(II)/Fe(II)/Ti(II) and reduction of Co(III)/Fe(III)/Ti(IV). Electron spin resonance (ESR) spectroscopy analysis confirmed that CoFe₂O₄@MXene nanohybrids can form more $\bullet\text{OH}$, SO₄^{•-}, and O₂^{•-} species and corresponding nonradical ¹O₂ compared to the individual CoFe₂O₄ and MXene by PS activation. A detailed reaction mechanism is shown in Fig. 16.

12.8. Chalcogenide nanocrystals

Chalcogenide nanocrystals are used for various applications such as energy storage and energy harvesting devices, thermoelectric devices, detectors, emissive materials, sensors, biomedical devices etc. Among various chalcogenide nanocrystals, the applications of the compound copper chalcogenide nanocrystals are widely investigated and accepted. This is because of their compositional and structural versatility. Their band structure and defect concentration play the vital role in property development [430]. Cui et al. [431] reported synthesis of various copper based chalcogenide nanocrystals for near-infrared plasmonic-enhanced solar energy harvest. Investigation exhibited strong near-infrared absorption plasmonic absorption of Cu₇S₄@Pd providing hot carrier from Cu₇S₄ to Pd, which resulted in catalytic reactions on Pd surface. This enhancement may improve the sunlight use in a wide range of photocatalytic reactions, such as Suzuki coupling reaction, oxidation of benzyl alcohol and hydrogenation of nitrobenzene. Fig. 17 shows the possible photocatalytic reactions of copper chalcogenide heteronanostructures.

12.9. Quantum dots

Quantum dots are fascinating nanostructures of different materials. These nanomaterials have applications in various areas such as energy conversion and storage, medical and biological applications, environmental applications, catalysis, food Science, flexible devices, chemiluminescence etc. Among others, the applications of quantum dots of carbon and graphene-based materials are more common. Chemistry of chemiluminescence is fascinating, as these reactions emit light (lumi-

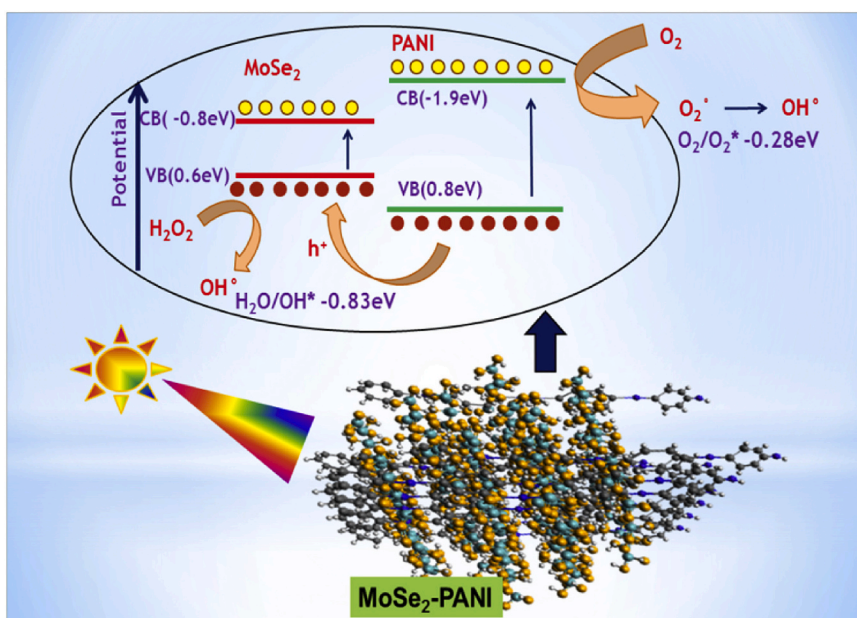


Fig. 15. Photodegradation mechanism of dyes by using MoSe₂ PPy nanocomposite in presence of light [426].

