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Recent advances on properties and utility of nanomaterials generated from industrial and biological activities

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Abstract

Today is the era of nanoscience and nanotechnology, which finds applications in the field of medicine, electronics, or environmental cleanup. Even though the nanotechnology is in its emerging phase, but still it provides solutions to numerous challenges. Nanotechnology and nanoparticles are found very effective because of their unique chemical and physical properties, high surface area, but their high cost is one of the major hurdles in its wider application. So, the synthesis of nanomaterials especially 2D nanomaterials from the industrial, agricultural and other biological activities could provide a cost-effective technique. The nanomaterials synthesized from such waste not only minimizes the pollution but also provides an eco-friendly approach towards the utilization of the waste. In the present review work, the emphasis has been given on the types of nanomaterials, different methods for the synthesis of 2D nanomaterials from the waste generated from industries, agriculture and their application in electronics, medicine and catalysis.

Keywords: Nanomaterials; Carbon nanotubes; Rice husk; Agriculture waste; Carbon nanofibres

Abbreviations

0-D: 0-dimensional

1-D: 1-dimensional

2-D: 2-dimensional

3-D: 3-dimensional

AFM: atomic force microscopy

$AgNO_3$: silver nitrate

Al_2O_3: aluminum oxide

BaO: barium Oxide

BET: brunauer emitter teller

^0C: degree celsius

Ca: calcium

CaO: calcium Oxide

Cd: cadmium

CO: carbon monoxide

Co_3O_4: cobalt (II, III) oxide

CNTs: carbon nanotubes

Cr: chromium

CVD: chemical vapor deposition

DMF: N, N-dimethylformamide

Fe: ferrous

Fe_2O_3: ferric oxide

Fe_3O_4: ferric oxide

Ga: gallium

GO: grapheme oxide

HER: hydrogen evolution reaction

HRTEM: high resolution Transmission Electron microscopy

InSe: Indium selenide

K: kelvin

LCVD: laser chemical vapor deposition techniques

LEDs: light emitting diodes

Mg: magnesium

MgO: magnesium oxide

µm: micrometer

Mn: manganese

MnO: manganese oxide

Mo: molybdenum

MoO_3: molybdenum trioxide

MoS_2: molybdenum disulfide

MWCNT: multi walled carbon nanotubes

Na: sodium

Ni: nickel

Nm: nanometre

NMs: nanomaterials

NSMs: nano structured materials

NSs: nanosheets

NPs: nanoparticles

NSs: nanostructures

ORR: oxygen reduction reaction

Pb: lead

Pd: palladium

PEM: polymer electrolyte material

P_2O_5: phosphorus pentoxide

Pt: platinum

PVP: polyvinyl pyrrolidone

QD: quantum dots

Rice Husk: rice husk

SB: sugarcane bagasse

Se: selenium

SEM: scanning Electron microscopy

SERS: surface enhanced Raman scattering

SiO_2: silicon dioxide (silica)

SnO: stannous oxide

SnO2: stannic oxide

SPR: surface plasmon resonance

SQUID: superconducting quantum interface device

SS: standard size

SVR: surface volume ratio

TEM: transmission electron microscopy

TGA: Thermo gravimetric analysis

TiO_2: Titanium dioxide

TPPs: thermal power plants

WO_3: Tungsten trioxide

WS_3: Tungsten (VI) Sulfide

XRD: x-ray diffraction

Zn: zinc

ZnO: zinc oxide

ZnS: zinc sulfide

1. Introduction

Nanotechnology deals with the design and development of the materials at the nanoscale (1-100 nm) or one dimension in the nanoscale [1]. The word nano was derived from the Greek word meaning "dwarf" [2] and denoted as nm. By using such measurement, the size of viruses are about 100 nm (30-100) nm [3] and to that of a human hair is 1000 nm in diameter. Nanotechnology and nanoscience allow the researchers to manipulate the properties of materials at the atomic level [4]. Nanomaterials can be produced in a variety of methods like chemical, physical and biological with different classes such as: carbon-based nanomaterials [5], nanocomposites [6], metals, alloys, nanopolymers [7], nanoglassses [8] and nanoceramics [7].

Nanomaterials are typically those materials having at least anyone dimension at the nanoscale (<100 nm). Nanomaterials can be either synthesized in the laboratory or could be derived from the natural resources [9]. The nanomaterial synthesized from the commercial precursor materials makes the product as well as process expensive. Moreover, the source of nanomaterial is also depleting, so there is a need to rely on the natural and alternative sources of nanomaterial. The natural nanomaterial [10] act as a potential candidate for the development of nanomaterials. The nanomaterial derived from such processes are cost-effective [11], biocompatible [12] and environment friendly [13]. The waste materials that are commonly used for nanomaterial synthesis includes industrial waste like fly ash [14], red mud, agricultural waste [15] (rice husk and straw, wheat husk and straw, coconut shell) and plastic waste [16]. Most of these waste materials mainly act as a pollutant to the environment, which are produced in tonnes annually around the globe. The utilization of such products for the synthesis of carbon nanomaterials reduces the pollution from the environment and simultaneously provides an environment-friendly and economical approach.

These nanostructured materials based on their purities can find application in the electronics [17], wastewater treatment [18], medicine [19] and catalysis [19].

2. Classification of nanostructured materials

Nanostructured materials (NSMs) have gained a huge consideration in fundamental science and technological applications due to their multifunctionality and unique chemical, physical, electronic and magnetic properties at the nanoscale [20]. Like every day new novel nanomaterials are synthesized so the classification is an utmost need for this.

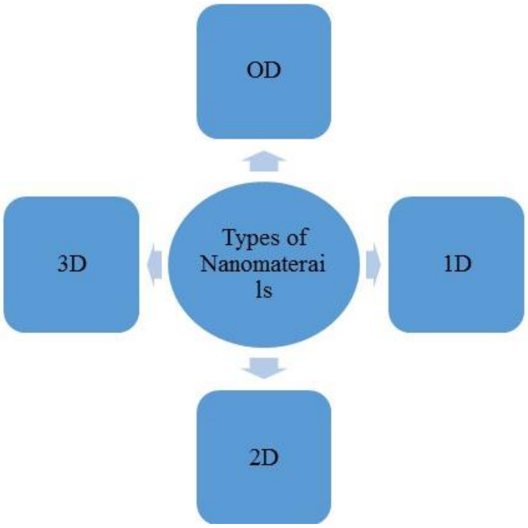

Fig.1 Classification of nanomaterials

The density of the state varies considerably for different nanomaterials which are based on the degree of freedom/confinement [21]. Based on the nanostructural elements and their physical and chemical properties; the nanomaterials have been classified into four classes i.e. 0-D, 1-D, 2-D, and 3-D by Pokropivny.

