MULTIDIMENSIONAL NANOMATERIALS FOR SUPERCAPACITORS:

NEXT GENERATION ENERGY STORAGE

Editors:
Sanjeev Verma
Shivani Verma
Saurabh Kumar
Bhawna Verma

Bentham Books

CHAPTER 1

Introduction of Next-Generation Materials

Neeraj Kumar[1,3], **Shailendra Kumar Dwivedi**[2,4,*], **Om Prakash**[5] and **Shivani Verma**[6]

[1] *School of Studies in Chemistry, Jiwaji University, Gwalior (M.P), India*
[2] *School of Studies in Physics, Jiwaji University, Gwalior (M.P), India*
[3] *IPS group of colleges, Shivpuri Link Road, Gwalior (M.P) India*
[4] *Madhav Institute of Technology & Science, Gola ka Mandir,Gwalior-474005, India*
[5] *Regional Ayurveda Research Institute, Ministry of Ayush, Gwalior, 474009, India*
[6] *Department of Chemistry, School of Physical Sciences, Doon University, Dehradun-248012, Uttarakhand, India*

Abstract: The "next-generation materials" are those materials that have high efficiency, high-performance structural stability, easy manufacturability, and multifunctional capabilities. These new materials can be classified based on dimension, shape, composition, and nanostructure like 0D, 1D, 2D, and 3D. These materials have unique enhanced properties *viz.* electronic, optical, mechanical, magnetic, optoelectronics, vitrification, thermal properties, *etc*. Due to these outstanding features, these smart materials could be a game changer for prospects. Tuning the properties of such advanced materials provides a wide variety of fascinating opportunities. This chapter aims to provide a comprehensive overview of materials used to fabricate supercapacitor point of view and several other latest applications. The nanomaterials, discussed in this chapter along with their properties are Graphene, nanotubes, nanocomposites, microwave-absorbing materials, nanoparticles, biomaterials, and self-healing polymers. It also discusses future directions for the development of advanced materials that perform well to anticipate future trends and highlight their relevance in real-world contexts. This chapter could become the torchbearer for new researchers working in the field of multifunctional advanced materials.

Keywords: Functional & smart materials, Flexible electronics, Multifunctional, Nanomaterials & nanofluids, Optoelectronics.

---

[*] **Corresponding author Shailendra Kumar Dwivedi:** School of Studies in Physics, Jiwaji University, Gwalior (M.P), India and Madhav Institute of Technology & Science, Gola ka Mandir,Gwalior-474005, India;
E-mail: shail.dew04@gmail.com

Sanjeev Verma, Shivani Verma, Saurabh Kumar & Bhawna Verma (Eds.)

INTRODUCTION

The “Next-generation materials” or advanced materials are those materials that have the properties of high efficiency, high-performance structural stability, easy manufacturability, and multifunctional capabilities. The basic characteristics of these materials include being very light, intelligent, more durable, and active materials that can adjust appropriately to their surroundings. In recent years, the development of new materials and technologies has been associated with innovation, creativity, originality, and forward thinking. A self-assembly process is specifically designed to produce advanced materials comprising nanoscale structures [1, 2]. These materials are of great interest in scientific research efforts and industrial development because of their innovative potential applications in various fields. Advanced materials are future materials with improved properties that are consciously designed for superior performance. The major scientific contributions of the 21st century, and a new understanding of atomic and subatomic levels, laid the foundation for the creation of advanced materials. The development of such advanced future materials can even lead to the design of completely advanced products, such as portable supercomputers, mini electronic gazettes, flexible electronics and optoelectronic devices, automatic lightweight weapons, fire registrant materials, medical implantable devices, gas sensors, lightweight industrial equipment, intelligent robotics, *etc*.

Nowadays, the materials such as graphene, carbon nanotube, men, nanofluids, quantum dots, nanoparticles, metal-organic frameworks (MOFs), aerogel, nanocomposites, microwave absorbing materials, self-healing polymers, artificial spider silk, metal foam, synthetic fuel and lubricants, shrilk and many more have emerged as advanced materials for human beings. These materials have the potential to sort out human futuristic problems and are useful for the better advancement of human civilization. Advanced nanomaterials are very desirable in these domains because of their controllable production and beautiful design. Due to its vast applicability in a range of sectors, such as energy storage, electronics, optics, optoelectronics catalytic, absorption and separation, biomedical, luminescence, sensing, and environment, nanotechnology has gained a lot of attention in recent decades. The key features of advanced nanomaterials are their active surfaces, dimensions, and reaction conditions [3, 4].

The physical and chemical properties of advanced nanomaterials are greatly influenced by their dimensions and reaction conditions [3]. Thus, it is the right time to think about not only synthesizing materials but also tuning their physicochemical properties (Fig. **1a**) to develop next-generation materials. The beauty of advanced nanomaterials is their tunable properties; therefore, by changing the shape, size, and reaction conditions of the nanomaterials, one can change their functionality accordingly. So, to utilize these nanomaterials for the development of a new world, we need to develop advanced synthetic techniques so that more features of those materials can be explored in various fields for human beings.

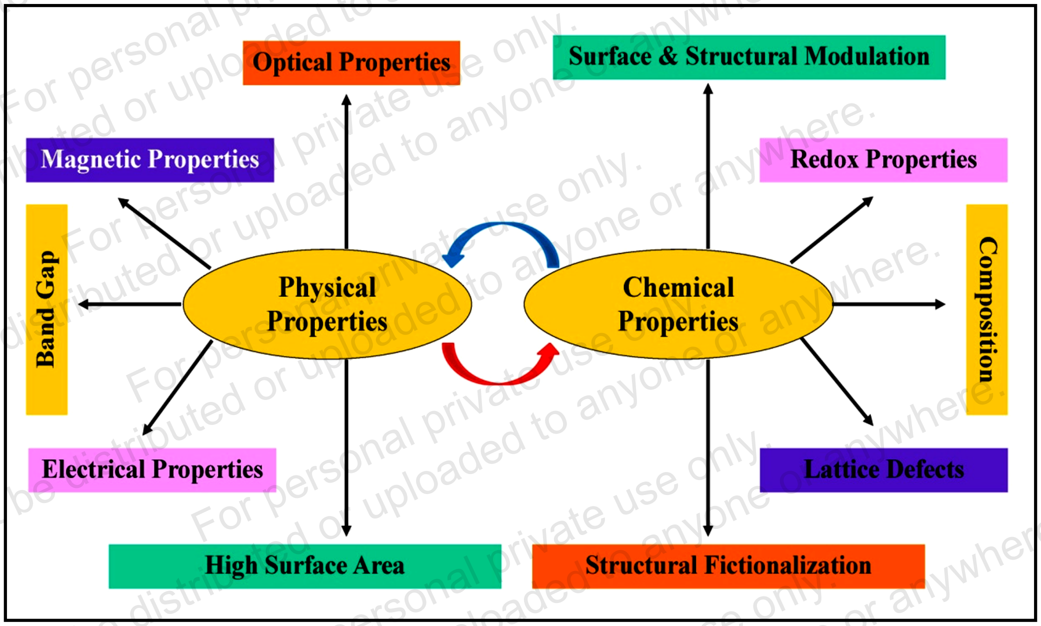

Fig. (1a). Physicochemical properties of nanomaterials.

Scientific legend; Andre Geim and Konstantin Novoselov in 2004 at Manchester University discovered a wonder material called "Graphene" by playing with a lump of graphite and Scotch tape. At that time, both did not know how to deal with and what to do. But nowadays, Graphene has become one of the extraordinary materials for the future world because of its properties like immensely strong, flexible, transparent, and conductivity. Shrilk could be another wonder material for the future world [4]. Shrilk is a biodegradable solution to plastic and is mainly made up of silk proteins and chitin developed by Javier Fernandez and Donald Ingber at the Wyss Institute of Biologically Inspired Engineering, Harvard University [5]. A material with huge absorption capability of electromagnetic radiations (microwave) was discovered named metamaterials. It is an advanced or a new class of materials that can have electromagnetic features including the negative value of permittivity, permeability, and refractive index that do not occur naturally. In 2011, another wonder material called Mxenes was discovered by two research groups led by Y.Gogotsi and M.Barsoum at Drexel University. Generally, Mxene is a 2D transition metal-based compound of carbides, carbonitrides, and nitrides used for wastewater treatment, energy storage, detection of various gases (gas sensors), and electronic applications [6, 7].

Nowadays, the continuous developments in high-performance energy storage devices have gained much attention from the scientific world and environmental security agencies of different countries. To fulfill the energy demand, various alternatives have come into existence but supercapacitor technologies could be the best alternative among all which can offer high power densities, large life cycles, quick charge and discharge response time as well as a clean and safe electrochemical energy storage [8 - 10]. This chapter aims to provide a comprehensive overview of several latest functional materials used for supercapacitors, storage mechanisms, criteria of formation and design fabrication, different electrodes and electrolyte materials, along with their properties, synthesis, applications, and future scopes.

Fundamental Theory of Supercapacitor

A supercapacitor (Fig. **1b**) is a device having a higher capacitance value than conventional capacitors at lower voltage limits. It fulfils the gap between rechargeable batteries and electrolytic capacitors and has 10-100 times more energy storage capacity per unit volume or mass than electrolytic capacitors [11]. A supercapacitor consists of a bi-electrode system that is separated from each other by an electrolyte separator. The supercapacitor device is composed of many parts like a current collector, two electrodes, a separator, and an electrolyte solution. Its characteristics are based on these constituents.

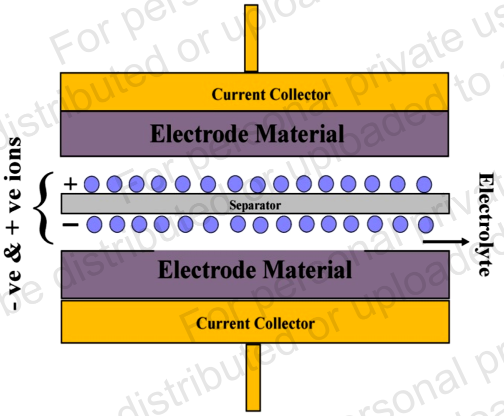

Fig. (1b). Basic device structure of supercapacitor.

The basic function of the separator is similar to that of the battery. It keeps apart the two electrodes to avoid a short circuit between the electrodes and allows ions to pass through. The basic principle of energy storage in supercapacitors is based on the charging-discharging cyclic process which happens at the electrode-electrolyte interface. In comparison with conventional capacitors, supercapacitor electrodes possess a highly effective surface area which leads to enhancement in capacitance value by a huge factor of 10000 than conventional capacitors [12, 13].