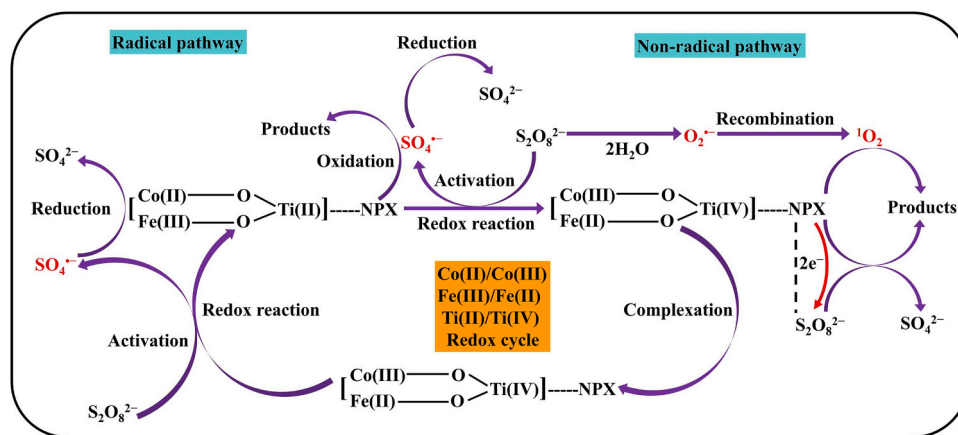


Fig. 16. Radical and nonradical-mediated NPX degradation with persulfate activated by CoFe2O4@MXene nanohybrids [429].

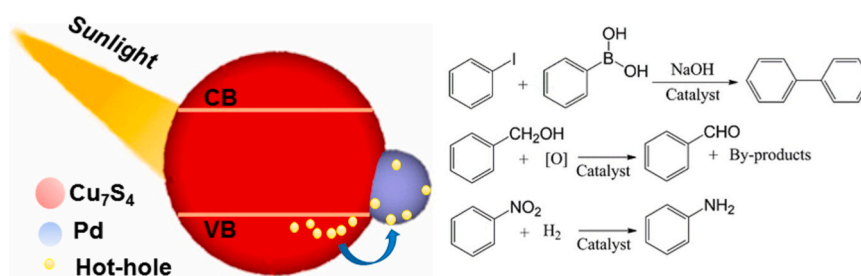
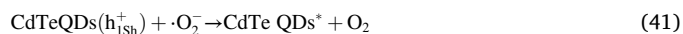
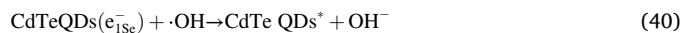
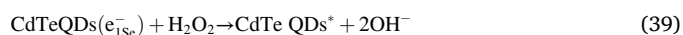
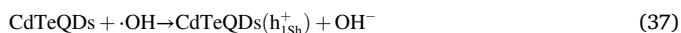
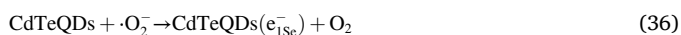
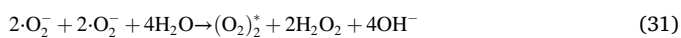
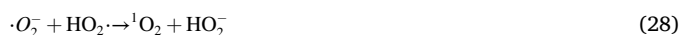
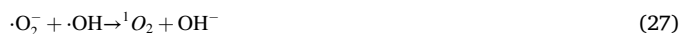
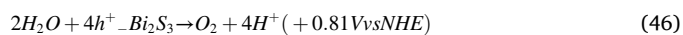
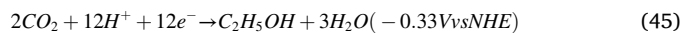
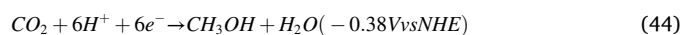
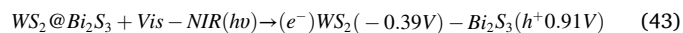


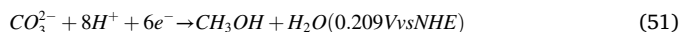
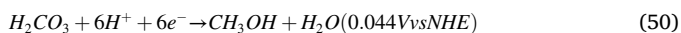
Fig. 17. Possible reaction mechanisms for photocatalytic reactions by using Cu7S4/Pd nanostructures [431].

nescence). Let us take an example of chemical reactions of NaHCO₃-H₂O₂-CdTe quantum dots system for chemiluminescence as shown in Eqs. (23)–(42) [432].



Another aspect of use of quantum dots is the environmental remediation, this includes but not limited to wastewater treatment and CO₂ mitigation. In the environmental remediation technologies, the quantum dots can be used as photo-catalysts, metal ion indicators, membranes and adsorbents [385]. For quantum dots of Tungsten disulfide (WS₂) seeded over Bismuth(III) sulfide (Bi₂S₃), it is reported that in WS₂@Bi₂S₃ structure, exposed S atoms in WS₂ quantum dots combined Bi³⁺ ions to produce Bi–S bonds, and results S-sharing between WS₂ and Bi₂S₃ unit cells. This results low resistance for fast electron transfer on the interface leading to efficient separation of electron-hole pairs. The detailed reaction chemical reactions for photocatalytic reduction of CO₂ over WS₂@Bi₂S₃ are provided in Eqs. (43)–(51) [433]:





Nie et al. [434] reported photocatalytic degradation of organic pollutants like p-nitrophenol (4-NP), diethyl phthalate (DEP) and ciprofloxacin (CIP) by using graphene quantum dots/Mn-N-TiO₂/g-C₃N₄ composite (GQDs/TCN-0.4). Along with photodegradation of pollutants, reactions also resulted in evolution of hydrogen gas. It is reported that $\bullet\text{OH}$ and h^+ were the active species in the degradation process. However, the major contributor to the degradation of 4-NP and CIP was $\bullet\text{OH}$ and h^+ was effective in degradation of DEP. The proposed photocatalytic degradation of organic pollutants over GQDs/TCN-0.4 is exhibited in Fig. 18.