2.1 Zero-dimensional nanomaterial (0-D nanomaterial)

In 0-D material (quantum dot) [QD], there is confinement of electrons in all the three directions [22]. Zero dimensional nanomaterial has gained a huge attention in the field of research and in material based industries [23]. Such material finds applications in the light emitting diodes (LEDs) [24], solar cells [25], single-electron transistors [26], and lasers. The common example of zero dimensional nanomaterial are spheres (including hollow spheres) and nanoclusters [27], quantum dots that includes core-shell QDs also [28], heterogeneous particles arrays, onions [29], and nanolenses.

2.2 One dimensional nanomaterial (1D-Nanomaterial)

One dimensional nanomaterial is those materials which are confined in two dimension but free in one dimension [30]. Some of the common examples of 1D nanomaterial are wires, nanowires [31], nanotubes, nanofibres [32], nanobelts [33], nanoribbons [33], nanorods [34] and hierarchical nanostructures**.** From the last decade, such nanomaterial has gained huge considerations because of their remarkable properties and such a wider applicability in the research and development and material development. Such materials have wider impact in nanoelectronics [35], nanodevices and systems [36], nanocomposite materials [37], and alternative resources of energy. The 1D nanomaterials are the most preferred material for exploring the properties at the nanoscale. It is also used for the investigation of size and dimensionality dependence of functional properties [38].

2.3 Two-dimensional nanomaterials (2D nanomaterials)

2D nanomaterials have only one dimension in the nano range while the other two dimensions are out of nano range [39]. 2D Materials are said to be the thinnest materials, which possess the highest surface area. In recent years, not only the synthesis but also the applications of 2D NSMs have drastically dawn attentions in materials research because of their several interesting properties at the nanoscale. In comparison with bulk materials, two-dimensional (2D) nanomaterials own rare physiochemical assets develops due to their high aspect ratio (SVR) [40], distinctive surface chemical properties, and quantum confinement effect [41]. The 2D NSMs finds applications in sensing materials, photocatalysis, nanocontainers and nanoreactors [28]. Most preferably, the metallic based 2D NSMs have exploited widely in sensing, catalysis, photothermal therapy, surface-enhanced Raman scattering (SERS), bioimaging, and solar cells [42], due to their phenomenal properties. The common examples of 2D nanomaterials are nanoprisms [43], nanoplates [44], nanosheets [45, 46], nanowalls [46], and nanodisks [47].

2.4 Three Dimensional nanomaterials (3D-Nanomaterials)

The 3D NSMs three dimensional nanomaterials are those materials which have their free dimensions in all the three directions and there is no confinement and limitations [28]. The common examples of three 3D nanomaterials are powders [48], multilayer [49], fibrous and poly crystalline materials [9]. The 3D nanomaterials exhibit have large specific surface area [50] and because of which such nanostructures provide adequate surface absorption sites for the molecules in a small area. The 3D NSMs are extensively used for catalysis in nanomaterials finds applications in the field of catalysis [51], magnetism and for development of electrode material for batteries [52]. Additionally, the porosity in the three dimensions, helps in the easy transport of the molecules. The examples of 3D NMSs are nanoballs (dendritic structures) [53], nanocoils [54], nanocones [28], nanopillers [55] and nanoflowers [55].

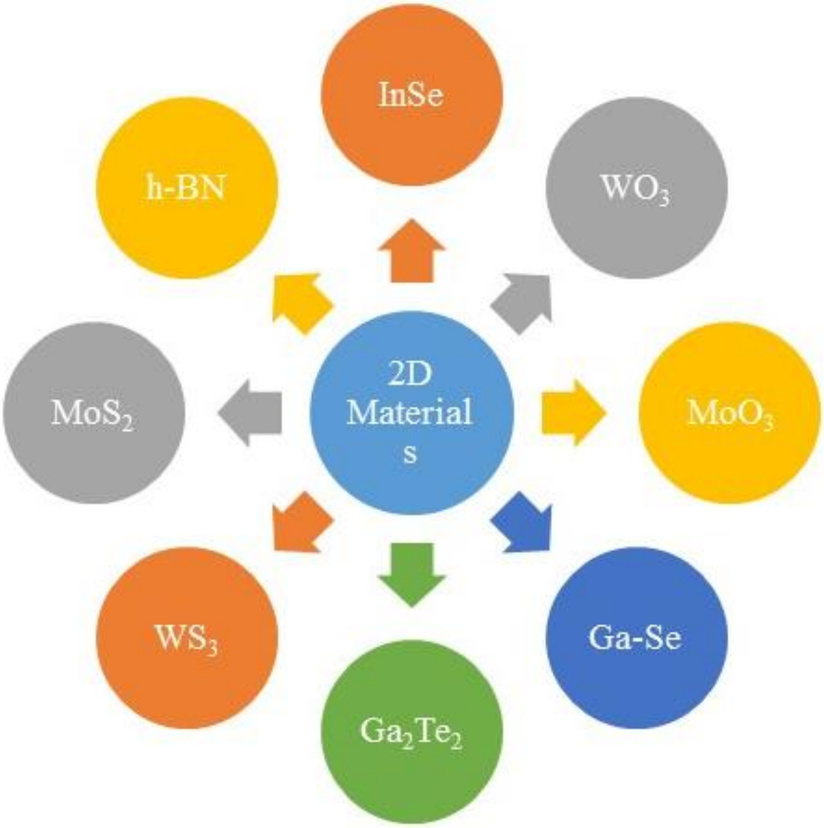

Fig.2 Examples of 2D materials

3. Different methods of nanomaterials synthesis

The nanomaterials could be developed by all the three means i.e. chemical, physical and biological methods. Among them the physical approaches includes sputtering [56], laser ablation [57], pyrolysis [58], lithography [59], and hot and cold plasma [59]. While, the chemical methods that are used most frequently are lyotropic liquid crystal templates [60], electrochemical deposition [61], electroless deposition [62], hydrothermal [63] and solvothermal techniques [64], sol–gel technique [65, 66], laser chemical vapor deposition technique [67], laser pyrolysis [68] and chemical vapor deposition [69]. The nanomaterials could also be synthesized by the biological approaches like microbial [70] and plant derived materials [71]. The microbial synthesis of nanomaterials [72] employs the utilization of microorganisms like algae [73], fungi [46] and bacteria [74]. The main drawback is that when there is utilization of commercial precursor for the synthesis of nanomaterials by any of the above mentioned approaches there the process as well as the product become expensive. So, in order to get a cost-effective material the precursor should be lower in cost. One such materials are the industrial waste [75], biological waste or agricultural waste [15].