Classifications of Supercapacitor

There are two major classification standards for the supercapacitors. The first classification is based on the energy storage mechanisms of the different electrode materials, and the second classification is based on the different electrolytes. A supercapacitor based on different electrode materials can have different possible designs and leads to the production of symmetric supercapacitors, asymmetric supercapacitors, and hybrid supercapacitors. In case of a symmetric supercapacitor, the anode and cathodes are made of the same material (basically carbon materials) whereas, an asymmetric supercapacitor can have various possible combinations of electrode materials. If the combination of these two electrodes is in such a way that one is the capacitive type and the other is a capacitive Faradic (pseudocapacitive) or non-capacitive Faradic type, then that combination leads to the formation of hybrid capacitors [14]. Furthermore, the electrolyte-type supercapacitors are divided based on aqueous and organic electrolyte media. The aqueous electrolytes include acidic electrolytes (H_2SO_4 aqueous solution, 36%), basic electrolytes (strong bases KOH and NaOH), and the neutral electrolytes (KCl, NaCl, and other salts) which are mostly used in case of manganese oxide electrode material along with water as a solvent. The organic electrolyte commonly uses lithium salts, and quaternary amine salts along with solvents such as ACN, PC, GBL, THL, *etc* [15]. Based on the above discussion, supercapacitors can be classified based on charge-storage mechanism into three basic types as follows: (**i**) Pseudocapacitors (PCs), (**ii**) Hybrid capacitors (HCs), and (**iii**) Electric double-layer capacitors (EDLCs) [16 - 18] as shown in Fig. (**1c**).

H. Becker developed a “Low-voltage electrolytic capacitor in 1957 by using a porous carbon electrode system. At that time, he did not know the energy storage process and believed that a charge was stored in the carbon pores which provide energy. Later on, numerous scientists worked on this and finally electric-double layer mechanism came into existence. The first supercapacitor having low internal resistance was designed for military applications in 1982 by the Pinnacle Research Institute (PRI) and was commercialized under the brand name “Ultracapacitor- PRI” [19]. Supercapacitors have promising potential because of their excellent charge storage properties and high-power density for various energy storage applications. Supercapacitor devices can be widely used in photovoltaic, electric hybrid, wind power generation, *etc*. These are also used as power supplies in portable devices such as computers, digital cameras, mobile phones, and notebooks because of their lightweight and small size [20]. In addition, supercapacitors have many advantages compared to electrochemical batteries and fuel cells, such as short charging times, long cycle stability, and high-power density. Therefore, it is necessary to understand their energy storage mechanism.

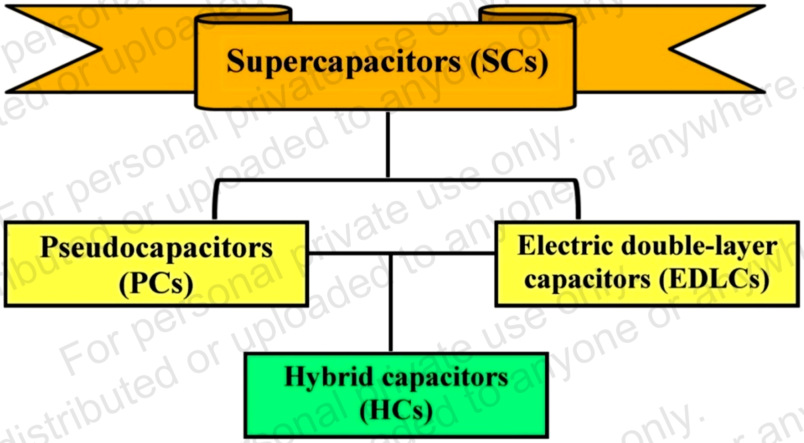

Fig. (1c). Types of supercapacitors.

Charge Storage Mechanism on Supercapacitors

Electrochemical Double-layer Capacitors

Electrostatic ion adsorption/desorption at the interface of electrode and electrolyte is the concept of energy storage used in EDLCs. When voltage is applied, there was no charge accumulation on the surface of the electrode, hence, opposite charges attract each other due to potential difference as a result of this the diffuse of electrolyte ions takes place over the separator as well as on the opposite charged electrode. A charge's double layer was formed to prevent ion recombination in electrodes. Thus, the charge storage takes place directly across the double layer of the electrode material without any charge transfer across the interface, and hence the capacitance value increases due to the capacitance effect [21].

Pseudocapacitors

Pseudocapacitors are completely non-electrostatic and obey the Faradaic redox mechanism for charge transfer between the electrode and the electrolyte. Commonly, transition metal oxide (MnO_2, RuO_2, Fe_3O_4, $MnFeO_2$, *etc.*) and conducting polymer (PANI–PANI, PPY/MWCNT, PANI/MWCNT, *etc.*) electrodes show high electrochemical pseudocapacitance behavior. When a potential is applied to the pseudocapacitor, redox reaction takes place on the electrode material interface and hence charge's passage across a double layer. In addition, due to this redox Faradic mechanism, pseudocapacitors possess high specific capacitance as well as energy densities in comparison to EDLCs [22].

Hybrid Supercapacitors

This type of supercapacitors was designed to achieve enhancement in energy density as compared to EDLC. HCs supercapacitors are based on the mechanism of double-layer ion adsorption/desorption and reversible Faradic reaction. The hybrid supercapacitor formation results from the coupling of different redox and EDLC materials like graphene or graphite, magnetic metal oxides, conducting polymers, and activated carbon [23]. Graphene and carbon nanotubes are very popular carbon-derived nanomaterials that are being used as efficient electrode materials in the design of supercapacitors. These materials have many outstanding features like high mechanical properties with great specific surface area and most importantly competent electrical properties [24]. Furthermore, carbon fiber, carbon derivatives, xerogel, activated carbon, and template carbon have been applied as efficient electrode materials in the design of supercapacitors. These materials possess durable power density, powerful lifecycles, lasting cycle durability, and desirable coulumbic reliability [25]. Nowadays, magnetic metal oxide nanoparticles have received great attention from energy storage devices like supercapacitors with high specific capacitance. Magnetic metal oxide nanoparticles are class of an attractive type of material because they are cheap and easy to prepare in large quantities [26].

Recently, the spinel ferrite which has nominal composition MFe_2O_4, where M is magnesium, copper, manganese, nickel, zinc, and cobalt. This has been successfully synthesized and exhibited a notable discharge of capacitance up to 1000 mA hg^{-1}, which is about three times higher than commercial anodes made from graphite [27]. Yao *et al.* [28] have successfully developed a carbon-coated Zn ferrite/graphene composite by a general multistep strategy. During the anodic process, one broad peak rises at ~ 1.50-2.10 V, exhibiting the oxidation of the base zinc ions (Zn^0 to Zn^{2+}) and iron ions (Fe^0 to Fe^{3+}). The electrochemical studies have revealed that the electrode offers a discharge capacity with a value of 1235 mA h g^{-1} and a loss of about 465 mA h g^{-1} over 150 cycles with good cycling performance. The nickel molybdate $NiMoO_4$ has been studied as one of the most popular candidates for supercapacitor electrodes. 2D nickel molybdate like-nanoflakes synthesized *via* rapid microwave-assisted, have achieved 1739 F g^{-1} of specific capacitance at 1 mV s^{-1} of scan rates. Huang *et al.* [29] have demonstrated that the three-dimensional interconnected nickel molybdate-lik--nanoplate arrays revealed a specific capacitance as high as 2138 F g^{-1} at a current density of 2 mA cm^{-2}.

Classifications and Types of Nanomaterials

Nature is a wonderful gift from God to human beings. The observation and examination of nature, natural processes, and evaluation of verities of elemental structures inspired us to solve human futuristic problems. Researchers aim to replicate something in nature that they find to be incredibly amazing (Biomimicry). Human inventions have been influenced and created by natural structures [8]. Controlled organization and properties with nano-scale precision have led to the creation of multi-functional advanced nanomaterials with miniaturization. Thus, nanomaterials are broadly classified based on three basic criteria; (1) Classification of nanomaterials based on origin [9]; (2) dimensionality, and (3) on the material used in the synthesis process. The existing classifications are based on research articles, textbooks, internet sources, and expert's knowledge of the various disciplines. According to the first approach called dominant bond type (in technical disciplines), the materials are divided into four categories Ceramics, Metals, Polymers, and Composites. According to the International Organization of Standardization ISO norms and the German Institute for Standardization (GIS) norms materials are classified as Materials of Glass (Ceramic, Metal, Stone, Paint and Color, Paper, Leather, Plastic, Textile, and Wood), Composite Materials and Raw Materials [30 - 33].

Classification of Nanomaterials Based on Origin

In everyday life, materials are important. Most of the time, people interface with these materials through products knowingly or unconsciously, voluntarily or involuntarily. Based on the origin of the materials, they are broadly classified into types; natural and synthetic. Natural materials (biotic) exist in nature and are produced by bio-geochemical or mechanical processes. They are not chemically changed as much. For example, a wooden table, its shape might be changed, but the material is still wood. Similarly, glass might be considered as a natural substance due to its origin from sand, which has been melted and then cooled. Synthetic materials are also made from natural resources and may or may not be chemically identical to a naturally occurring substance. These materials are produced by anthropogenic processes. The succession of chemical processes used to transform natural resources into synthetic goods is termed chemical synthesis. Fig. (**2a**) gives an idea of the classification of materials along with some examples.

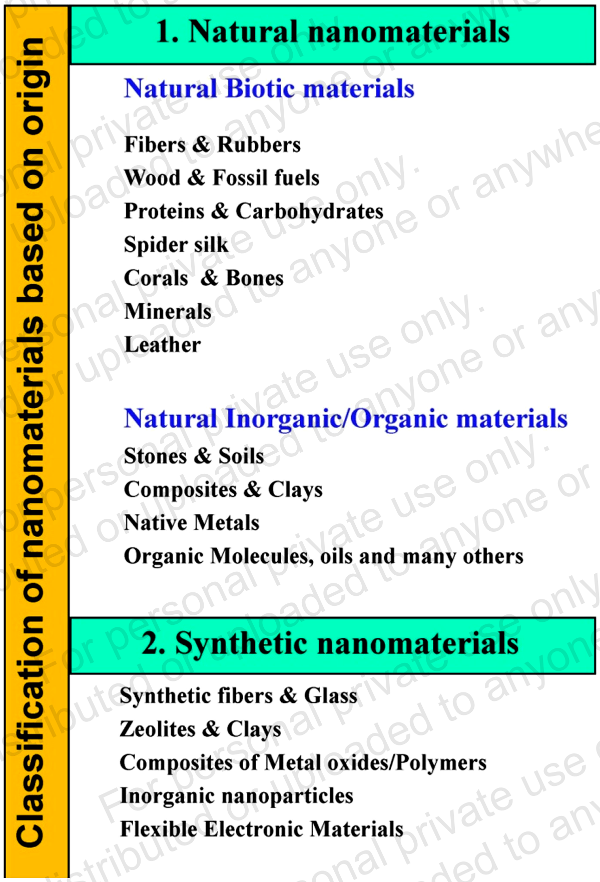

Fig. (2a). Classification of nanomaterial materials based on Origin.