13. Nanomaterials: toxicity, environmental impact, and waste-handling & recycling

13.1. Toxicity

Nanoparticles are fabricated and formed naturally during various processes, for instance, volcanic eruption, erosions, and forest fires. Generally, contamination is linked with human activities involving industries, for example, charcoal and fuel burning, and natural events, such as dust storms [435]. Nanoparticles' toxicity mainly depends on their root source, durability, dimension, and dose, moreover, intake, or exposure via different pathways. Toxicity may depend on various parameters that include size, bulk or surface chemistry, mass, aggregation, and surface area [436]. Few other essential parameters which affect their toxicity are aspect ratio, modification, surface coating, and crystalline morphology.

Toxicity of the nanomaterials is one of the major challenges for chemists, engineers, and scientists involved in nanomaterial development. The toxicities of the nanomaterials include cytotoxicity, dermal toxicity, pulmonary toxicity, genotoxicity, carcinogenic toxicity, liver toxicity, cardiovascular toxicity, hemolytic toxicity, and immune toxicity [437,438]. The potential mechanisms of the toxicities of the nanomaterials are apoptosis, reactive oxygen species, free radical formation, formation of granuloma, increased inflammatory response [439,440]. The administration routes of nanomaterials to human beings are intravenous, intraperitoneal, and oral [441,442]. Toxicity varies with the type of the nanomaterial, their physiochemical characteristics like morphology, electrical properties, magnetic properties, optical properties, surface properties, charge, size and size distribution, surface chemistry, oxidation, composition and crystalline structure,

aggregation, and concentration, dispersion state, synthesis methods, etc. [443–445]. The size and shape of the nanomaterials are reported to affect the cellular uptake. Particle size affects the mass diffusivity, sedimentation velocity, attachment efficiency, and deposition velocity over the biological surfaces [441]. The different particle sizes may behave differently for different cells. For example, silver nanoparticles of sizes 10, 50, and 100 nm are reported to induce toxicity in HepG2 cells through autophagy lysosomal system and inflammasome activation [446]. Whereas, for the same cell, the silver nanoparticles of less than 10 nm in size induced toxicity through oxidation changes or stress [447, 448]. The toxicities of the nanomaterials increase with an increase in their concentration [449]. The proteins, biomolecules, and micro-nutrients might get altered by the presence of different functional groups [437]. The synthesis methods are also reported to affect the toxicities of the nanomaterials, due to impurity residues and improper finishing. The nanomaterials can be dangerous for human beings and badly affect their cardiovascular and central nervous system, malfunctions in different organ systems, cause neurotoxicity, or immunotoxicity. The toxicity flow framework is presented in Fig. 19.

To assess the toxicity of nanomaterials, the comparison of their noxious effects with nanoparticles and different bulk types can be

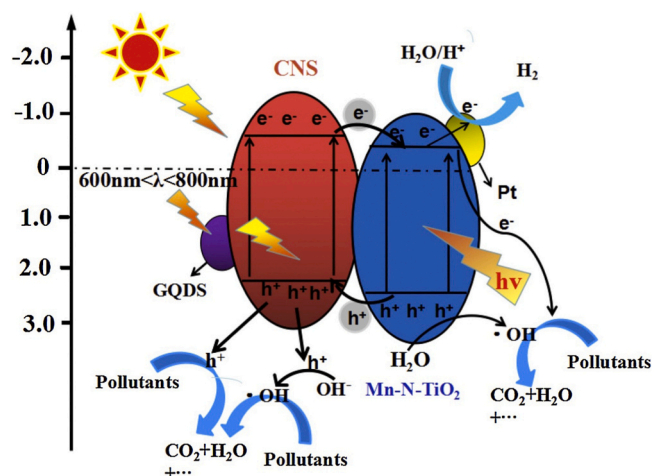


Fig. 18. Photodegradation of organic pollutants and hydrogen evolution over GQDs/TCN-0.4 [434].