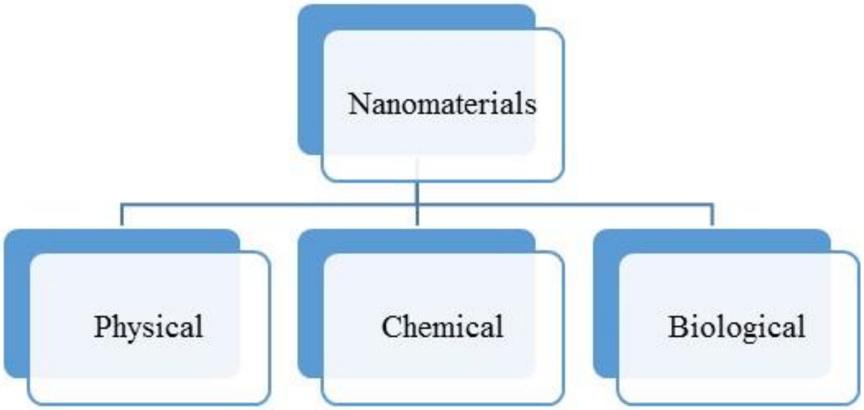

Fig. 3 Different methods of synthesis of nanomaterials

3.1. Physical methods for synthesis of 2D NSMs

The 2D NSMs could be synthesized by various physical methods [76] such as evaporation [77], lithography [78], sputtering, phase condensation, hot and cold plasma spray pyrolysis [79], inert gas phase condensation [80], pulsed laser ablation method [81] and sonochemical reduction [82]. These methods (physical) are generally used for the synthesis of nanowalls [46], nanoprisms [83], nanosheets [84], nanoplates [85], and nanodisks [28]. The nanomaterials synthesized by physical method are homogenous in nature and ordered. Dai et al., 2002 developed the SnO nanodisks [56]-alumina plates using thermal evaporation method under optimized environmental conditions [86]. Here firstly, SnO or SnO_2 powders were kept in an alumina boat which in turn placed in a quartz tube reactor (evaporation source), where alumina act as a substrate which was placed one by one in the downstream. The physical techniques provides an environment friendly approach for the development of 0D; 1D; 2D; and 3D nanomaterials which are shown below in Figure 5.

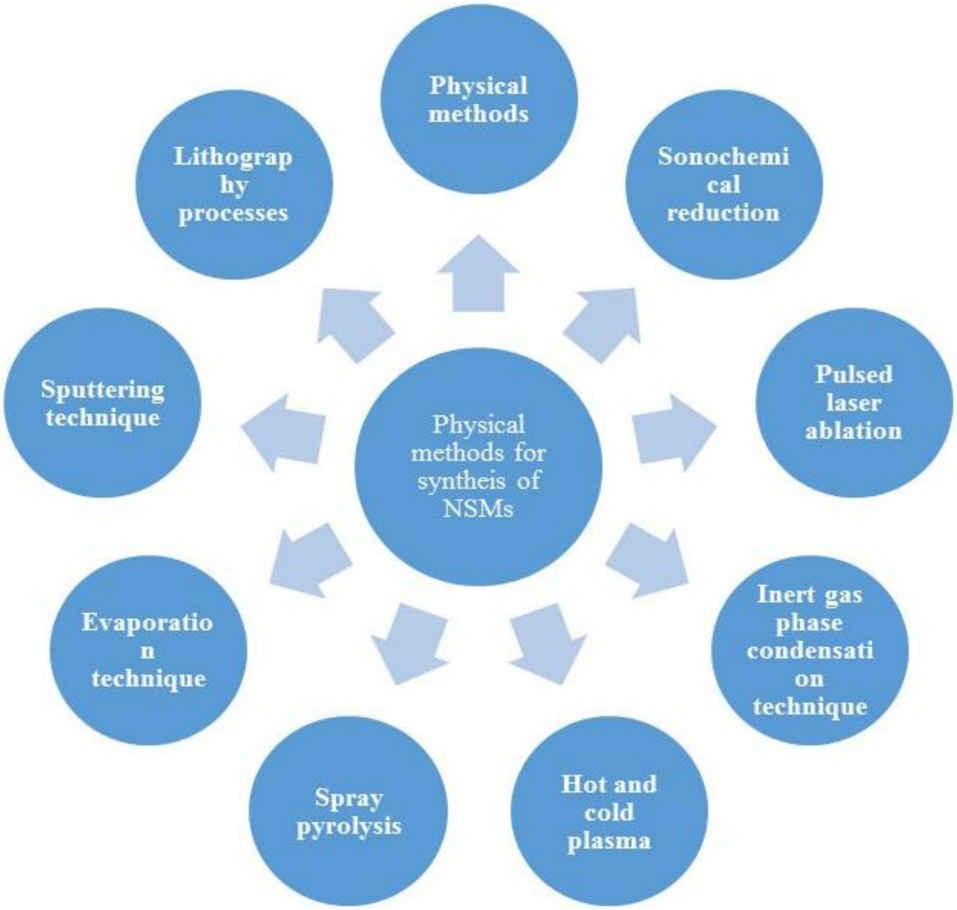

Fig. 5 Physical methods for the synthesis of 2D nanomaterial

3.2. Chemical methods for synthesis of nanomaterials

Chemical methods have contributed to the fabrication of materials at nanoscale [87]. The Chemical methods have several advantageous properties over physical methods as the previous one involves mixing of chemical at molecular level which ensures good chemical homogeneity [66, 88]. Chemical reduction methods are reported to have numerous drawbacks for instance utilization toxic reagents and solvents, generation of unwanted by products due to which there are several extra step is needed for removal of impurities, time consuming [89]. The most common chemical methods are electroless deposition [90], lyotropic liquid crystal templates [28], hydrothermal and solvothermal method, sol-gel technique , electrochemical deposition, chemical vapor deposition (CVD), laser pyrolysis and laser chemical vapor deposition techniques (LCVD) which are utilized frequently for the production of different NSMs. The above-mentioned techniques are shown in the Figure 6.