Classification Based on Dimensionality

Dimensionality is another criterion for the classification of nanomaterials. The shape and size of nanomaterials, ranging from 1-100 nm, are the basis of their classification. Further, they can be divided into four classes, based on their dimensionality and shape, *i.e.*; 0D, 1D, 2D, and 3D (Fig. **2b**).

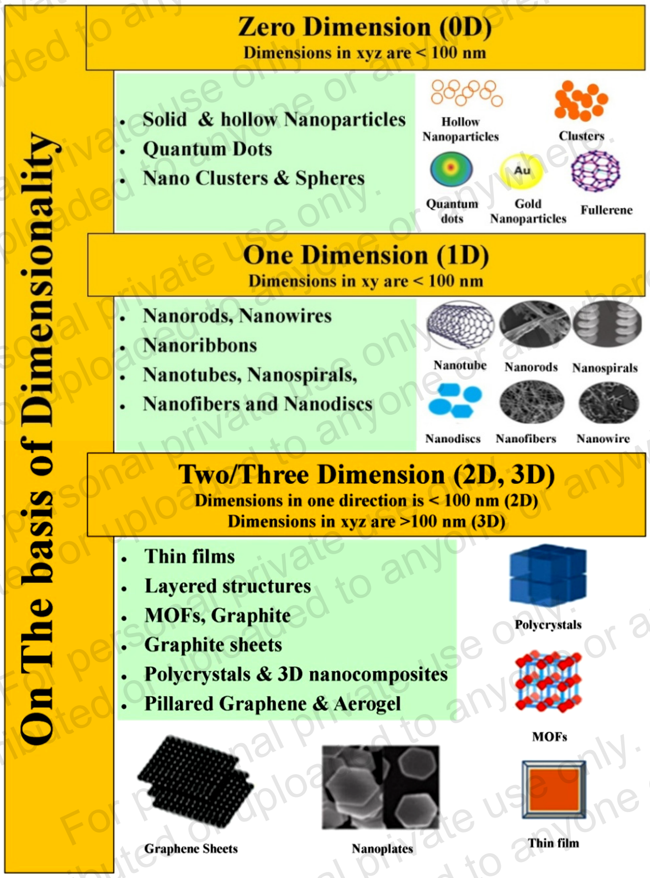

Fig. (2b). Schematic representation of the classification of nanomaterials based on dimensionality (adopted from refs. [34-37]).

Zero-dimensional (0D) nanomaterials are materials with all of their dimensions at nanoscale, or below 100 nm in size. Spherical NMs, nanorods, Cubes and polygons, hollow spheres, metal nanoparticles, fullerenes, and quantum dots are all included in 0D. Materials having only two dimensions in the nanoscale range are included in one-dimensional (1D) nanomaterials. The common examples are carbon nanotubes, ceramic, metallic nanodiscs, nanorods, nanofibers, and nanowires. Two-dimensional (2D) nanomaterials are those which have only one dimension in nanoscale while the other two are not. Some common examples of 2D materials are single and multi-layered structures, thin films, nanoplates, MOFs, *etc* [38]. Further, three-dimensional (3D) nanomaterials are those having dimensions in different directions with all of their dimensions beyond 100 nm.

Classification Based on Material Used

Intentionally created functional nanomaterials come in a wide range of varieties, and more are predicted to be developed in the future. Fig. (**2c**) displays some frequently used materials and it is expected that by tuning their basic properties, these materials have the potential to generate revolutionary advanced material for future generation.

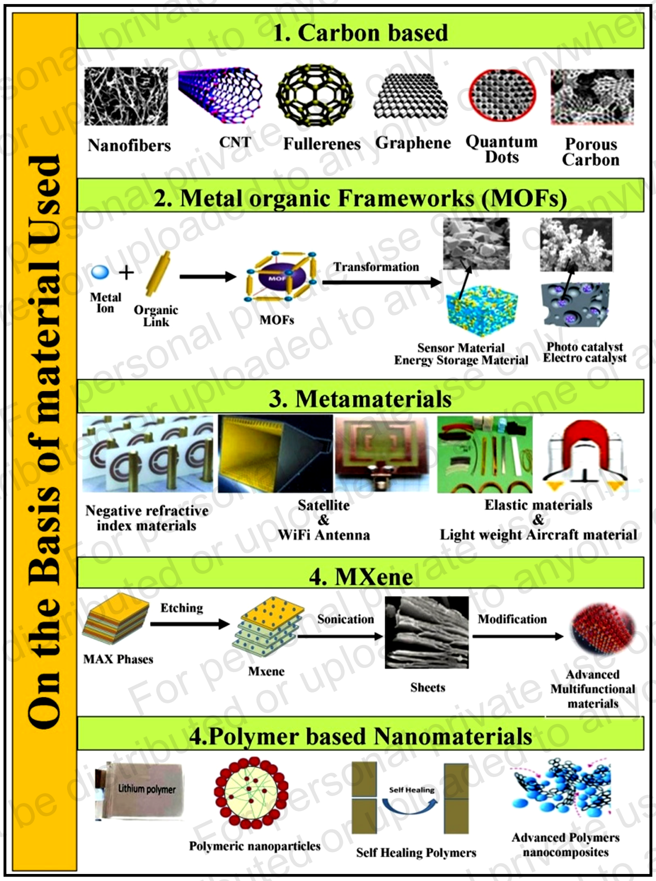

Fig. (2c). Classification of materials based on the route of synthesis (adapted from refs. [41-45, 63, 71, 77, 81-82, 91-93]).

Multifunctional Future Materials, Their Properties, and Applications

Various above-mentioned functional materials such as Graphene, Mxene, MOFs, perovskites, self-healing polymers, Shrilk, Metameterias, quantum dots, and advanced nanomaterials, have been developed for future generation. However, many properties of these materials still need to be explored for the development of a new world with new technologies. Here, various properties and applications (Fig. **3a**) of highly demanded materials with their functionality are discussed.

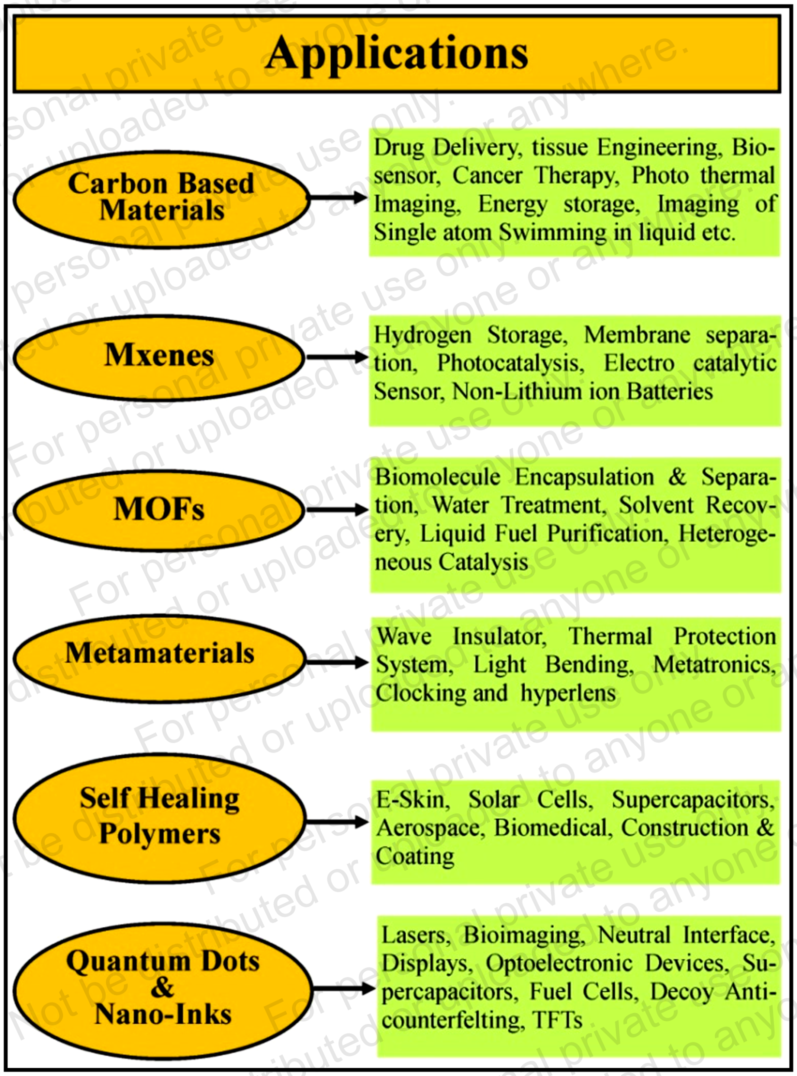

Fig. (3a). Application areas of multifunctional materials.

Carbon Based Materials

Carbon-based nanomaterials have outstanding properties such as high surface area, lightweight, high electrical conductivity, high thermal and chemical stability, corrosion resistive and non-oxidizing nature. Carbon materials provide a vast range of forms and textures, and they are simple to produce. Carbon is a solid-state allotrope that provides a wide variety of structures and is easy to process.

The carbon material is an ancient but a new substance with ongoing and continuous discoveries. Carbon materials include activated carbons, carbon black, graphite, carbon nanofibers, glassy carbons, fullerenes, carbon nanotubes, and wonder material graphene [39, 40]. Graphene, a monolayer of sp^2-bonded carbon atoms has attracted significant scientific interest due to its outstanding properties such as excellent enormous specific surface area (2620 m^2 g^{-1}), mechanical properties (Young's modulus of $1TP_a$ and intrinsic strength of $130GP_a$), high electronic conductivity (electron mobility of $2.5x10^5$ cm^2 $V^{-1}s^{-1}$at room temperature), high thermal conductivity (above 3000 WmK^{-1}), along with many other properties [41 - 44]. It is easily prepared from graphite flakes. Many researchers investigate the dispersion behavior of graphene and its oxide in organic solvents such as NMP (N-methyl-2- pyrrolidone), THF (tetra hydro furan), Acetone, N-N-dimethylformamide, ethylene glycol, and many others to expand its processability. However, there is still a challenge to understand how graphene disperses in these liquids [45].

Graphene quantum dots (GQDs) are a very smart and latest zero-dimensional (0D) member of the carbon family consisting of single to few layers of graphene sheets with lateral dimensions of 10 nm [46]. GQDs have demonstrated extraordinary physiochemical properties including non-zero band gap, edge effect, and quantum confinement effect. GQDs have a lot of potential in the electronic and optical industries due to their exceptional characteristics. Pan *et al.* [47] have demonstrated a facile hydrothermal route for the synthesis of GQDs having blue luminescent features and analyzed their fluorescent properties for the first time. The applicability of GQDs in fluorescence imaging, magnetic resonance imaging, bioimaging, dual-modal imaging, and two-photon imaging can be explored using this research work. Recently, scientists from the University of Manchester have fabricated a novel nano-Petri dish by adopting graphene-decorated 2D MoS_2 materials to develop a new technique for observing how atoms swim in liquids [48]. Moreover, the team at the National Graphene Institute successfully captured the images of a single atom swimming in liquid for the first time. This finding could have a great impact on the future development of green technology such as hydrogen technology. Moreover, to translate the underlying information into practical applications, it is essential to integrate carbon elements, especially nanocarbons, with other components to build functional or structural materials. Carbon composites, for instance, are used in cylinders for high-pressure hydrogen storage that can operate at 50 MPa due to their high specific mechanical characteristics. Functional materials for energy storage that combine a carbon substance with a different element, such as a metal oxide or conductive polymer, are a hot topic of research. Future research in carbon-based materials will undoubtedly be vigorous due to the numerous challenging topics that exist today. The creation of novel carbons with various structures and textures, as well as the comprehension and customization of surface chemistry, are all incredibly significant and closely related to the creation of new applications.