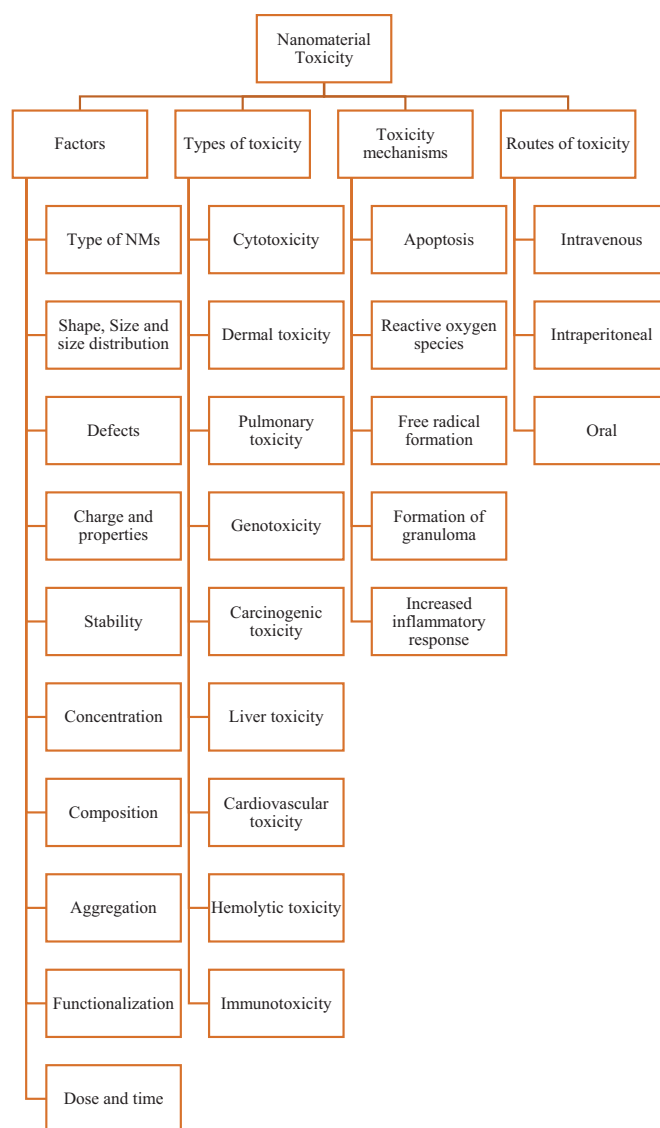


Fig. 19. Toxicities of nanomaterials, their mechanisms, routes, and factors affecting damage [437,450–452].

examined. Many research studies have been conducted and examined in other reviews. Hoet and co-associates' studies observed that breathe in 20 nm (TiO_2) nanoparticles with a minimum dosage of 10 mg/m^3 can cause greater lung tumor than 250 mg/m^3 (30 nm) [453]. The amount of nanoparticles that reach a biological system, can be associated with exposure or concentration of nanoparticles in food, air, and water, and increased via contact duration [454]. It has been reported that carbon nanotubes are more toxic than carbon black silver, Fe_2O_3 , Si_3N_4 , Al_2O_3 , and ZrO_2 . Hence, carbon nanotubes' toxicity differs depending on their types, diameters, and functionalities. Silver nanoparticle aggregate was noted to be more noxious than zirconia, iron oxide, alumina, and asbestos [455].

Besides, the small size of nanomaterials can cause a problem and have harmful effects on the environment. Research conducted on the toxicity of nanomaterial by Sidiropoulou and co-associates showed that iron nanoparticles can accumulate in organisms and source many effects, for example, apoptosis, reactive oxygen species, and oxidative stress production. The mechanism of growth of nanomaterials in organisms can arise by ingestion or inhalation and can spread to different organs and tissues and source toxicological effects on the body [456]. Yet, many studies have performed the study of toxicological effects of nanomaterials on animal and plant cells, however, toxicological works of magnetic nanoparticles in plants are still limited. Dai and co-associates have conducted the transformation of copper oxide (CuO) nanoparticles during association with plant cells [457]. The study concluded that the toxicity level from nanoparticles is affected through conversion during association with fragments of the plant cell. CuO can be decreased to Cu_2O with the existence of galacturonic acid in the protoplasts. Conversion into other metal oxides will offer higher toxicity than CuO . Active surface area, and size and shape of particles, and the connected functional group on the material's surface directly affected the toxicity of the nanoparticles, particularly in biotechnology, due to their potential to control the protein mechanism and binding. The binding method can develop several other distressing biological compounds, subsequently reduction of enzymatic activities and also protein degradation. In terms of environmental parameters, nanomaterials are highly inclined by the form of water such as hard water or seawater, moreover, elements of organic compounds may affect the aggregation process of the material. Few other factors are pH, salinity, and colloidal-producing compounds [458]. Additional research works on bio-chemical interaction and kinetics of nanoparticles are imperative to expand on research associating nanoparticles accumulation.