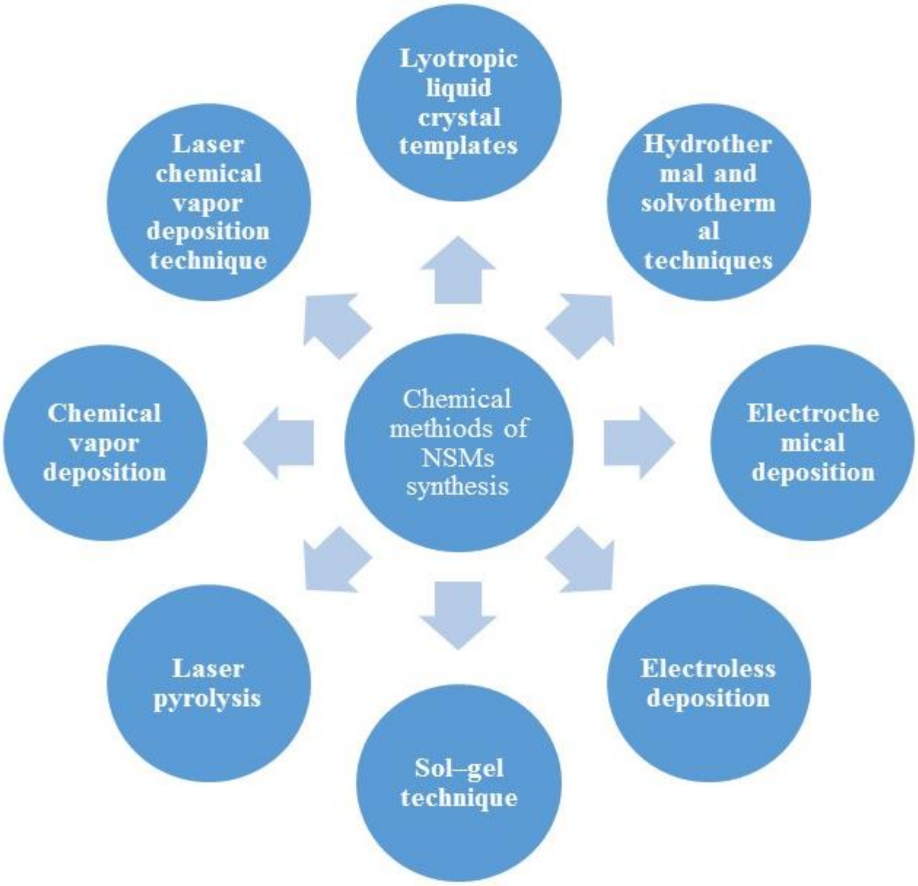

Fig. 6 Chemical methods of synthesis of nanomaterials

Among all the metallic nanoparticles silver nanoparticles has gained used consideration due to their exceptional properties and applications. Silver nanoparticles of different shapes and sizes have important role in medicine, biomedical field and drug delivery [91]. Till now silver NPs of various shapes and sizes has been reported by the numerous investigators. Nanoprisms are one of the example of 2D nanomaterial, which had gained huge attention in the biomedical field [91]. Silver nanoprisms were synthesized silver salts by chemical reduction and photochemical method where the earlier method is more preferred than the later one due to their more controlled growth of nanoprisms which finds application in the industries [92]. Monodispersed hematite (a-Fe_2O_3) nanodiscs of size (50±10 nm in diameter and thickness of 6.5 nm) synthesized under a mild conditions through a facile hydrothermal method i.e. hydrolysis of ferric chloride [93]. The reported method was quite unique as there was no use of surfactants, no toxic or hazardous chemical precursors, no high temperatures decomposition of iron precursors in non-polar solvents. The synthesized hematite nanodiscs were further characterized by the atomic force microscopy (AFM), X-ray diffraction (XRD), Scanning Electron microscopy (SEM), Transmission Electron microscopy (TEM), Brunauer Emitter Teller (BET), and superconducting quantum interface device (SQUID). The synthesis of Ta_3N_5 nanoplates was reported by Jie Fu and Sara E. Skrabalak, 2016, for the photocatalytic application [94]. A simple technique developed for the production of hexagonal-shaped Ag nanoplates whose diameter was in the range of 15-20 nm with a smooth nanobulk of 120 nm [95]. The silver nanoplates were prepared by a kinetically controlled solution growth method under following conditions; polyvinyl pyrrolidone (PVP) as a capping agent, dextrose as reducing agent, and urea as a habit modifier at 50 ^{0}C and the crystalline structure of silver nanoplates analyzed by the XRD and TEM.

Xin He et al., 2009 synthesized triangular/hexagonal silver nanoplates, nanobelts and chain-like nanoplate assemblies by utilizing N,N-dimethylformamide (DMF) along with PVP [96]. The results revealed that due to the strong interaction between Ag^+ and PVP, there was the formation of individual nanoplates and external features of nanoplates were controlled by the ratio of $AgNO_3$

and PVP. Sial et al., 2018 synthesized multimetallic nanosheets which was utilized for the manufacturing of fuel cells [97]. Zheng et al.,2011 synthesized Palladium NSs by using CO as a reducing agent [98]. Yansong Zhou et al., 2016 reported an ultra-facile and generalized approach for the synthesis of metal oxide nanosheets (TiO_2, Co_3O_4, Fe_2O_3, ZnO, and WO_3) with larger surface and applied them for the for energy applications [99]. Jianxing Liu, He Yang, Xiangxin Xue 2018, reported the synthesis of hematite nanosheets by using a large sized particles of iron red and found that the shape of hematite have important effect on the magnetic and optical properties [100]. All the above mentioned chemical processes revealed simple, reliable and useful approach towards synthesis of 2D NSMs. The shape, size and composition of the 2D NSMs can be varied by precursor solutions, conditions of deposition and substrate materials [76].

3.3 Biological methods for the synthesis of 2D NSMs

Biological synthesis of nanomaterials involves the synthesis from plants and their parts, microbes for instance algae, fungi and bacteria. In comparison to the chemical and physical method biological methods are eco-friendly and there is minimum utilization of hazardous chemicals. Besides this the nanomaterials synthesized by biological methods are biocompatible. There are several reports where the nanomaterials have been synthesized by biological methods [101].

4. Carbon nanomaterials

Carbon is not only the most abundant element on earth crust but it also acquires exceptional properties because of its hybrid orbitals. The allotropes of carbon is mainly due to the hybridization of bonds formed after the combination of atomic orbitals (s and p) into new hybrid orbitals as sp, sp^2, and sp^3. The different allotropes of carbon are buckyballs (0D), CNTs (1D), graphene sheets (2D), and diamond (3D) [102]. Due to the allotropy, carbon forms a separate class of 2D nanomaterials that includes graphene, GO, CNTs, buckyballs and its derivatives which are shown in the Figure. 7 and the properties of graphene oxide (GO) is shown in Figure 8. All these nanocarbons finds applications in electronics, environmental cleanup, drug delivery, agriculture, research and catalysis [103]. The wider applications of nanocarbons are also due to presence of wide range of structural and textural properties in them. Out of all, nanocarbons, CNTs and graphene are the most widely used nanomaterials in the field of nanotechnology [103].