Self-healing Polymers

The ability of a substance to repair physical loss is known as self-healing. To produce self-healing polymers, both physical and chemical methods have been chosen. These include covalent-bond reformation and rearranging heterogeneous self-healing systems, shape-memory effects, diffusion and flow, and supramolecular chemistry dynamics [49]. Due to their tendency to repair scratch-damaged or maintain their original physico-chemical and mechanical characteristics, smart self-healing polymers have gained a lot of research interest in recent years [50, 51]. Self-healing polymers became a hot topic of the current scenario after the first international conference on “self-healing materials” held at Delft University of Technology, Netherland, in 2007 [52]. These self-healing polymers are a unique class of intelligent materials having automatic healing properties much similar to human skin, as these materials can repair internal flaws, cracks, or damage caused by any matrix and can rebuild the mechanical properties (such as tensile strength) of the damaged area. Carolyn Dryin 1996 reported the first autonomic healing polymer. Recently (in 2015), a group of NASA scientists named Scott R. Zavada and his co-workers developed a polymer that has bulletproof properties. Moreover, a bullet will rupture the polymer, but at the same time, the temperature impact causes the polymer to flow and rejoin, closing the gap once the bullet has passed through [53]. Such kind of polymers could be helpful for healing damage in satellites and spacecraft caused by high-speed debris. The self-healing properties of polymers allow them to repair cracked or damaged material parts, extending the durability and life of many materials, decreasing waste, and improving performance while using them in real-world applications like construction, automotive, aerospace, biomedical engineering, and defense. Recently, significant progress has been made in the design and development of new self-healing polymers using a variety of chemical techniques. These polymers can spontaneously mend cracks and damage in moderate circumstances, which is desirable in many applications [54 - 56]. Ginting M. *et al.* reported a self-healable polyacrylic acid/polypyrrole-Fe (PAA/PPy-Fe) composite utilized for antibacterial and electrical conductivity properties. The antibacterial activity was studied against *E. coli.* revealing a 1.26-1.56 cm zone of inhibition after 12 hours of incubation. The composite exhibited reversible restorability when applied in an electrical circuit powered by 3V batteries, consisting of an LED [57]. Self-healing polymers have excellent potential for applications to space suits. Habitats and inflatable structures as reported by Pernigoni*et al.* The data for hyperelastic and viscoelastic response and damage and healing time was recorded. An effective self-healing ability was shown by the polymer (ASTM 1708) with polyamide under pressurized conditions [58]. Recently, Gao H. *et al.* explored the mechanical and conductive properties of solid, stretchable, and self-healable poly (oxime-urethane) and graphene composite. The self-healing composite showed a tensile strength of 6 MPa, 1000% elongation, and 48 MJ m^{-3} toughness [59]. The self-healing polymers also demonstrate protective properties. Owing to these properties, a composite based on PDO-2,5 polymer and oxime-urethane, as a protective film on the inner wall of the tire was utilized by Liu X. *et al.* [60] The composite was found to be self-healing and puncture-resistant. Hence, these materials can be successfully used as protective coatings for automobiles, electronics, and diplomas. Wang S. *et al.* developed a dynamically cross-linked polyurethane hot melt adhesive (DPU-HMA) possessing superior solvent resistance, high bonding strength, fast curing speed, and excellent bonding effects on wood, plastic, metal, and composite substrates [61]. These polymers are of great interest in biomedicine due to their self-healing properties. Jiang C *et al.* designed a self-healing poly(oximeurethane) elastomer having biocompatible, biodegradable, and mechanically adjustable properties. It was used for in vivo repair of the tissues. The results were validated in three animal models for nerve coaptation, bone immobilization, and aortic aneurysm, providing a new perspective to biomedical engineering [62].

Metal-organic Frameworks (MOFs)

A class of porous materials with exceptional chemical and structural tunability composed of metal anodes and organic linkers belonging to metal-organic frameworks (MOFs). Because of their porosity, stability, long-range order, conductivity, particle morphology, and synthetic adaptability, MOFs could be excellent platforms for identifying design features for advanced functional materials for specific applications. For cost-effective technologies, MOFs are the worthiest candidates to replace materials such as ordered silica, zeolites, and highly porous materials in various fields like fuel cells, sensors, gas storage, catalysis, and purification [63]. Radhakrishnan S. *et al* studied the electrochemical applications of Cobalt phenylphosphonate (CP) - MOF, such as energy storage and electrocatalysis. The CP-MOF exhibited excellent catalytic performance toward the electro-oxidation of methanol with a good catalytic constant (7.79 x $10^5 cm^3 mol^{-1} s^{-1}$) and higher oxidation peak current (2.97 ± 0.11 mA cm^{-2}). A high specific capacity of 218 C g^{-1} at 0.25 A/g current density and 82% cyclic stability up to 8000 cycles was observed when used as electrode materials revealing its excellent energy storage properties [64]. Jamil *et al.* utilized Co and Ca- based MOF as catalysts for the production of biodiesel from waste cooking oil. The results demonstrated good agreement with the predicted results for the yield of biodiesel (84.5%) with a percentage error of less than ± 5%. The regenerated catalyst exhibits a notable biodiesel production drop of up to 7% after three cycles

[65]. MOFs have also been successfully used for sensing applications such as sensing antibiotics, pesticides [66], hydrogen peroxide [67], nitroaromatic compounds [68], *etc*. The application of MOFs in fuel cells has been of great utility. Wang H. *et al.* prepared Zn-MOF for H_2O_2 fuel cells [69] with a power density of 212 mW cm^{-2} and a current density of 630 mA cm^{-2}. Ziang Z.*et al.* reported the adsorbent properties of cage-based MOF for separation and purification of natural gas and C_2H_2 showing adsorption selectivities for C_2 hydrocarbons over CH_4 above 17.7, 5.0 for CO_2/CH_4 and 4.4 for C_2H_2/CO_2. The studies also revealed good hydrolytic stability of MOF under harsh chemical conditions, making it suitable for practical future applications [70].

Mxenes

Mxenes have been investigated as one of the potential materials for a wide range of applications. Mxenes have many outstanding features including high miscibility, availability of active sites, high surface area to volume ratio, high electrical conductivity, electron-rich density, surface charge state, enabling stable colloidal solutions in water, negative zeta-potential, mechanical properties of transition metal carbides/nitrides, effective absorption of electromagnetic waves and functionalized surfaces that make MXenes hydrophilic and easily bind to different species. Energy storage was the first MXene application that was investigated, and it still accounts for a sizable amount of MXene operations. MXenes' distinctive layered structures offer transition metal-active redox sites on the surface, while simultaneously improving electrolyte ion transport. Due to these characteristics, MXenes have become an attractive candidate for high-performance electrodes for electrochemical capacitors [71]. Yu. L *et al.* used a 2D screen printing technique for energy storage application of pure MXene-N ink with low viscosity having a capacitance value of 70.1 mF cm^{-2}. The supercapacitor exhibited the energy density and power density of 0.42 mWh cm^{-2} and 0.83 mWh cm^{-3} respectively [72]. Apart from this, Chen L. *et al* examined the electronic properties of $Ti_3C_2T_x$ MXene. A strong dispersion of more than 1 eV was shown by the electronic structure of $Ti_3C_2T_x$. Also, the work function measured for $Ti_3C_2T_x$ was found in the range of 3.9 to 4.8 eV [73]. MXenes bound to PVA showed an increased electrical conductivity of 7.25×10^{-3} Sm^{-1} as compared to pure PVA (1×10^{-13} Sm^{-1}) and the optical absorption coefficient was calculated to be in the range 4000-5000 cm^{-1} [74]. The mechanical properties of MXenes are also the focus of attention. Ti_3C_2/polyacrylamide nanocomposite hydrogels exhibited fracture strengths of 66.5 to 102.7 kPa, compressive strengths of 400.6 to 819.4 kPa, and elongations at break of 2158.6% to 3047.5%, revealing its impressive mechanical properties [75]. Yue Y. *et al* studied the magnetic properties of Zr_2N MXene. The studies revealed that the ground state of Zr_2N MXene is antiferromagnetic, but a magnetic state with applied strain greater than

(>) 4% tends to be ferromagnetic [76]. Based on the above properties, it can be concluded that MXene is a fascinating candidate for futuristic materials and can be applied for various applications.

Composite Materials

Composites are an important class of multifunctional materials consisting of more than one phase bonded together. These materials can be categorized into four classes based on matrix composition: metal, carbon, polymer, and ceramic matrix composites. These materials can be modified and utilized accordingly for various applications owing to their excellent physical and mechanical properties. Characteristics such as resistance to creep, creep rupture, wear, corrosion and fatigue, high modulus, high strength, low coefficient thermal expansion, and low density make composite materials reliable for countless applications such as aerospace, energy production, infrastructure, architecture, automotive, transportation, energy storage, marine, *etc*. Along with these applications, the composite materials also show good biological activity as reported by Abhilash M.R. *et al.* The antibacterial activity of Fe_2O_3/Cu_2O against *E. coli*, *P. aeruginosa*, *Staphaureus*, and *B. subtilis* was studied and the material was found to be less toxic against *Musmusculus* skin melanoma cells. The composite also exhibited a short time span for photocatalytic degradation of Rhodamine-B and Janus green dyes [77]. Similarly, a composite material based on chitosan, glutaraldehyde, reduced graphene oxide, and palladium was prepared by Ge L. *et al.* for catalytic degradation of organic pollutants [78]. Carbon-based composite materials are well-suited for energy storage properties with high cyclic stability as reported by Vidhya M.S. *et al.* [79]. A composite material of cobalt hydroxide with reduced graphene oxide was prepared as electrode material which delivered a high specific capacitance of 1100 Fg^{-1} at 0.5 Ag^{-1} current density and 98.1% cyclic stability after 2000 cycles. Nevertheless, carbon-based composites are also utilized as microwave absorbers by Feng A. *et al.* They prepared a hierarchical carbon fiber@cobaltferrite@manganesedioxide ($CF@CoFe_2O_4@MnO_2$) composite for microwave absorption, exhibiting a superior performance with minimum reflection loss value up to -34 dB [77]. Sankar S. *et al.* developed polymer-based composite materials for gas sensing and electrical properties. A composite of poly(aniline-co-indole) with varying contents of copper alumina exhibited excellent performance towards ammonia gas sensing and formation of p-n junction in the material. The composite revealed high electrical conductivity, gas sensing, and thermal stability making it a promising candidate for electronic and sensing applications [80].