13.2. Environment impacts

Nanomaterials sneak into open environments and waterbodies through different sources and routes. The sources of nanomaterials may be natural, which include volcanic activities, forest fires, clay minerals, soil erosion, weathering, and dust storms, and anthropogenic activities for example burning fossil fuels, automobile traffic, mining/demolition, and nanomaterial production and their waste streams. The nanomaterials produced are used for different applications, which have either direct or indirect contact with an open environment. For example, nanomaterials are used in biomedical applications, electronic appliances, chemical industries, cosmetics, clothes, and in operations like cleaning, packing, sonication, mixing, and spraying, etc. [459,460]. The majority of these nanomaterials end up in the sewage [461]. For example, titanium is reported to accumulate in biosolids, whereas silver nanoparticles can accumulate in biosolids too and turn into Ag_2S if anaerobic conditions prevail. Several, other nanoparticles may enter soil through fertilizers and plant protection products [462]. Soil sedimentation takes place through various roots like STP sludge, direct sedimentation through sanitary landfills, export of matter from incineration plants, particle emissions, etc. [463]. A major portion of biosolids generated in wastewater plants is used for agricultural land purposes. Biosolids carry nanoparticles from wastewater treatment plants hence

deposit them in the soil. Solid waste handling landfill sites host the exhausted or used textiles and fabric containing nanotextile materials. Different studies report that more than 50% of the nanoparticles get carried with wasted textiles to landfill sites [461]. The accumulation or aggregation of the nanoparticle depends on their type, size, and surface characteristics, and the soil properties like pH, ionic strength, and organic matter. The higher pH (around 10 or above) has been observed to retain the nanoparticle from transport, however, the pH range of 5–9 makes the nanoparticle transport faster. Hence, the soils with a pH range of 5–9 may allow the transport of nanoparticles readily into groundwater [464]. Due to chemical and physical processes taking place in the soil due to organic matter, water, oxygen, sunlight, and minerals, the aggregation of nanoparticles may lead to the formation of higher size nanoparticles due to chemical and physical changes. It is also alarming that in sediments, the nanoparticles may get absorbed in soil particles and degrade through biotic and abiotic processes leading to their eventual release in water bodies [465,466]. Even though plants have the natural capability of refusing the toxic components, however, some experiments show that these nanoparticles may be translocated from roots to the leaves and edible parts leading to the toxicity of the food chain [467]. Fig. 20 illustrates the release of nanomaterials from different sources and endangered ecosystem.

Because of their remarkable features, the impacts and noxiousness of nanomaterials on the environment in terms of their association with biological constituents are yet relatively defined. Inclining usage of nanomaterials in various commercial purposes and consumer products tends to incline the likelihood of their contact with humans in direct and indirect ways [468]. Issues have also been highlighted whether the development of nanomaterials can give rise to additional hazards in the lights of their worth, positive and negative effects of nanomaterials on the environment has been described in the section below:

13.2.1. Positive impacts of nanomaterials

Nanotechnology offers considerable social, financial, and environmental advantages. Nanotechnology may eventually be introduced to assist lower the human footprint on the environment by offering more efficient and eco-saving innovations. For instance, nanomaterials are employed in air-craft as an alternate of traditional composites to aid reduce the aircraft weight, saving tons of fuel [469]. Moreover, nanomaterials are introduced in the wind turbine blades to reduce their weight and increase mechanical strength thus helping raise their energy conversion efficiency. Nanomaterials are also used in petroleum refining and automotive exhaust system to lift chemical reactions, whereas, decreasing expenses and pollution. Furthermore, nanotechnology also serves in the production of energy-saving and efficient products in a range of applications. Enormous efforts have been dedicated by the scientific society in the development of carbon nanotube (CNT) 'scrubber' to segregate carbon dioxide (CO_2) from power plant emissions [470]. Besides, several researchers are at work to produce low resistance wire with CNTs, which may have the potential to lessen the transmission power loss. Also, with nanomaterials, a solar panel can be developed in flexible rolls instead of isolated panels and are even printable. Nanomaterials are being sought to transform the waste heat of power plants, and automobiles into a useful source of electrical power [471].