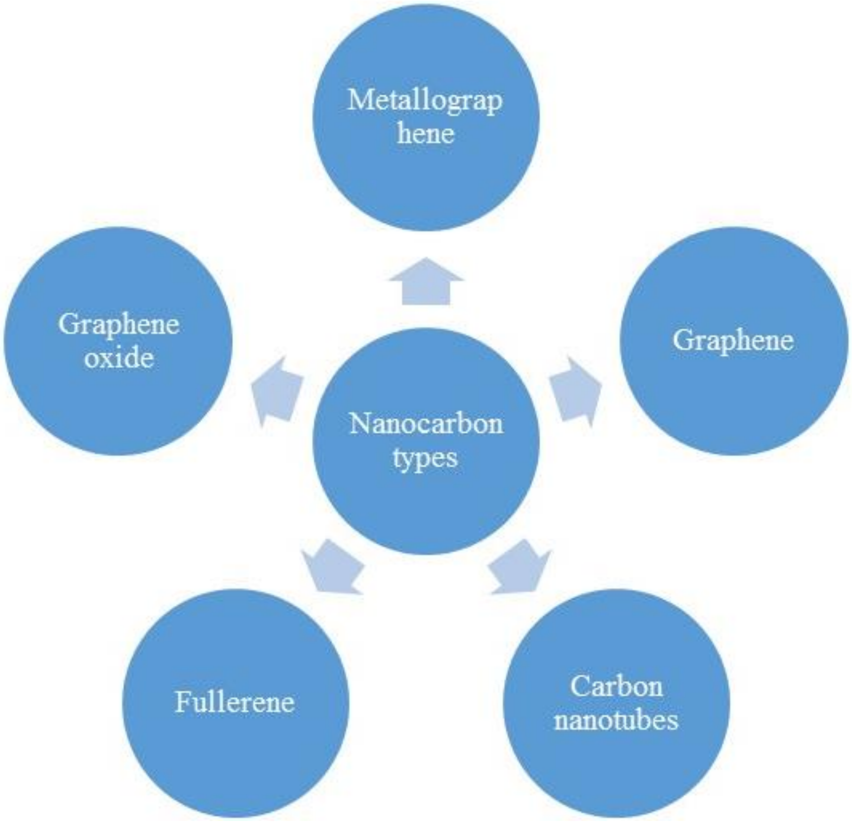

Fig.7 Different types of nanocarbons

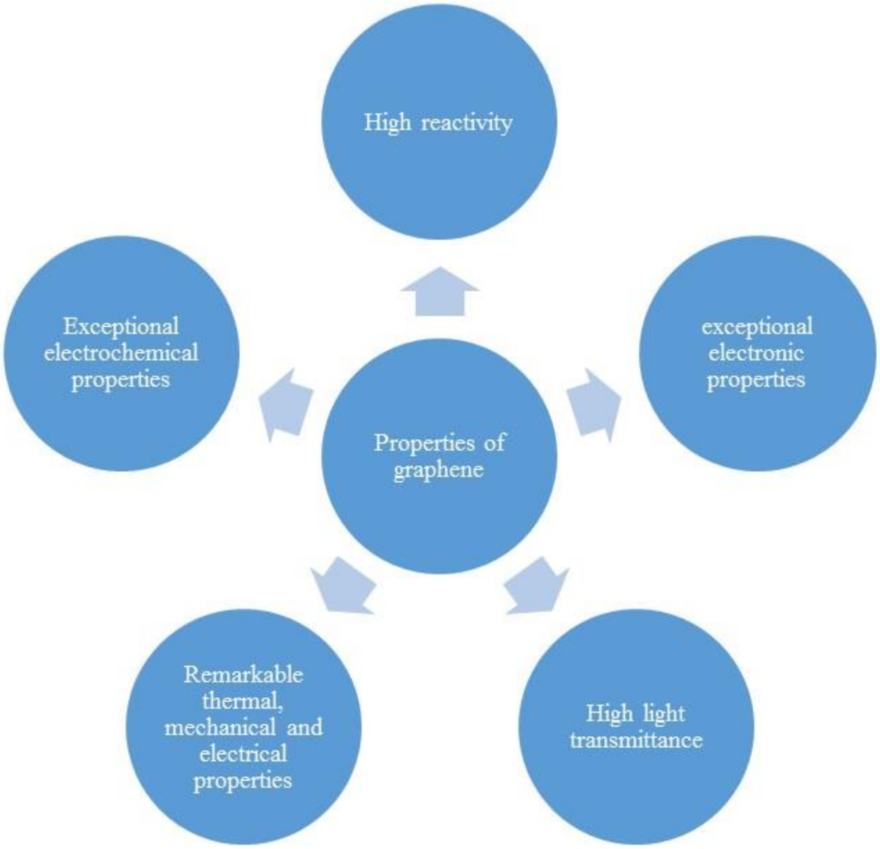

Fig. 8 Properties of graphene

4.1 Synthesis of GO from agro waste

Sugarcane bagasse (SB) [104] is an agricultural waste which is rich in carbon content. Every year it is produced in million tonnes around the whole world and challenges a potential threat for the environment. The recovery of nanocarbons and GO from such waste will reduce the pollution from the environment. The recovery of GO from sugarcane bagasse includes following steps, collection of the fiber, crushing followed by grinding to obtain a powder, repetition of these two steps in order to increase the fineness of the powder [105]. Grounded SB and ferrocene was mixed in 5:1 ratio by weight, in a crucible and calcination was done in a muffle furnace at 300 ^{0}C for 10 min under atmospheric conditions. The as produced black solid was collected and the final product was analyzed.

4.2 Carbon nanotubes/carbon nanofibers

One of the most systematically studied nanostructures, carbon nanotubes (CNTs) are cylindrically shaped materials with lengths in the order of few microns while the cross-sectional diameters are in the nanometer range [106, 107]. Elongated surface of these materials makes them robustly versatile for their functionalization driven need based applications. Although the hybridization of constitutive carbon atoms is sp^2 (similar to graphene), but the arrangement of atoms is relatively distinct (that does not form layers). The two known variations are single walled and multiwalled, with a high purity and cost of former. The most extraordinary feature of these materials is their structural toughness, imparted by inherently high rigidity, Young's Modulus, coefficient of elasticity which together are the reasons for their robust suitability in civil, defense, aeronautic and many other strategic applications [107, 108]. It is because of such remarkable properties that these materials are widely preferred for developing immobilization based assays, with high detection sensitivities. An interesting aspect of these nanomaterials is that based on their geometry and chiral carbon vicinity, these can be electrically conductive, semi-conductive or insulated [107]. These adjustable electronic properties form the basis of their usage in single electronic transistors, flexible automated diodes where electron flow needs to be manipulated [109]. Comprised of only carbon, a variety of substrates have been used to obtain nanotubes *via* differently explored mechanisms. The most widely used methods of preparation are laser ablation, CVD [110], and electric discharge which necessitate the provision of specific stoichiometric mix of precursors. Though there are some concerns regarding the drug delivery application of these materials (with a potential risk of toxicity initiation), still the ability of functionalization has minimized such concerns and enabled a dose and location specific drug delivery with them. Readers are suggested to concern more specific literature sources regarding the biological applications of these nanomaterials. Substrates as common as biscuits, chocolates, waste tyres, rubber and manifold carbon comprising substances have been used to prepare carbon nanotubes [111-113].

4.3 CNTs from fly ash

Fly ash constitutes one of the most primitive by products, most widely produced through pulverized coal combustion at the time of electricity generation in thermal power plants (TPPs) [114]. Other than coal combustion, industrial activities such as mining and metallurgical operations also contribute to fly ash generation. Compositionally, fly ash comprises of diverse minerals and carbon materials either in single or combined form. The toxicity risk of fly ash has recently been in news pertaining to deteriorating environmental quality in many developed and developing nations across the globe. In these circumstances, a potential utilization of these materials towards preparation of nanomaterials like CNTs [115], fullerenes [56] and several others could be a significant breakthrough remedy to improve the pollution and toxicity extents and contents of environment. Traces of carbon in the fly-ash are derived from organic contents and incomplete combustion of coal, soots and charcoal combustion end products [116]. Several studies report the preparation of CNTs from fly ash, with a 2016 study claimed the utility and aptness of Saudi Arabian fly ash to provide CNTs using chemical vapor deposition method, provided all reaction conditions are maintained [117]. The preparation of CNTs from fly ash could be considered as an alternative to famous electric arc-discharge method, with significant reports of transition metals (Mn, Mg, Ca, Na, Pb, Cd, Cr, Co, Ni, Zn and Mo), present as traces in the fly ash. Depending on the regional geography and parent source of generation, the transition metal composition and diversity extents may vary amongst different sources. A generalized idea of typical fly ash composition is mentioned in Table 1. This synthesis of CNTs serves dual purpose, one being the minimization of hazardous waste in the environment while the other being the cost effectiveness and minimized use of energy. So, this approach is fittingly a green solution to minimize the undesired environmental risks of fly-ash by means of sustainable approach. Research on particulate matter pollution does pose a concern of significant respiratory complications from inhaling fly-ash.