Nano-Inks and Quantum Dots

Nanoparticle conductive inks and composites of nanomaterials are no longer a technology that is just used in academic labs; firms are now developing these formulations and putting them to use in real-world goods. Owing to their outstanding features such as high optical absorption coefficients ($> 104\ \text{cm}^{-1}$) and tunable direct band gaps ranging from 1.1 to 1.5 eV [81 - 83], ternary and quaternary chalcogenides materials, Cu_2SnSe_3 (CTSe) and Cu_2ZnSnS_4 (CZTS), have received research attention to become an effective photovoltaic material [84 - 86]. Recently, ternary and quaternary semiconductor compounds CTSe and CZTS, have been used as efficient photoactive layers in heterojunction thin film solar cells. A combination of inorganic nanoparticles and conjugated polymers was used in the past to develop low-cost photovoltaic (PV), energy storage, and electrochemical sensors. Organic semiconductors that have undergone solution processing and inorganic/organic composite materials have the potential to lower the cost of solar energy devices and sensors significantly. The semiconductor nanocrystals and their nano-inks offer suitable energy band alignment for the fast exciton dissociation rate and charge transport as well as wide coverage of spectral region [87]. It has also been reported that the performances of solar cells are strongly dependent on electron/hole selective layers used. To create a buffer layer, various thin layers including ZnO, ZnS, CdS, and TiO_2, have been successfully incorporated into thin film solar cells. In thin films, the buffer layer is mainly used for the formation of a junction with an observer layer to allow the maximum number of photons in the absorber layer. Currently, rGO–CNF/Ce–TiO_2, Sr-CeTiO_2/CNF, and PANI/MOR emerged as an efficient charge carrier's selective layers [88]. Therefore, nano-inks based on these materials could be beneficial for multidisciplinary applications.

Quantum dots (QDs) are nanocrystals of semiconducting materials having a size resumed less than 10 nm. Currently, QDs have gained great research interest in a wide variety of different applications such as photovoltaic cells, photodetectors, biological imaging, and LEDs. Due to their minute size, a physically confined electron cloud is produced, called quantum confinement effect, and various properties such as optical, electronic, and chemical, can be enhanced to a great extent. The phrase "quantum dot" was first used in 1986. Legend Alexey Ekimov created QDs in a glass matrix in 1981, while Louis Brus created them in a colloidal solution in 1983. At the beginning of the twenty-first century, Prof. Xiaogang Peng, who worked at the Department of Chemistry, University of Arkansas developed a "Green Synthesis" method by replacing $CdMe_2$ with CdO with a non-coordinating solvent ODE. This allowed "QD synthesis" to be used in laboratories and industries all around the globe. In 2014, GaN was used to develop efficient blue light emitting diodes (LED), brilliant and energy-efficient white light sources, by employing high vacuum and temperature-controlled epitaxial growth of a multilayer semiconductor single crystal on a sapphire substrate. A Nobel Prize in Physics was awarded for the same. But the price is outrageous! It is anticipated that the benefits of both organic light-emitting diode and GaN-LED will be combined if the QDs-based devices (*i.e.*, QLED) can attain high performance comparable with GaN-LED (OLED). Recent research by Xiaogang Peng and his team supported this theory by producing a high-performing, low-cost QLED utilizing a "solution-processed synthesis approach". The photo luminescent QDs technology has been substantially commercialized in lighting and displays during the past ten years [89]. This was a revolutionary change in the field of ODs.

Metamaterials

The term "meta" means "beyond" in Greek. "Metamaterials" have unique qualities that go beyond those of natural materials. The properties of metamaterials are due to their structure rather than the construction materials. The most remarkable contribution in this field is V. G. Veselago's statement in 1968 that materials with both negative permittivity and negative permeability are theoretically feasible [90]. These materials have unique spatial alterations in their constituent components as they are man-made substances. These materials are extensively used for the modification of elastic, acoustic, or electromagnetic properties of materials. Metamaterials often used in microwave engineering, waveguides, dispersion compensation, smart antennas, and lenses also produce low/high-frequency band gaps to control wave propagations with varying wavelengths. For example, the metamaterial's permittivity and permeability can have positive or negative values. The selected frequency of surface-based metamaterials is exploited for wave guiding since the single-cell dimensions of these materials are less than their wavelength. Metamaterials have a wide variety of applications in different fields such as public safety, sensor identification, high-frequency combat communications, enhanced ultrasonic sensors, solar energy management for high-gain antennas, and distant aerospace applications [90, 91].

SYNTHESIS TECHNIQUES

Nanomaterials can be synthesized using two types of approaches; top down and bottom approach (Fig. **3b**). As the name suggests, the top-down approach uses bulk materials to produce nano-size particles. Various dispersion and aggregation techniques are employed to structure macroscopic particles to a nanometer scale. Physical methods are involved in this approach including mechano-chemical dispersion, plasmo-chemical method, and condensation from the gas phase. The original structure of the compact material is retained in this type of approach.

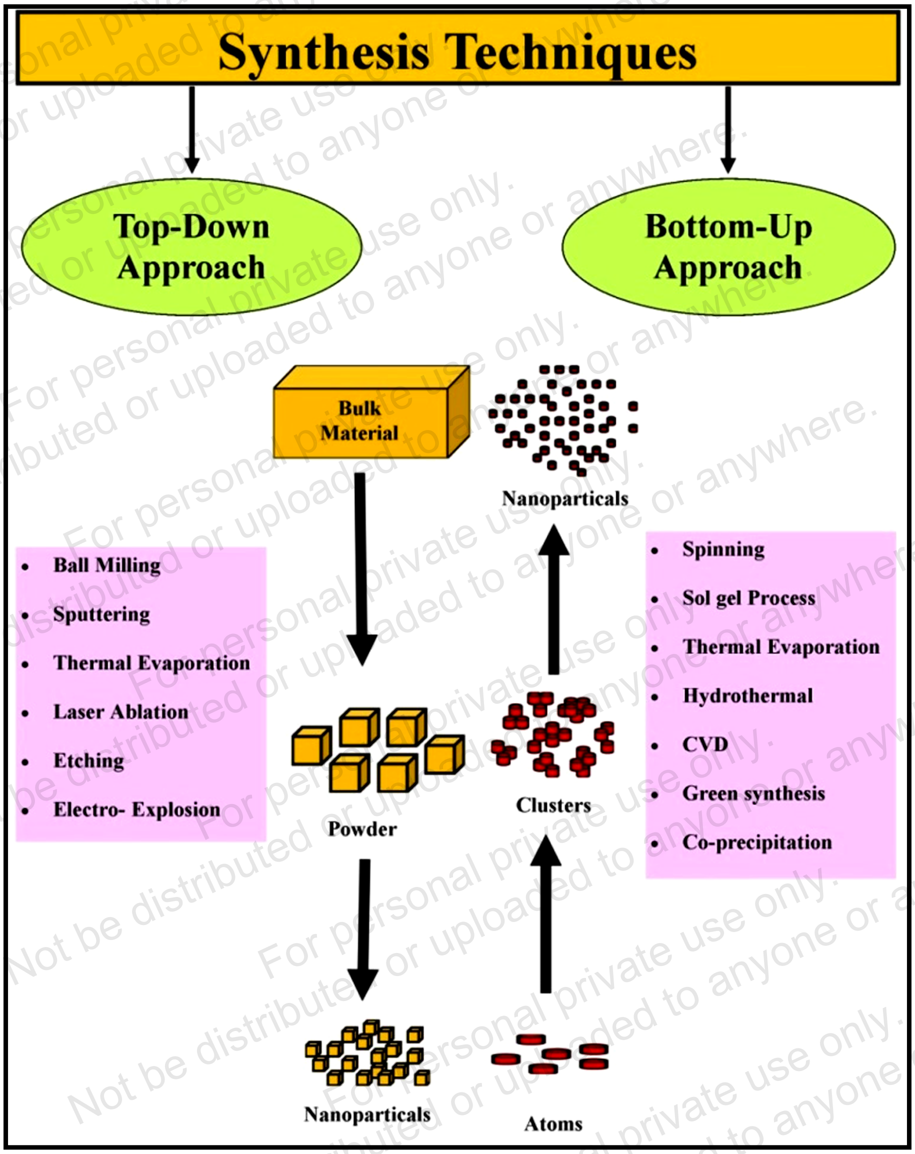

Fig. (3b). Synthesis techniques for synthesis of nanostructures.

In a bottom-up approach, basic building blocks *i.e.*; atoms and molecules are organized to build up nanostructures. This approach is largely about chemical methods for nanomaterial synthesis. Chemistry expertise is required in this method for assembling and structuring these nano-objects into nanomaterials. The electrical structure of nanoparticles may be affected due to variations in the position of atoms in nanoparticles created by aggregation of atoms. The objective of this approach is to prepare materials with excellent chemical, mechanical, optical, and magnetic properties, by using small-sized materials in the beginning [92 - 98].

FUTURE SCOPE OF NANOMATERIALS

Nanotechnology is considered to be the major technological advancement of the twenty-first century and has sparked interest worldwide. Today's nanotechnology is much more advanced than what is imagined in science fiction. Although the current focus of nanotechnology is primarily on new material composition, their prospective applications are extremely broad. The usage of nanotechnology has grown significantly, and it has the potential to become crucial shortly. It is anticipated to inspire a wide range of application domains across practically all industries and technological fields. It will open up new possibilities for producing life's necessities (such as electronics, medications, goods, cars, and homes) more effectively and affordably while utilizing fewer raw materials. There will be significant advancements in a variety of fields, including robotics, computing, energy, and food. Perhaps Richard Feynman's innovative lecture, which inspired others to investigate this technology and helped establish this industry, can be credited with making this possible. Due to its distinctive properties, future applications of nanotechnology are anticipated to be far more sophisticated. As nanomaterial-based engineering techniques progress, the goal of producing clean energy is becoming more and more attainable. Nanomaterials have produced promising outcomes, enabling the development of new types of solar and hydrogen fuel cell technologies, serving as effective catalysts for water splitting, and displaying outstanding hydrogen storage capabilities. Nanomedicine holds a bright future for nanomaterials. Therapeutic compounds can be delivered *via* nanocarriers. The future of advanced technology is linked with advancements in the field of nanotechnology. Although nanotechnology is maturing rapidly, it is still in a formative phase. Nobody can predict how quickly will these novel concepts finish the R&D stage and reach the market. However, with certainty, we can state that nanotechnology is here to stay and that it uses and applications can be produced in a way that is morally upright and beneficial to mankind.