Because of the energy diversification and supportable development systems and resources, there has been a rise in investment in eco-friendly substitute energy systems. In regards to this, microbial fuel cells (MFCs) are a promising approach that can provide the prospect of generating electricity via complex organic effluents and renewable biomass. To enhance the electrical resistivity to corrosion, mechanical strength, and electrical conductivity of MFC, the use of a variety of materials has been taken into account as the element of MFC such as carbon rods, graphite felt, carbon paper, nickel and copper sheet, and stainless-steel mesh. Nanomaterials also display promise for fuel cell applications, hence, to upgrade the properties of few nanomaterials, particularly, CNTs and reduced graphene oxide, they have been

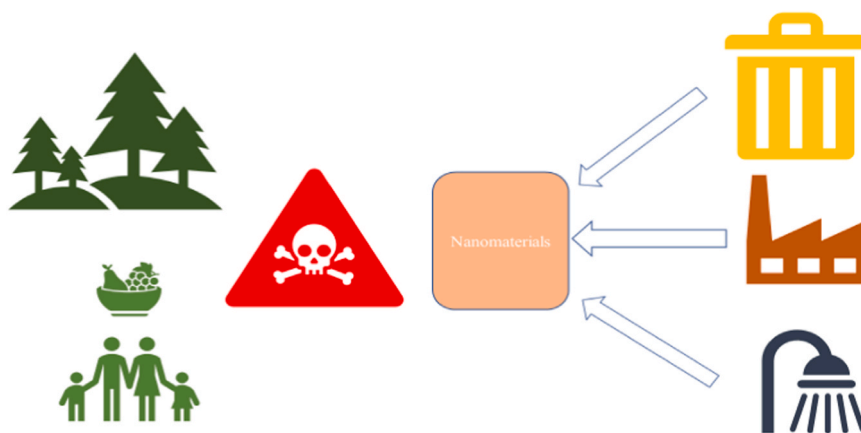


Fig. 20. Major sources of release of nanomaterials and endangered ecosystems.

embedded in various materials to add beneficial features such as mechanical strength, thermal stability, resistivity to corrosion, and conductivity. Ghangrekar and co-associates investigated CuZn microparticles as cathode catalysts in MFC [472]. The results concluded that CuZn a suitable candidate as a cathode catalyst for laboratory and industrial scale. Besides, displayed 64 times higher power density and entitled as the low-cost cathode catalyst. Tang and co-associates developed an anode material in MFC using TiO_2 and egg-white protein-derived carbon assembled core-shell nanoparticles [473]. The prepared anode materials displayed a power density of 2.59 W/m^2 , which was relatively 201% time higher than the control group. Due to the remarkable physical and chemical features of nanomaterials in terms of size and surface effect, hence, allowing its application as cathode and anode materials in laboratory and industrial scale MFC.

Nanomaterials are successfully employed for the cleaning of air and water utilizing filtration, adsorption, and oxidation methods with higher efficiency, compared to traditional methods [474]. One of the main aspects of nanomaterials is that they can be used to respond to pollutants impurities, eventually following to change into non-toxic particles. Nanomaterials coating can fight with the pollutants and display self-cleaning aspects [475]. Moreover, nanomaterials are also utilized in sensing technology to spot pollutants at minor concentrations. Besides, nanomaterials are also used to develop eco-friendly and efficient batteries. Besides, through breaking down oil into biodegradable compounds, nanomaterials can play a vital role in cleaning up oil spills [476]. Fig. 21 illustrates a few of the positive impacts of nanomaterials:

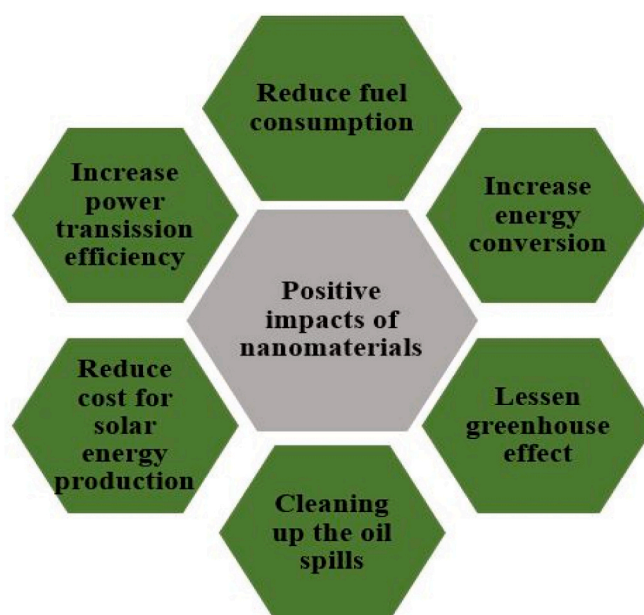


Fig. 21. Positive impacts of nanomaterials.