Table 1 Elemental composition of fly ashes

Elements	**Composition (wt. %)**
SiO_2	40-60%
Al_2O_3	20-40%
Fe_2O_3-Fe_3O_4	5-15%
TiO_2	2-5%
Carbon	5-20%
CaO, BaO, MgO, MnO, P_2O_5	Traces

4.4 CNTs from plastic waste and tyres

Carbon based everyday gadgets, such as plastic materials, tyres [67], rubber end products and several other forms can be readily used for making CNTs, using several modifications in their subsequent chemical treatment approaches. The generation of plastic wastes to the tune of billion tones on an everyday basis is one of the most pulsating concerns, since plastic wastes often encounter a disposal problem due to their biodegradability concerns. Plastics are viciously produced as waste products from industries, household routines, laboratories, hospitals and eateries. Although the non-biodegradable nature of these materials has resulted in their substantial recycling, but the recycled plastics often lose their plasticity. Many studies have nevertheless used the plasticity intact waste materials to make CNTs *via* processing under varying oxygen environments. In one such study, plastic waste was readily decomposed to propylene which subsequently catalyzed the MWCNT formation over the surface of metal catalysts [118]. Growth mechanism is well known with reportedly following a tip-growth or base-growth pattern in course of a vapor-liquid-solid reaction [119, 120]. Nevertheless, there is still no clarity regarding the utilization of carbon atoms whether in the bulk catalyst or react within the top surface of catalyst. The reaction was mediated by the utilization of reactor material (SS 316 tube of a CVD reactor), with the confirmatory studies revealing that removal of Cr from the reactor vessel resulted in MWCNT growth. Similar studies on SS 316 mesh surface found an involvement of Fe and Ni in the CNT formation. The results were in agreement of the works by *Levendis and co-workers* with a further ensuring of metal catalyst prevalence along the tip of MWCNTs inside the tubes [121]. Similarly, a 2016 study by *Zhang and Williams* reports the synthesis of MWCNTs along with hydrogen generation by the catalytic pyrolysis of waste tyres. The study employed a catalyst system comprising of a Ni/Al_2O_3 prepared via impregnation of Ni on Al_2O_3 surface. The experimental procedure was optimized by varying the temperature from (700 to 900) ^{0}C, alongside varying the tyre to catalyst ratios from 1:0.5 to 1:1 and 1:2 and using steam input *via* injection of hot water at 0,2 and 5 mL per hour injection rates. Estimation of the carbon fractions (formed as product) revealed 253.7 mg per gram tyre to be comprising of filamentous carbons at 1:1 tyre to catalyst ratios at a catalyst temperature of 900 ^{0}C. Microscopic screening of the product showed a significant proportion of deposited filamentous carbons as MWCNTs. The procedure also released hydrogen at compatible rates that met the fuel and energy scarcity, making this overall approach a reliable an efficient methodology to utilize the tyre waste. An important aspect of this approach was that it firstly processed the nickel nitrate as nickel precursor by its dissolution in ethanol on alumina support that gradually converted into slurry *via* continuous stirring. Final catalyst was prepared on overnight drying of this slurry at 90 ^{0}C in an oven, at 2 ^{0}C per minute till the temperature reached 750 ^{0}C. This process took nearly a three hour holding time following which the solid material collected was crushed into (0.05-0.18) mm sized granules. It is interesting to note that the smaller size of catalyst particles conferred a higher surface area to the reacting species, so whether a different physical form of the particles would be able to provide the product in same morphology with a similar yield, remains a significant concern [113].

Quite recently, the synthesis of CNTs was reported from waste rubber based substrates, with the experimental procedure utilizing the blended form of acrylonitrile butadiene and styrene butadiene rubbers (NBR and SBR). The blend could not be conventionally decomposed due to its stronger mechanical strength and thermal resistance, however the pyrolysis of the disposable form of blend was optimized at 450 ^{0}C in a horizontal CVD pyrolyzer with a cautiously maintained nitrogen supply to yield hydrocarbon fractions. Upon allowing the CVD of these hydrocarbon fractions on different catalytic systems at 850 ^{0}C for half an hour, the screening of formed product using HRTEM, Thermo gravimetric analysis (TGA) and Raman spectroscopy inferred a significant formation of SWCNTs in an efficient extent. Subsequently, in course of physical analysis, it was noted that adjusting the crystallinity of Fe-Ni catalyst on different zeolites was critical factor affecting the structure and diameter of as formed CNTs [67]. So, approaches like these are all potential solutions to synthesize nanotubes in desired yields from robust, cheap and biocompatible materials ensuring minimal pollution risk and higher output yields compared to costly and energy intensive conventional methods.

4.5 CNTs from agro waste: rice husk

In the different parts of world, rice husk (RH) shows as one of the most dominant crop residues and the disposal of which often results in crucial environmental risks [122-124]. The major constituent of RH as well as it burnt ash is silica (up to 90%) (widely used as fillers and area enhancement specific applications). So, efforts to utilize RH in its native as well burnt forms as reliable material providing energy are on a rapid high. Furthermore, the global RH production registered a nearly 6% increase from 2010 to 2014, which concerns with its alarming threat as environmental hazard [125]. The utilization of rice husk (substantially comprising carbon, nitrogen and hydrogen) commences with gasification (or pyrolysis), which generates fragments suitable for power generation and biologically compatible charcoal. The one deemed fit for power generation could be utilized as such *via* landfilling and fertilizer application. However, the fraction acting as bio-reduced char, contributes significantly in industrial activities. This fraction provides three potential materials, active carbon, porous carbon and amorphous silica, all of which have highly good absorption characteristics conferred by their significant surface area contributions. While amorphous silica finds peculiar suitability in soil improvement and cement industry the active and porous carbon fractions are highly efficient adsorbents and used for waste water treatment applications. So, with a carbon texture, the normally waste RH could be potentiated into manifold useful industrial products. Readers can have a detailed look about the RH utilization and processing methodology in a highly informative *Nguyen et al* contribution, reported in 2019 itself. This is a review article that comprehensively discusses the engineering and industrial potential of RH and its derivative fractions (such as silicon nitride, magnesium silicide and others) as refractory materials, filler agents in thermoplastics, as reinforcement agent, adsorbent in polymer composites and many others.