CONCLUSION

Overall, the advanced and multifunctional materials field is growing exponentially across the scientific community owing to their fascinating flexible electronics and optoelectronic devices, lightweight weapons, fire registrant materials, gas sensors, energy storage and biomedical, *etc*., which facilitate them to be qualified as the key materials for the next generation. These materials show high-level performance because of their unique properties. To achieve progress and growth in fundamental research and their practical applications, the exploration of the design of these advanced and multifunctional materials and their assemblies is facing more and more challenges. In this review, we summarized the basic properties, synthesis techniques, classifications, and recent applications in various fields. Finally, the continuous developments of elaborate design and assembly and enhancement in properties of such materials offer unprecedented opportunities for new applications as well as provide next-generation solutions.

REFERENCES

[1] J.Y. Cheong, S.H. Cho, J. Lee, J.W. Jung, C. Kim, and I.D. Kim, "Multifunctional 1D nanostructures toward future batteries: A comprehensive review", *Adv. Funct. Mater.,* vol. 32, no. 49, p. 2208374, 2022.
[http://dx.doi.org/10.1002/adfm.202208374]

[2] M. Hasan, J. Zhao, and Z. Jiang, "Micromanufacturing of composite materials: A review", *Int. J. Extreme Manuf.,* vol. 1, no. 1, p. 012004, 2019.
[http://dx.doi.org/10.1088/2631-7990/ab0f74]

[3] M. Sajid, "Nanomaterials: Types, properties, recent advances, and toxicity concerns", *Curr. Opin. Environ. Sci. Health,* vol. 25, p. 100319, 2022.
[http://dx.doi.org/10.1016/j.coesh.2021.100319]

[4] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, and A.A. Firsov, "Electric field effect in atomically thin carbon films", *Science,* vol. 306, no. 5696, pp. 666-669, 2004.
[http://dx.doi.org/10.1126/science.1102896] [PMID: 15499015]

[5] J.G. Fernandez, and D.E. Ingber, "Unexpected strength and toughness in chitosan-fibroin laminates inspired by insect cuticle", *Adv. Mater.,* vol. 24, no. 4, pp. 480-484, 2012.
[http://dx.doi.org/10.1002/adma.201104051] [PMID: 22162193]

[6] J.A. Kumar, P. Prakash, T. Krithiga, D.J. Amarnath, J. Premkumar, N. Rajamohan, Y. Vasseghian, P. Saravanan, and M. Rajasimman, "Methods of synthesis, characteristics, and environmental applications of MXene: A comprehensive review", *Chemosphere,* vol. 286, no. Pt 1, p. 131607, 2022.
[http://dx.doi.org/10.1016/j.chemosphere.2021.131607] [PMID: 34311398]

[7] A. Kirchon, L. Feng, H.F. Drake, E.A. Joseph, and H.C. Zhou, "From fundamentals to applications: A toolbox for robust and multifunctional MOF materials", *Chem. Soc. Rev.,* vol. 47, no. 23, pp. 8611-8638, 2018.
[http://dx.doi.org/10.1039/C8CS00688A] [PMID: 30234863]

[8] B.E. Conway, *Electrochemical supercapacitors: Scientific fundamentals and technological applications.* Springer US, 1999.
[http://dx.doi.org/10.1007/978-1-4757-3058-6]

[9] I.V. Barsukov, C.S. Johnson, J.E. Doninger, and V.Z. Barsukov, *New carbon based materials for electrochemical energy storage systems: Batteries, supercapacitors, and fuel cells.* Springer Netherlands: Dordrecht, 2006.
[http://dx.doi.org/10.1007/1-4020-4812-2]

[10] C.K. Chan, H. Peng, G. Liu, K. McIlwrath, X.F. Zhang, R.A. Huggins, and Y. Cui, "High-performance lithium battery anodes using silicon nanowires", *Nat. Nanotechnol.,* vol. 3, no. 1, pp. 31-35, 2008.
[http://dx.doi.org/10.1038/nnano.2007.411] [PMID: 18654447]

[11] F. Häggström, and J. Delsing, "IoT energy storage - A forecast", *Energy Harvesting and Systems,* vol. 5, no. 3-4, pp. 43-51, 2018. [http://dx.doi.org/10.1515/ehs-2018-0010]

[12] L.L. Zhang, and X.S. Zhao, *Carbon-based materials as supercapacitor electrodes.* vol. Vol. 38. Chemical Society Reviews, 2009, pp. 2520-2531.

[13] J. Huang, B.G. Sumpter, and V. Meunier, "Theoretical model for nanoporous carbon supercapacitors", *Angew. Chem. Int. Ed.,* vol. 47, no. 3, pp. 520-524, 2008. [http://dx.doi.org/10.1002/anie.200703864] [PMID: 18058966]

[14] E. Hornbogen, G. Eggeler, and E. Werner, *Werkstoffe, "Aufbau und eigenschaften von keramik, metal, polymer und verbundwerkstoffen" (materials: Structure and properties of ceramics, metals, polymers and composite materials).* Springer: Berlin, 2017.

[15] Z. Su, H. Guo, and C. Zhao, "Rational design of electrode–electrolyte interphase and electrolytes for rechargeable proton batteries", *Nano-Micro Lett.,* vol. 15, no. 1, p. 96, 2023. [http://dx.doi.org/10.1007/s40820-023-01071-z] [PMID: 37037988]

[16] L. Jiang, S. Shanmuganathan, G.W. Nelson, S.O. Han, H. Kim, I. Na Sim, and J.S. Foord, "Hybrid system of nickel–cobalt hydroxide on carbonised natural cellulose materials for supercapacitors", *J. Solid State Electrochem.,* vol. 22, no. 2, pp. 387-393, 2018. [http://dx.doi.org/10.1007/s10008-017-3723-z]

[17] B.E. Conway, *Electrochemical supercapacitors: Scientific fundamentals and technological applications.* Springer US, 1999. [http://dx.doi.org/10.1007/978-1-4757-3058-6]

[18] M. Zhi, C. Xiang, J. Li, M. Li, and N. Wu, "Nanostructured carbon–metal oxide composite electrodes for supercapacitors: A review", In: *Nanoscale* vol. 5. , 2013, pp. 72-88. [http://dx.doi.org/10.1039/C2NR32040A]

[19] H.I. Becker, *Low voltage electrolytic capacitor,* 1957.

[20] S. Liu, L. Wei, and H. Wang, "Review on reliability of supercapacitors in energy storage applications", *Appl. Energy,* vol. 278, p. 115436, 2020. [http://dx.doi.org/10.1016/j.apenergy.2020.115436]

[21] N.I. Jalal, R.I. Ibrahim, and M.K. Oudah, "A review on Supercapacitors: Types and components", *J. Phys. Conf. Ser.,* vol. 012015, p. 2021, 1973.

[22] A. Muzaffar, M.B. Ahamed, K. Deshmukh, and J. Thirumalai, "A review on recent advances in hybrid supercapacitors: Design, fabrication and applications", *Renew. Sustain. Energy Rev.,* vol. 101, pp. 123-145, 2019. [http://dx.doi.org/10.1016/j.rser.2018.10.026]

[23] D.P. Chatterjee, and A.K. Nandi, "A review on the recent advances in hybrid supercapacitors", *J. Mater. Chem. A Mater. Energy Sustain.,* vol. 9, no. 29, pp. 15880-15918, 2021. [http://dx.doi.org/10.1039/D1TA02505H]

[24] P. Chen, J-J. Yang, S-S. Li, Z. Wang, T-Y. Xiao, Y-H. Qian, and S-H. Yu, *Hydrothermal synthesis of macroscopic nitrogen doped graphene hydrogels for ultrafast supercapacitor.* vol. Vol. 2. Nano Energy, 2013, pp. 249-256.

[25] J. Yin, D. Zhang, J. Zhao, X. Wang, H. Zhu, and C. Wang, *Meso-and micro-porous composite carbons derived from humic acid for supercapacitors.* vol. Vol. 136. Electrochimica Acta, 2014, pp. 504-512.

[26] O. Masala, and R. Seshadri, "Synthesis routes for large volumes of nanoparticles", *Annu. Rev. Mater. Res.,* vol. 34, no. 1, pp. 41-81, 2004. [http://dx.doi.org/10.1146/annurev.matsci.34.052803.090949]

[27] S. Yuvaraj, R.K. Selvan, and Y.S. Lee, "An overview of AB 2 O 4 - and A 2 BO 4 -structured negative electrodes for advanced Li-ion batteries", *RSC Advances,* vol. 6, no. 26, pp. 21448-21474, 2016.

[http://dx.doi.org/10.1039/C5RA23503K]

[28] L. Yao, Q. Su, Y. Xiao, M. Huang, H. Li, H. Deng, and G. Du, "Facial synthesis of carbon-coated ZnFe2O4/graphene and their enhanced lithium storage properties", *J. Nanopart. Res.,* vol. 19, no. 7, p. 261, 2017.
[http://dx.doi.org/10.1007/s11051-017-3935-2]

[29] L. Huang, J. Xiang, W. Zhang, C. Chen, H. Xu, and Y. Huang, "3D interconnected porous NiMoO 4 nanoplate arrays on Ni foam as high-performance binder-free electrode for supercapacitors", *J. Mater. Chem. A Mater. Energy Sustain.,* vol. 3, no. 44, pp. 22081-22087, 2015.
[http://dx.doi.org/10.1039/C5TA05644F]

[30] B. Mekuye, and B. Abera, "Nanomaterials: An overview of synthesis, classification, characterization, and applications", *Nano Select,* vol. 4, no. 8, pp. 486-501, 2023.
[http://dx.doi.org/10.1002/nano.202300038]

[31] B.E. Marschallek, and T. Jacobsen, "Classification of material substances: Introducing a standards-based approach", *Mater. Des.,* vol. 193, p. 108784, 2020.
[http://dx.doi.org/10.1016/j.matdes.2020.108784]

[32] V. Singh, P. Yadav, and V. Mishra, "Recent advances on classification, properties, synthesis, and characterization of nanomaterials", In: *Green synthesis of nanomaterials for bioenergy applications*, 2020, pp. 83-87.
[http://dx.doi.org/10.1002/9781119576785.ch3]

[33] F. Asghari, Z. Jahanshiri, M. Imani, M. Shams-Ghahfarokhi, and M. Razzaghi-Abyaneh, "Antifungal nanomaterials: Synthesis, properties, and applications", In: *Nanobiomaterials in antimicrobial therapy.* William Andrew Publishing, 2016, pp. 343-383.
[http://dx.doi.org/10.1016/B978-0-323-42864-4.00010-5]

[34] R. Aversa, M.H. Modarres, S. Cozzini, R. Ciancio, and A. Chiusole, "The first annotated set of scanning electron microscopy images for nanoscience", *Sci. Data,* vol. 5, no. 1, p. 180172, 2018.
[http://dx.doi.org/10.1038/sdata.2018.172] [PMID: 30152811]

[35] B.W. Shiau, C.H. Lin, Y.Y. Liao, Y.R. Lee, S.H. Liu, W.C. Ding, and J.R. Lee, "The characteristics and mechanisms of Au nanoparticles processed by functional centrifugal procedures", *J. Phys. Chem. Solids,* vol. 116, pp. 161-167, 2018.
[http://dx.doi.org/10.1016/j.jpcs.2018.01.033]

[36] S. Saha, S. Bansal, and M. Khanuja, *Book Chapter -2 "Classification of nanomaterials and their physical and chemical nature.* Nano-enabled Agrochemicals in Agriculture, 2022, pp. 7-34.