13.2.2. Negative impacts of nanomaterials

As the environmental impacts of nanomaterials cannot be visibly examined and there are several variables to account for, for instance, low detection limit and identification. It is extremely difficult to come up with any conclusion regarding the ecological effects as well as environmental stability of nanomaterials. Although a minor alteration in the chemical structure of nanomaterials may radically alter their features, transforming them into noxious compounds. Based on the United States Environmental Protection Agency (USEPA) statement, nanomaterials' toxicity is difficult to identify due to their distinct chemical properties, high reactivity, and do not disperse in liquid'. As known that nanomaterials are extremely reactive, therefore, nanomaterials properties in environmental specimen would change between collecting and examining the specimen. Sometimes, it is extremely problematic to discover the root source of nanomaterials in the specimen as well. Lately, researchers have examined the ecological effects of silver sulfide (Ag_2S) nanoparticles. Consequently, it was observed that plant may consume nano-silver if exist in soil, particularly *Cucumis sativus* and *Triticum aestivum* L. The consumption of nano-silver directed to the upregulation of genes, fall in plant growth was accompanied. Furthermore,

nanomaterials helped the upregulation of plant resistance system, which also reduced the plant growth. As the majority of the Ag_2S were gathered at the leaves of the examined plant, such phenomenon inclined the possibility of trophic transfer of these structures via the food chain. The transport of certain nanoparticles, for example, titanium oxide (TiO_2) was also observed to root a genotoxic effect to damage the DNA of the plants, especially *Nicotiana tabacum*. Hence, several researchers stated that the nanomaterials' toxicity is primarily linked with the dispersed materials or metals leached from the nanoparticles.

After nanomaterials are released into the environment, they may react with various contaminants to produce a mixture of materials. The noxiousness of these mixtures must be evaluated to understand such a combination. To this stage, nano-copper oxide (n-CuO) and/or nano-zinc oxide (n-ZnO) were mixed either separately or as a mixture with nano-titanium oxide (n- TiO_2), nano-ferric oxide (n- Fe_2O_3), and nano-chromium oxide (n- Cr_2O_3) for the evaluation of toxicity on plants in regard to root growth inhibition and seed germination. It was concluded that nanomaterials in the blended form possessed low toxicity on the examined plant species, compared to applied as a mixture or individual.

The existence of nanomaterials was also verified to exert low to high toxicity impacts on marine life. In regard to the toxicological

investigation, nanomaterials can affect the uni-cellular marine species and organisms. Kwok and co-associates studied the toxicity effects of nano-cadmium (n-Cd) on the *Daphnia magna*. The result concluded that n-Cd dosage-dependent toxicity on *Daphnia magna*. Besides, nanomaterials have toxic effects on many micro-organisms, such as *Aeromonas hydrophila*. Both n-ZnO and n-TiO₂ exerted noxious effects on the marine bacteria through disturbing bacterial cell membranes. Similarly, nanomaterials showed anti-bacterial activity to cause microorganism's death via the growth of oxygen species close to the bacterial surface. Despite plant and marine systems, nanomaterial's effects on the life of soil were also assessed. To demonstrate the toxicity of nanomaterial on soil organisms, nano-cerium oxide (n-CeO₂) (concentration: 1–100 mN) was used on *Caenorhabditis elegans*. The result concluded that at a low concentration of n-CeO₂, life span decreased by 12%, whereas, at higher concentration, an 18% reduction in life span was observed. Fig. 22 exhibits negative impacts of nanomaterials.

Also, nanomaterials showed negative impacts on the atmosphere. The nanomaterials played a vital role in the development of dust clouds after being discharged into the environment. The limitations linked with the applications of nanomaterials are illustrated in Fig. 22. Inclusive, nanomaterials displayed negative effects on the environment via complicating various environmental systems. Therefore, it can be asserted that unregulated and unmonitored usage of nanomaterials could pose a drastic threat to environment.