4.6 CNTs and graphene synthesis from oil

Oils are one of most used commodities which are basically natural hydrocarbon precursors having varying carbon chain fatty acids. The carbon skeleton of oils, accompanied by a range of physical and chemical modifying technologies such as fractional crystallization, fractional distillation, chromatographic separation, aqueous two phase attraction are the incentives for their reduction procedures that could enable a range of products. Several kinds of oils, such as turpentine, eucalyptus, palm, turpentine, neem and sunflower, have been reported to enable efficient scale synthesis yields of CNTs and graphene [126]. The use of turpentine oil in the making of CNTs has been proposed by *Chatterjee et al*, through its decomposition on the surface of finely dispersed Co catalyst at 675 ^{0}C optimized the CVD method to synthesize CNTs. The study also proposed the application of synthesized CNTs in making efficient electrochemical double layer capacitor [127]. In several interesting modifications, scientists have optimized the use of neem, sunflower, sesame, camphor and castor oils as the parent carbon sources for CNT synthesis. Utilization of sesame oil has attracted significant scientific attention, owing to its edible nature, clean methodology and formation of hollow CNTs with diverse shapes and morphology [128]. The formed nanotubes had no Fe nanoparticles in the interior, had diameters within (50-60) nm and sheet-like structure showing an intricate long-range array of folds. Thus, synthesis of nanotubes from oil represents the renewable, energy efficient, cost effective and most importantly, much more compatible to environment and laboratory personnel [129]. So, since the CNTs inception, making CNTs in big yields is now no more a herculean task like in the beginning years.

4.7 CNTs and graphene from poultry waste

Poultry products or waste are also rigorous sources of carbon materials and their derivatives and are mostly comprised of carbohydrates and proteins, along with a dense supplement in the form of calcium [130]. Regarding the utilization of these materials to meet the energy concerns, egg shell material promises to be a very rich source of providing carbon skeleton, it has been used with significant interest to optimize the microbial growth for designated yields of biofuels. Though CNTs are concretely not reported as being synthesized from these materials, yet a modified version, namely, C-dots (inherently carbon comprising quantum dots) have successfully been synthesized using this natural resource. Primary advantage of these nanomaterials compared to conventional quantum dots is their low toxicity. A 2012 study reported from China has optimized the microwave assisted approaches (providing intensive and efficient energy) to process egg shell material for a reduced reaction time to obtain C-dots [131]. The study aimed at the microwave treatment of egg shell material to form C-dots, having a maximum fluorescence peak (at 450 nm) alongside a quantum yield of ~14%. The modification of operational parameters like reaction time (microwave duration), temperature, the relative contents of egg shell material could be the significant leads in obtaining many other variations in the products, for obtaining the biologically and biophysically more robust product designs.

5. Applications of 2D nanomaterials

The specialty of nanomaterials lies in their tunable nanoscale dimensionality, on the basis of which these are considered as one, two or three dimensional [132]. Thus, two dimensional nanomaterials are typically those materials which have two of their three dimensions restricted to < 100 nm [133]. There is not clear consensus regarding the upper limit of this restriction. This implies that in these materials, it is feasible to retrieve the quantum scale effects on two dimensions, i.e. the restriction of the electronic motions of excited state electrons (more conventionally known by the terminology “quantum confinement”). The examples of these materials include nanosheets, fibrous networks having nanometric widths and heights with lengths in the order of micrometers. Popular applications of these materials include their inclusion as catalysts, electronic/battery devices, hydrogen sensing, laser protection, magnetic memory devices and other domains, based on surface plasmon resonance (SPR) attributes [134].

5.1 Catalytic applications of 2D nanomaterials in fuel cells

In the present day energy savvy scenario, everyone is anxious to obtain quicker and greater product formation, minimizing not only the operational steps but also the energy requirements. 2D NMs serve as ideal solutions to all these concerns in having a high aspect ratio, high electron mobility, unsaturated surface coordination, and unique material properties (especially physical, chemical and electronic) [135]. The ultrafine thickness of these materials confers them with ultrahigh specific surface areas and high surface energy, making them appropriate towards numerous surface active applications such as for those in fuel cells. For efficient working of these cells, oxygen generation and transport has to take place at reasonably good rates. The catalytic approaches in most general cases employ platinum (Pt) nanoparticles (NPs) immobilized on the surface of carbon substrate. However, due to their high costs and slow reaction kinetics, use of Pt NPs is not economically as well as commercially viable. To tackle these issues, developments of new methods like alloying and nanostructured engineering which could ensure a maximum activity, stability along with cost minimization has emerged to be a priority [97]. Amongst the several different shapes attainable by noble metal alloys, ultrathin 2D sheet like structures having a single or few atoms thickness are acquiring significant interest because of their large size, high electron mobility and surface energy. These features confer a high surface area to volume ratio to the ultrathin 2D sheet like materials thereby giving rise to a high density of unsaturated atoms. For instance, *Hong et al* have reported faster ethanol oxidation using ultrathin free standing Pd-Pt-Ag (ternary) noble metal alloy [136]. Similarly, *Din et al* proposed a suitability of quaternary noble metal alloy Pt-Cu-Bi-Mn (porous nanosheets) having (3 to 4) nm thickness as novel catalysts having high oxygen (reduction and oxidation) capabilities apart from a significant methanol tolerance [137].

Sial et al., have rigorously compiled the several methods of making nanosheets (NSs) and their limitations in the present scenario (pertaining to energy considerations and economic constraints). Different methods of synthesizing 2D NSs are carbon monoxide (CO) confined growth, hydrothermal/solvothermal synthesis, wet chemical synthesis, self-assembly of NPs, topo chemical reduction method, template based synthesis, seeded growth and microwave assisted growth. Well even though each of the methods provides specific characteristics of products in terms of morphology, the unanimous factors affecting their implementation are the need of robust catalysis (which offers lesser reaction time and is less costly) and the requirement of energy from external agency. For example, CO assisted growth method allows the preferential growth on the substrate due to a good surface adsorption of CO. These methods are workable through a feasibility of interactional distinctions of water and non-aqueous solvents, such as viscosity and dissociation constant. The process is characterized by selective oxidative etching enabling an attainment of specific anisotropic growth. Two critical requirements of these methods are optimum reaction temperature maintenance alongside the steady action of reducing agent. Likewise wet chemical synthesis offers layered patterns of ultrathin NSs, with industrially scalable products allowing no CO requirement (unlike the CO assisted growth method and hydrothermal/solvothermal method). Another mechanism of interest is self-assembly which provides NSs regulated by weak binding interactions and comparatively larger sizes. But the advantage in this method is that requirement of energy from external end is very low and the constituent species themselves acquire a minimum energy configuration. Likewise, the topo chemical reduction approach is specifically suited for making single crystalline metal alloy NS utilizing Ni and Co as combined catalyst in aqueous medium while template synthesis method is an efficient strategy to obtain layered nanostructures and extensively utilizes graphene and its derivatives as templates. Comparing the basic requirements of these two methods, it is quite evident that template synthetic approach offers much higher control with every successive step being regulated by the chemical composition of preceding deposited material layer. Another benign approach for making 2D NSs is the use of microwave technology, which is specially preferred for making inorganic nanomaterials having high quantum yield and high precision. Although this is green approach but yet again dependent on energy input from outside. Often template based synthesis mechanisms utilizing hydrothermally fabricated catalysts are relied for commercial purposes.