[37] M. Inagaki, and F. Kang, *Materials science and engineering of carbon: Fundamentals Butterworth-Heinemann.*, 2014.

[38] K. Khan, A.K. Tareen, M. Aslam, Y. Zhang, R. Wang, Z. Ouyang, Z. Gou, and H. Zhang, "Recent advances in two-dimensional materials and their nanocomposites in sustainable energy conversion applications", *Nanoscale,* vol. 11, no. 45, pp. 21622-21678, 2019.
[http://dx.doi.org/10.1039/C9NR05919A] [PMID: 31702753]

[39] M. Inagaki, and L.R. Radovic, "Nanocarbons", In: *Letter to Editor/Carbon* vol. 40. , 2002, pp. 2263-2284.

[40] Y. Hernandez, M. Lotya, D. Rickard, S.D. Bergin, and J.N. Coleman, "Measurement of multicomponent solubility parameters for graphene facilitates solvent discovery", *Langmuir,* vol. 26, no. 5, pp. 3208-3213, 2010.
[http://dx.doi.org/10.1021/la903188a] [PMID: 19883090]

[41] G.K. Dimitrakakis, E. Tylianakis, and G.E. Froudakis, "Pillared graphene: A new 3-D network nanostructure for enhanced hydrogen storage", *Nano Lett.,* vol. 8, no. 10, pp. 3166-3170, 2008.
[http://dx.doi.org/10.1021/nl801417w] [PMID: 18800853]

[42] M.D. Stoller, S. Park, Y. Zhu, J. An, and R.S. Ruoff, "Graphene-based ultracapacitors", *Nano Lett.,*

vol. 8, no. 10, pp. 3498-3502, 2008.
[http://dx.doi.org/10.1021/nl802558y] [PMID: 18788793]

[43] R.R. Nair, P. Blake, A.N. Grigorenko, K.S. Novoselov, T.J. Booth, T. Stauber, N.M.R. Peres, and A.K. Geim, "Fine structure constant defines visual transparency of graphene", *Science,* vol. 320, no. 5881, p. 1308, 2008.
[http://dx.doi.org/10.1126/science.1156965] [PMID: 18388259]

[44] J.I. Paredes, S. Villar-Rodil, A. Martínez-Alonso, and J.M.D. Tascón, "Graphene oxide dispersions in organic solvents", *Langmuir,* vol. 24, no. 19, pp. 10560-10564, 2008.
[http://dx.doi.org/10.1021/la801744a] [PMID: 18759411]

[45] R. Zhang, and Z. Ding, "Recent advances in graphene quantum dots as bioimaging probes", *J Anal Methods Chem ,* vol. 2, pp. 45-60, 2018.

[46] D. Pan, J. Zhang, Z. Li, and M. Wu, "Hydrothermal route for cutting graphene sheets into blue-luminescent graphene quantum dots", *Adv. Mater.,* vol. 22, no. 6, pp. 734-738, 2010.
[http://dx.doi.org/10.1002/adma.200902825] [PMID: 20217780]

[47] M.R. Younis, G. He, J. Lin, and P. Huang, "dots for bioimaging applications", *Front Chem.,* vol. 8, p. 424, 2020.
[http://dx.doi.org/10.3389/fchem.2020.00424] [PMID: 32582629]

[48] S. Wang, and M.W. Urban, "Self-healing polymers", *Nat. Rev. Mater.,* vol. 5, no. 8, pp. 562-583, 2020.
[http://dx.doi.org/10.1038/s41578-020-0202-4]

[49] H. Jiang, G. Zhang, X. Feng, H. Liu, F. Li, M. Wang, and H. Li, "Room-temperature self-healing tough nanocomposite hydrogel crosslinked by zirconium hydroxide nanoparticles", *Compos. Sci. Technol.,* vol. 140, pp. 54-62, 2017.
[http://dx.doi.org/10.1016/j.compscitech.2016.12.027]

[50] E. Su, and O. Okay, "Hybrid cross-linked poly(2-acrylamido-2-methyl-1-propanesulfonic acid) hydrogels with tunable viscoelastic, mechanical and self-healing properties", *React. Funct. Polym.,* vol. 123, pp. 70-79, 2018.
[http://dx.doi.org/10.1016/j.reactfunctpolym.2017.12.009]

[51] C. Dry, "Procedures developed for self-repair of polymer matrix composite materials", *Composite Structures,* vol. 35, pp. 263-269, 1996.

[52] S.R. Zavada, N.R. McHardy, K.L. Gordon, and T.F. Scott, "Rapid, puncture-initiated healing via oxygen-mediated polymerization", *ACS Macro Lett.,* vol. 4, no. 8, pp. 819-824, 2015.
[http://dx.doi.org/10.1021/acsmacrolett.5b00315] [PMID: 35596502]

[53] Y. Yang, H. Wang, L. Huang, M. Nishiura, Y. Higaki, and Z. Hou, "Terpolymerization of ethylene and two different methoxyaryl-substituted propylenes by scandium catalyst makes tough and fast self-healing elastomers", *Angew. Chem. Int. Ed.,* vol. 60, no. 50, pp. 26192-26198, 2021.
[http://dx.doi.org/10.1002/anie.202111161] [PMID: 34751988]

[54] S.R. White, J.S. Moore, N.R. Sottos, B.P. Krull, W.A. Santa Cruz, and R.C.R. Gergely, "Restoration of large damage volumes in polymers", *Science,* vol. 344, no. 6184, pp. 620-623, 2014.
[http://dx.doi.org/10.1126/science.1251135] [PMID: 24812399]

[55] Y.L. Rao, A. Chortos, R. Pfattner, F. Lissel, Y.C. Chiu, V. Feig, J. Xu, T. Kurosawa, X. Gu, C. Wang, M. He, J.W. Chung, and Z. Bao, "Stretchable self-healing polymeric dielectrics cross-linked through metal-ligand coordination", *J. Am. Chem. Soc.,* vol. 138, no. 18, pp. 6020-6027, 2016.
[http://dx.doi.org/10.1021/jacs.6b02428] [PMID: 27099162]

[56] M. Ginting, S.P. Pasaribu, I. Masmur, J. Kaban, and Hestina, "Self-healing composite hydrogel with antibacterial and reversible restorability conductive properties", *RSC Advances,* vol. 10, no. 9, pp. 5050-5057, 2020.
[http://dx.doi.org/10.1039/D0RA00089B] [PMID: 35498274]

[57] L. Pernigoni, and A.M. Grande, "Development of a supramolecular polymer based self-healing multilayer system for inflatable structures", *Acta Astronaut.,* vol. 177, pp. 697-706, 2020. [http://dx.doi.org/10.1016/j.actaastro.2020.08.025]

[58] H. Gao, J. Xu, S. Liu, Z. Song, M. Zhou, S. Liu, F. Li, F. Li, X. Wang, Z. Wang, and Q. Zhang, "Stretchable, self-healable integrated conductor based on mechanical reinforced graphene/polyurethane composites", *J. Colloid Interface Sci.,* vol. 597, pp. 393-400, 2021. [http://dx.doi.org/10.1016/j.jcis.2021.04.005] [PMID: 33892422]

[59] X. Liu, X. Liu, W. Li, Y. Ru, Y. Li, A. Sun, and L. Wei, "Engineered self-healable elastomer with giant strength and toughness via phase regulation and mechano-responsive self-reinforcing", *Chem. Eng. J.,* vol. 410, p. 128300, 2021. [http://dx.doi.org/10.1016/j.cej.2020.128300]

[60] S. Wang, Z. Liu, L. Zhang, Y. Guo, J. Song, J. Lou, Q. Guan, C. He, and Z. You, "Strong, detachable, and self-healing dynamic crosslinked hot melt polyurethane adhesive", *Mater. Chem. Front.,* vol. 3, no. 9, pp. 1833-1839, 2019. [http://dx.doi.org/10.1039/C9QM00233B]

[61] C. Jiang, L. Zhang, Q. Yang, S. Huang, H. Shi, Q. Long, B. Qian, Z. Liu, Q. Guan, M. Liu, R. Yang, Q. Zhao, Z. You, and X. Ye, "Self-healing polyurethane-elastomer with mechanical tunability for multiple biomedical applications in vivo", *Nat. Commun.,* vol. 12, no. 1, p. 4395, 2021. [http://dx.doi.org/10.1038/s41467-021-24680-x] [PMID: 34285224]

[62] C.M. Oliva González, B.I. Kharisov, O.V. Kharissova, and T.E. Serrano Quezada, "Synthesis and applications of MOF-derived nanohybrids: A review", *Mater. Today Proc.,* vol. 46, pp. 3018-3029, 2021. [http://dx.doi.org/10.1016/j.matpr.2020.12.1231]

[63] S. Radhakrishnan, S.C. Selvaraj, and B.S. Kim, "Morphology engineering of Co-MOF nanostructures to tune their electrochemical performances for electrocatalyst and energy-storage applications supported by DFT studies", *Appl. Surf. Sci.,* vol. 605, p. 154691, 2022. [http://dx.doi.org/10.1016/j.apsusc.2022.154691]

[64] U. Jamil, A. Husain Khoja, R. Liaquat, S. Raza Naqvi, W. Nor Nadyaini Wan Omar, and N. Aishah Saidina Amin, "Copper and calcium-based metal organic framework (MOF) catalyst for biodiesel production from waste cooking oil: A process optimization study", *Energy Convers. Manage.,* vol. 215, p. 112934, 2020. [http://dx.doi.org/10.1016/j.enconman.2020.112934]

[65] G.D. Wang, Y.Z. Li, W.J. Shi, B. Zhang, L. Hou, and Y.Y. Wang, "A robust cluster-based Eu-MOF as multi-functional fluorescence sensor for detection of antibiotics and pesticides in water", *Sens. Actuators B Chem.,* vol. 331, p. 129377, 2021. [http://dx.doi.org/10.1016/j.snb.2020.129377]

[66] W. Dang, Y. Sun, H. Jiao, L. Xu, and M. Lin, "AuNPs-NH2/Cu-MOF modified glassy carbon electrode as enzyme-free electrochemical sensor detecting H2O2", *J. Electroanal. Chem.,* vol. 856, p. 113592, 2020. [http://dx.doi.org/10.1016/j.jelechem.2019.113592]