13.3. Waste handling and recycling

Nanomaterials being on the full attention of researchers, industries, and governments, unfortunately, has attracted less on their recycling and waste management strategies. A limited number of studies exist on the fate of nanomaterials after the end-of-life stage of nano-products. Nanomaterials have already exhibited environmental and health risks; hence their proper waste management and recycling can mitigate their toxicities. After the end-of-life a nanomaterial product may end up in a recycling system, incinerated or landfilled. These particles can flow through the air, water, and soil. Nanomaterials have the potential to become emerging pollutants if not managed, treated, or recycled properly [477]. Modeling studies indicate that the fate of metallic nanoparticles may be landfilled when they are incinerated [478]. Caballero-Guzman et al. [479] modeled flows of nano-TiO₂, nano-ZnO, nano-Ag, and CNT in the recycling system. The authors found that majority of the materials flow into landfills and incineration plants as waste and a very small portion of it gets recycled for the new products. For example, in the case of Switzerland, 43 tons/year of TiO₂ enters the recycling system, out of which 23 tons/year end up in waste incineration

plants and 13 tons/year goes into landfills, 2–3 tons/year outflows with plastics abroad or goes for production of cement and concrete aggregates and 2% of total gets into the wastewater. The good news is, several recovery processes have recovered significant portions of nanomaterials when the material is present in a recyclable waste [480]. For example, Xiang et al. [481] recovered Zn nanoparticles up to 99%, using thermal procedure-inert gas condensation and vacuum separation from waste Zn-Mn batteries. Similarly, Vermisoglou et al. [482] recovered purified carbon nanotubes up to 70% from supercapacitor materials' waste through filtration and extraction. However, recovery processes are often inefficient or nonexistent due to limits imposed by social behavior, cost, product design, recycling technologies, and the thermodynamics of separation [483]. Thomas and Kolodziejczyk [484] proposed disposal and recycling standards for nano-waste, which include policy to regulate the nanotechnology, precautionary principle for the development of nanomaterials, protocols to respond to potential threats to human health and wellbeing, environment and biodiversity, commercialization pathways and safe disposal. The nanotechnology seems to have a major share in emerging technologies in near future. With emergence and scope expansion, waste handling of nanomaterials becomes a daunting task. This needs significant research, consumer waste handling awareness and strategies, industrial recycling, cost effectiveness, policymaking, and political will.

14. Future perspective

The development of nanomaterials has been rapidly employed in several applications, ranging from micro-electronics to bioengineering industries, as nanomaterials are truly multidisciplinary subjects. Hence, there are still few concerns that need to be addressed before these nanomaterials are available commercially in near future. A few of them are listed below:

- Potential acute and chronic toxic effects; the potential toxicity of nanomaterials cannot be ignored. Therefore, it is essential to study intensively the long-term toxicity of nanomaterials before using them in the living system and environment applications.
- Most of the innovative nanomaterial are patented, therefore, their usage is restricted
- No active laws and regulations on the use of nanomaterials in different applications
- The development of robust, eco-friendly, and economical nanomaterials is also important.
- Inadequate capacities in developing countries to study nanomaterials
- Production of nanomaterial-based products from laboratory scale to industrial scale is also an obstacle that needs to be addressed.
- Economic evaluation of nanomaterials to estimate their viability on an industrial scale
- Understanding chemistry involved in applications

15. Conclusions

This review has enclosed different synthesis and characterization approaches to nanomaterials. Besides, different types of nanomaterials have also been discussed, comprehensively. As mentioned in the review, the nanomaterials possess remarkable prospect. Applications of nanomaterials include nanoprobe sensing, point-of-care devices, cancer biosensors, bone scaffolding, protein separation, water purification and remediation, microbial fuel cell, lithium batteries, electrochemical sensors, catalysis, chemiluminescence, etc. Although there are enormous, exciting potential and feasible applications of nanomaterials, several concerns and challenges stay unsolved up to date, and few of the concerns are listed above.

Regarding the extensive efforts by the scientific society from various science sectors such as medicine, chemistry, material science

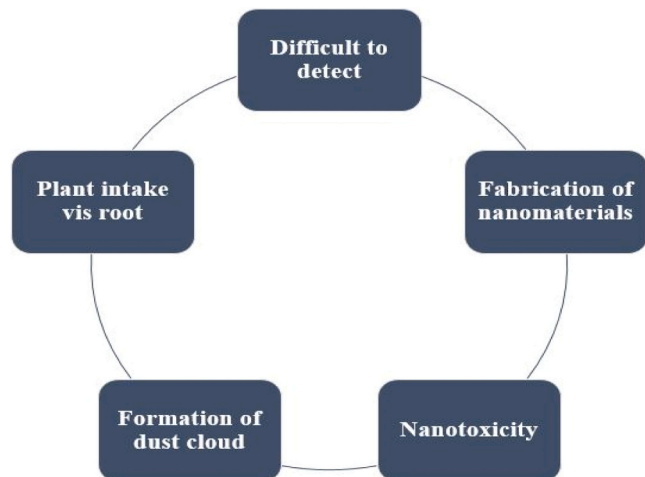


Fig. 22. Negative impacts of nanomaterials.

engineering, biology, and pharmacy, it is prognosticated that positive examples of nanomaterial-based products will be commercially available in the near future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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