The working of fuel cell involves rigorous electrochemical processes, characterized by electrocatalytic oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER), involving formic acid oxidation and alcoholic oxidation at cathode and anode. The major problems encountered in commercialized application of fuel cells are improvements in the electrode preparation with minimized use of precious metals, controlling the kinetics of electrochemical process which collectively reduces the output efficiency of a fuel cell. So, in general faster, more efficient and rigorous catalysis with minimized expenditure and care requirements are the key. With continuous better understanding, several alternative mechanisms have emerged as steady sources of energy provision, like microbial driven fuel cells which utilize the energy generated from microbial metabolism (the functioning of enzymes and key pathways). However, this recourse is also not free of constraints as there is a constant need to ensure optimum microbial activities through providing specific pH, temperature, humidity and minimizing the ion concentration [138]. Recently, a new methodology making use of CNT based composite materials have emerged. The concurrent hindrances related to dependence on water for conductivity, high methanol permeability, frequent disintegration (of conventionally used materials) in the presence of –OH radicals and low to moderate chemical stability have been the reasons to screen a safer, more reliable and efficient alternative. A novel attempt in this direction has been the use of nafion based membranes and its composite with inclusion of CNTs as polymer electrolyte material (PEM) has provided a solution to recurrent limitations, through its greater mechanical stability, greater tensile strength and stronger physical texture [139]. Thus, nanomaterials provide numerous structural benefits to improve the fuel cell working through improvement in catalysis and energy savvy functioning.

5.2. Applications related to surface plasmon resonance

SPR is the characteristic phenomenon driven by dominant surface effect of nanomaterials, and more specifically the metal or metal oxide NPs. These entities absorb light in maximum at a peculiar wavelength after which the constituent ions are excited and progressively move to high energy state. As the temperature increases (due to the input heat or light energy or *via* intermolecular frictional activities), these excited particles rapidly move with a net charge and remain in the semi-solid state, termed as plasma. The terminology plasmon is originated from the essence of ions existing in plasmonic state. The resonance implies an instant where the light energy absorption is maximum, owing to which the manifested surface effects are also greater. Each nanoparticle has a characteristic SPR corresponding to peculiar kind of incident light, so the SPR wavelengths are often used as identifiers for the formation of specific NPs. Since there is maximum energy absorbance in the SPR event, so the nanoscale effects are also highest at this particular instant, giving rise to maximum bioactivities or quantum confinement dependent properties. The applications of nanomaterials have been significantly improved after a clear understanding of this phenomenon, with bulk species or sensing moieties being swiftly replaced either by individual NPs (bound in membranes) or by combination of nanomaterials (such as assembled nanostructures or hybrid NPs and thin layers of nanomaterials. For detailed insights of SPR and its consequent applications, readers are suggested to refer more specific literature contribution [140].

5.3 Nanotechnology and solar energy

Probably, the most clean, unanimously accessible and even most used form of energy, the solar energy is a rigorous input agency for most of the daily life activities. From microbes to plants, animals and even human beings, all require solar energy directly or indirectly for sustenance of life. Commercial usage of solar energy presents exciting prospects, which are often limited by its low efficiency (substantially attributed to uncertainty of availability) and inabilities to being scaled up. Lots of progress has been made *via* use of nanomaterials in native and engineered form, to increase the absorption efficacy of sun's energy radiations. Most popular area has been the use of solar cell panels to provide electricity in which the functional circuit comprises of an assembly of solar cells in a rectangular pattern. The efficiency of original assembly is quite low owing to which Si wafers (with amicable impurities) are added to it, which collectively not only improve the absorption but also manifold the utilization extents. Similarly, nanoscale attenuators and converters have been drafted into calculators to improve their charging efficiencies and performance. Lots of bioassays and drug carrier systems are in the market working through photothermal attributes of metallic NPs and their constitutive assemblies. Thin layers or assemblies of nanomaterials have emerged as carriers of more uniform and regulated solar energy absorption that remain localized to the surface and do not cause any serious effect in the bulk. Piezoelectric materials (such as MgO and ZnS based nanostructures) have come to the forefront, making use of pressure influences from solar energy (as input) to conduct the electricity or perform mechanical works. Many of these conceptualizations are in the research phase with delay in optimization studies, meeting the scale-up regulations and constraints; owing to which commercialization of such innovations is being delayed. Considering the energy crisis scenario (in particular for developing world), these solutions could be potential remedies to eradicate the inadequate energy availability. Recently, the use of nanofluids (typically having either solid NPs or (1-100) nm sized nanofibers suspended in a liquid) has been on peculiar rise to enhance the utilization potential of solar energy [141]. These fluids having dissolved nanomaterial(s), are able to enhance the outlet temperature by (30-100) K, enabling an enhanced potential to absorb the sunlight without any damage to native structures of base material. One study claimed more than 100% enhancement in photo thermal efficiency of 0.01% graphite based nanofluid than without using it (normal functioning mode involving coating of an absorbing collector). The use of these fluidic materials has enabled improved photovoltaic application *via* long lasting existence in non-agglomerated form, having high stability without undergoing significant chemical changes in base fluid [142]. The use of nanofluids has significantly improved the efficiency of electrolysis manifolds by the replacement of conventional electrolytes, allowing faster and smoother conduct of chemical reactions [143].

6. Conclusions

The progress and better understanding of nanotechnology and its functional principles have slowly entered into the multiple inter and cross-domain disciplines, to improve the product life, design, performance and overall quality by considerable reduction in the raw materials. The use of nanostructures like CNTs, 2D nanosheets, several different kinds of NPs has provided stronger and more efficient materials, enabling multifunctional performance and increased outputs. Incorporation of CNTs along with graphene and their derivatives have bettered the present performance of materials by substantial improvement in their structural responses, mechanical strength, stress bearing capacity and physical load bearing capacities. The availability of these materials in multiple nanoscale dimensions has enabled the synthesis of desired materials with robust self-adjusting responses and flexibilities. Though much remains unknown and even unpredictable that sometimes poses a risk in their nanoscale manifested enhanced chemical reactivity, still regular research and continuous merger of scientific cross disciplines have significantly improved the understanding with respect to use of nanomaterials. Market scenario predicts hopeful aspects from consumer point of viewpoint while at the same time, appearing little gloomy for the reduced manpower requirement. So, better understanding of nanomaterials usage and applications definitely owes a bright future and better living standard for mankind.

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