[67] X.J. Zhang, F.Z. Su, D.M. Chen, Y. Peng, W.Y. Guo, C.S. Liu, and M. Du, "A water-stable Eu III -based MOF as a dual-emission luminescent sensor for discriminative detection of nitroaromatic pollutants", *Dalton Trans.,* vol. 48, no. 5, pp. 1843-1849, 2019. [http://dx.doi.org/10.1039/C8DT04397C] [PMID: 30648716]

[68] H. Wang, Y. Zhao, Z. Shao, W. Xu, Q. Wu, X. Ding, and H. Hou, "Proton conduction of nafion hybrid membranes promoted by NH 3 -modified Zn-MOF with host–guest collaborative hydrogen bonds for H 2 /O 2 fuel cell applications", *ACS Appl. Mater. Interfaces,* vol. 13, no. 6, pp. 7485-7497, 2021. [http://dx.doi.org/10.1021/acsami.0c21840] [PMID: 33543925]

[69] Z. Jiang, Y. Zou, T. Xu, L. Fan, P. Zhou, and Y. He, "A hydrostable cage-based MOF with open metal

sites and Lewis basic sites immobilized in the pore surface for efficient separation and purification of natural gas and C 2 H 2", *Dalton Trans.,* vol. 49, no. 11, pp. 3553-3561, 2020. [http://dx.doi.org/10.1039/D0DT00402B] [PMID: 32118237]

[70] Y. Chen, H. Yang, Z. Han, Z. Bo, J. Yan, K. Cen, and K.K. Ostrikov, "MXene-based electrodes for supercapacitor energy storage", *Energy Fuels,* vol. 36, no. 5, pp. 2390-2406, 2022. [http://dx.doi.org/10.1021/acs.energyfuels.1c04104]

[71] L. Yu, Z. Fan, Y. Shao, Z. Tian, J. Sun, and Z. Liu, "Versatile N-doped MXene ink for printed electrochemical energy storage application", *Adv. Energy Mater.,* vol. 9, no. 34, p. 1901839, 2019. [http://dx.doi.org/10.1002/aenm.201901839]

[72] T. Schultz, N.C. Frey, K. Hantanasirisakul, S. Park, S.J. May, V.B. Shenoy, Y. Gogotsi, and N. Koch, "Surface termination dependent work function and electronic properties of Ti3C2T x Mxene", *Chem. Mater.,* vol. 31, no. 17, pp. 6590-6597, 2019. [http://dx.doi.org/10.1021/acs.chemmater.9b00414]

[73] K.H. Tan, L. Samylingam, N. Aslfattahi, R. Saidur, and K. Kadirgama, "Optical and conductivity studies of polyvinyl alcohol-MXene (PVA-MXene) nanocomposite thin films for electronic applications", *Opt. Laser Technol.,* vol. 136, p. 106772, 2021. [http://dx.doi.org/10.1016/j.optlastec.2020.106772]

[74] P. Zhang, X.J. Yang, P. Li, Y. Zhao, and Q.J. Niu, "Fabrication of novel MXene (Ti 3 C 2)/polyacrylamide nanocomposite hydrogels with enhanced mechanical and drug release properties", *Soft Matter,* vol. 16, no. 1, pp. 162-169, 2020. [http://dx.doi.org/10.1039/C9SM01985E] [PMID: 31774104]

[75] Y. Yue, B. Wang, N. Miao, C. Jiang, H. Lu, B. Zhang, Y. Wu, J. Ren, and M. Wang, "Tuning the magnetic properties of Zr2N MXene by biaxial strain", *Ceram. Int.,* vol. 47, no. 2, pp. 2367-2373, 2021. [http://dx.doi.org/10.1016/j.ceramint.2020.09.079]

[76] M.R. Abhilash, G. Akshatha, and S. Srikantaswamy, "Photocatalytic dye degradation and biological activities of the Fe 2 O 3 /Cu 2 O nanocomposite", *RSC Advances,* vol. 9, no. 15, pp. 8557-8568, 2019. [http://dx.doi.org/10.1039/C8RA09929D] [PMID: 35518681]

[77] L. Ge, M. Zhang, R. Wang, N. Li, L. Zhang, S. Liu, and T. Jiao, "Fabrication of CS/GA/RGO/Pd composite hydrogels for highly efficient catalytic reduction of organic pollutants", *RSC Advances,* vol. 10, no. 26, pp. 15091-15097, 2020. [http://dx.doi.org/10.1039/D0RA01884H] [PMID: 35495471]

[78] M.S. Vidhya, G. Ravi, R. Yuvakkumar, D. Velauthapillai, M. Thambidurai, C. Dang, B. Saravanakumar, A. Syed, and T.M. Dawoud, "Functional reduced graphene oxide/cobalt hydroxide composite for energy storage applications", *Mater. Lett.,* vol. 276, p. 128193, 2020. [http://dx.doi.org/10.1016/j.matlet.2020.128193]

[79] A. Feng, T. Hou, Z. Jia, and G. Wu, "Synthesis of a hierarchical carbon fiber@cobalt ferrite@manganese dioxide composite and its application as a microwave absorber", *RSC Advances,* vol. 10, no. 18, pp. 10510-10518, 2020. [http://dx.doi.org/10.1039/C9RA10327A] [PMID: 35492930]

[80] S. Sankar, A. George, and M.T. Ramesan, "Copper alumina @ poly (aniline- co -indole) nanocomposites: synthesis, characterization, electrical properties and gas sensing applications", *RSC Advances,* vol. 12, no. 27, pp. 17637-17644, 2022. [http://dx.doi.org/10.1039/D2RA02213C] [PMID: 35765439]

[81] S.K. Dwivedi, D.C. Tiwari, S.K. Tripathi, P.K. Dwivedi, P. Dipak, T. Chandel, and N.E. Prasad, "Fabrication and properties of P3HT: PCBM/Cu2SnSe3 (CTSe) nanocrystals based inverted hybrid solar cells", *Sol. Energy,* vol. 187, pp. 167-174, 2019. [http://dx.doi.org/10.1016/j.solener.2019.05.012]

[82] S.K. Dwivedi, S.K. Tripathi, D.C. Tiwari, A.S. Chauhan, P.K. Dwivedi, and N. Eswara Prasad, "Low

cost copper zinc tin sulphide (CZTS) solar cells fabricated by sulphurizing sol-gel deposited precursor using 1,2-ethanedithiol (EDT)", In: *Solar Energy.* vol. 224. , 2021, pp. 210-217.

[83] S.K. Dwivedi, D.C. Tiwari, N. Kumar, S.K. Tripathi, and N.E. Prasad, "Electrochemical-based studies of Cu2SnSe3 nanocrystals and P3HT:PCBM for hybrid solar cells", *Bull. Mater. Sci.,* vol. 46, no. 3, p. 163, 2023.
[http://dx.doi.org/10.1007/s12034-023-03000-7]

[84] P. Uday Bhaskar, G. Suresh Babu, Y.B. Kishore Kumar, and V. Sundara Raja, "Investigations on co-evaporated Cu2SnSe3 and Cu2SnSe3–ZnSe thin films", *Appl. Surf. Sci.,* vol. 257, no. 20, pp. 8529-8534, 2011.
[http://dx.doi.org/10.1016/j.apsusc.2011.05.008]

[85] S.K. Dwivedi, S.K. Tripathi, D.C. Tiwari, A.S. Chauhan, P.K. Dwivedi, and N. Eswara Prasad, "Low cost copper zinc tin sulphide (CZTS) solar cells fabricated by sulphurizing sol-gel deposited precursor using 1,2-ethanedithiol (EDT)", *Sol. Energy,* vol. 224, pp. 210-217, 2021.
[http://dx.doi.org/10.1016/j.solener.2021.04.046]

[86] D.C. Tiwari, S.K. Dwivedi, P. Dipak, and T. Chandel, "PEDOT: PSS: RGO nanocomposite as a hole transport layer (HTLs) for P3HT: PCBM based organic solar cells", *AIP Conference Proceedings,* vol. 1953, p. 100065, 2018.

[87] N. Kumar, S. Kumar Dwivedi, D. Chandra Tiwari, and R. Tomar, "Study of rGO-CNF/Ce-TiO2 based hetrojunction for optoelectronic devices", *Mater. Lett.,* vol. 315, p. 131945, 2022.
[http://dx.doi.org/10.1016/j.matlet.2022.131945]

[88] M.G. Bawendi, M.L. Steigerwald, and L.E. Brus, "The quantum mechanics of larger semiconductor clusters (“quantum dots”)", *Annu. Rev. Phys. Chem.,* vol. 41, no. 1, pp. 477-496, 1990.
[http://dx.doi.org/10.1146/annurev.pc.41.100190.002401]

[89] V.G. Veselago, "The electrodynamics of substances with simultaneously negative values of $$ and μ", *Sov. Phys. Usp.,* vol. 10, no. 4, pp. 509-514, 1968.
[http://dx.doi.org/10.1070/PU1968v010n04ABEH003699]

[90] X. Dai, Z. Zhang, Y. Jin, Y. Niu, H. Cao, X. Liang, L. Chen, J. Wang, and X. Peng, "Solution-processed, high-performance light-emitting diodes based on quantum dots", *Nature,* vol. 515, no. 7525, pp. 96-99, 2014.
[http://dx.doi.org/10.1038/nature13829] [PMID: 25363773]

[91] M.S. Zaini, J. Ying Chyi Liew, S.A. Alang Ahmad, A.R. Mohmad, and M.A. Kamarudin, "Quantum confinement effect and photoenhancement of photoluminescence of PbS and PbS/MnS quantum dots", *Appl. Sci.,* vol. 10, no. 18, p. 6282, 2020.
[http://dx.doi.org/10.3390/app10186282]

[92] W.K. Bae, Y.S. Park, J. Lim, D. Lee, L.A. Padilha, H. McDaniel, I. Robel, C. Lee, J.M. Pietryga, and V.I. Klimov, "Controlling the influence of Auger recombination on the performance of quantum-dot light-emitting diodes", *Nat. Commun.,* vol. 4, no. 1, p. 2661, 2013.
[http://dx.doi.org/10.1038/ncomms3661] [PMID: 24157692]

[93] Z. Vaseghi, and A. Nematollahzadeh, "Nanomaterials", In: *A book chapter-2, Green synthesis of nanomaterials for bioenergy applications.* John Wiley, 2020, pp. 23-82.
[http://dx.doi.org/10.1002/9781119576785.ch2]

[94] L.A. Kolahalam, I.V. Kasi Viswanath, B.S. Diwakar, B. Govindh, V. Reddy, and Y.L.N. Murthy, "Review on nanomaterials: Synthesis and applications", *Mater. Today Proc.,* vol. 18, pp. 2182-2190, 2019.
[http://dx.doi.org/10.1016/j.matpr.2019.07.371]

[95] S. Anu Mary Ealia, and M.P. Saravanakumar, "A review on the classification, characterisation, synthesis of nanoparticles and their application", *IOP Conf. Series Mater. Sci. Eng.,* vol. 263, p. 032019, 2017.
[http://dx.doi.org/10.1088/1757-899X/263/3/032019]