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Nanomaterials via Reconfiguration of Skeletal Matrix

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Abstract

Nanotechnology is an ever-expanding field, which offers novel avenues due to advance, unique, and myriad applications in science and technology. Especially composites procured from reconfigured matrixes appear as multiphase matter tendering augmented/new functionalities via chosen amalgamations. Hence, it is important to meticulously comprehend the interactive materials for the basic reconfiguration of their skeletal matrix to derive desired output to cater to the needs of S&T developments. Nanoscale material's systematic and rational designing gets fundamental as various material scale manipulations permit to recognize characters and functionalities that are not viable via conventional methods. Material's skeletal matrix reconfiguration is feasible through advanced biotechnology, physics, chemistry, and nanomaterial engineering mainly decisive to fabricate the particle, thing, and device at the atomic and molecular dimensions. These reconfigurations of material's matrix reduce its spatial dimension/captivity within crystallographic phase usually changing its physical, mechanical, thermal, optical, and electrical-electronic properties. Reconfigured material matrixes restrain three nanoporous skeletons, namely: 3D/zero dimensional (e.g., particle, grain, shell, capsule, ring, and colloidal), 2D/one dimension (e.g., quasi crystal, nanorod, filament, tubes, and quantum wire), and 1D/two dimensional (e.g., disc, platelet, ultrathin film, super lattice, and quantum well). Today, rational designing of smart nanomaterials obtained via flexible matrix's skeletal reconfiguration focus on desired applications in the advancement of science and technology.

Keywords: nanomaterial, nanotechnology, reconfiguration, 1-/2-/3-dimensional, metal-organic framework/matrix, graphdiyne, graphyne

1. Introduction

Nanotechnology aids in designing challenging functionally fabricated materials via skeletal matrix reconfigurations that offer integrated solutions for medical, biological, and engineering model applications [1]. The hierarchical structure alterations open/allow nanomaterial creations with comparable size to those that occurred naturally. Accordingly, advanced engineering/technological designing permits assorted skeletal reconfigurations to yield resultant matrixes (also abet to mimic intricate natural skeletal) proposed certain advanced utilities viz. drug delivery, gene capture, tissue release, cell labeling, and scaffold improvements [2].

2. Nanomaterials: classifications, characterizations and fabrications

'Advanced nanotechnology' offers novel tools, opportunities and scope in significant applications for diagnostic and therapeutic purposes. Rationally designed smart materials are well established for drug delivery, diagnostics, treatment and prognosis of illness via reconfigured/restructured devices and tools. Pharmaceutical nanotechnology is one of such fields embracing nanostructured products owing improved and requisite characteristics in its assorted sub-domains, viz. polymeric nanoparticle, magnetic/metallic nanoparticles, biosensors, biomarkers, liposome, carbon nanotube, quantum dot and dendrimers which are innovatory in medical/clinical usages [3]. Nano-pharmaceutically designed/reconfigured materials own vital applications in health risk-related issues like delivering therapeutic components at desired site in treatment of critical illness and crucial diseases. Nanoparticles are obtained via three techniques, viz. dispersion of preformed polymers, ionic gelation (hydrophilic polymeric coacervation) and monomeric polymerization. In order to control nanoparticle size/shape and composition industrially, certain methodology called supercritical fluid technology and particle replication in non-wetting templates [1–4] are also used to get reconfigured nanomaterials. Dispersive polymeric technique is well used to reconfigure biodegradable nanoparticles via dispersion of biodegradable polymers like polyglycolide, polylactic acid, polycyanoacrylate and polylactide-co-glycolide [5].

Reconfigured matrix acts as effective carriers vulnerable in drug delivery, targeting cell release and specific tissue liberation in biological samples. Moreover, the size reduced targeted formulations; besides, suitable drug delivery pathway designing can be easily performed through these reconfigured matrixes.

Through intrinsic skeletal reconfigurations yielding varied nanostructures which displayed sole physicochemical/biological features. Rationally designed nanoparticles own potential utility for such purpose, imparting peculiar advantages like less toxicity, more release capacity, improved solubility, bioavailability and better drug formulations [3, 4]. Nanotechnologically achieved reconfigurations offer assorted nano-range matrixes owing to augmented performance. There are certain notable rewards of reconfigurations in material skeleton attenuated in nanosize matrixes such as reduce fed/inconsistency, amplified surface area, improved solubility, better bioavailability, more dissolution, fewer doses and rapid therapeutic action [4, 5].

Nanotechnology field in combination with advanced electronic, physics, and engineering sciences can offer superior applications in the domain of biophysics, molecular biology, medicine, immunology, cardiology, endocrinology, ophthalmology, oncology, and pulmonology, targeting brain and tumor besides gene/cell/tissue delivery [5]. Science of materials/devices can be restructured, and the resultant matrix reveals novel and substantially transformed nanoscales owing to unique physical, chemical and biological phenomena. Thus, nanotechnological reconfigurations in materials are manipulated at atomic, molecular and supramolecular level linking design, production and characteristic functionality anticipated for novel science and technological advancements [1–6]. Such reconfigured matrixes are utilized in making molecular tools which preserves/improves our health through diagnosis, treatments and prevention of diseases, traumatic hurts and pain reliefs [1, 3]. The usage of assorted nanomaterials in the field of science and technology is mentioned in **Figure 1**.

Certain novel therapeutic and drug delivery systems are framed by the use of reconfigured nanoparticles in medicines which also extend its utility for remedial and diagnostic research. Varied advance nanoparticulates like paramagnetic nanoparticle, quantum dot, nanoshell and nanosome get reconfigured for cancer detection based on fluorescent material and contrast agent, targeting antibody besides molecular research which modernize and amend landscape of

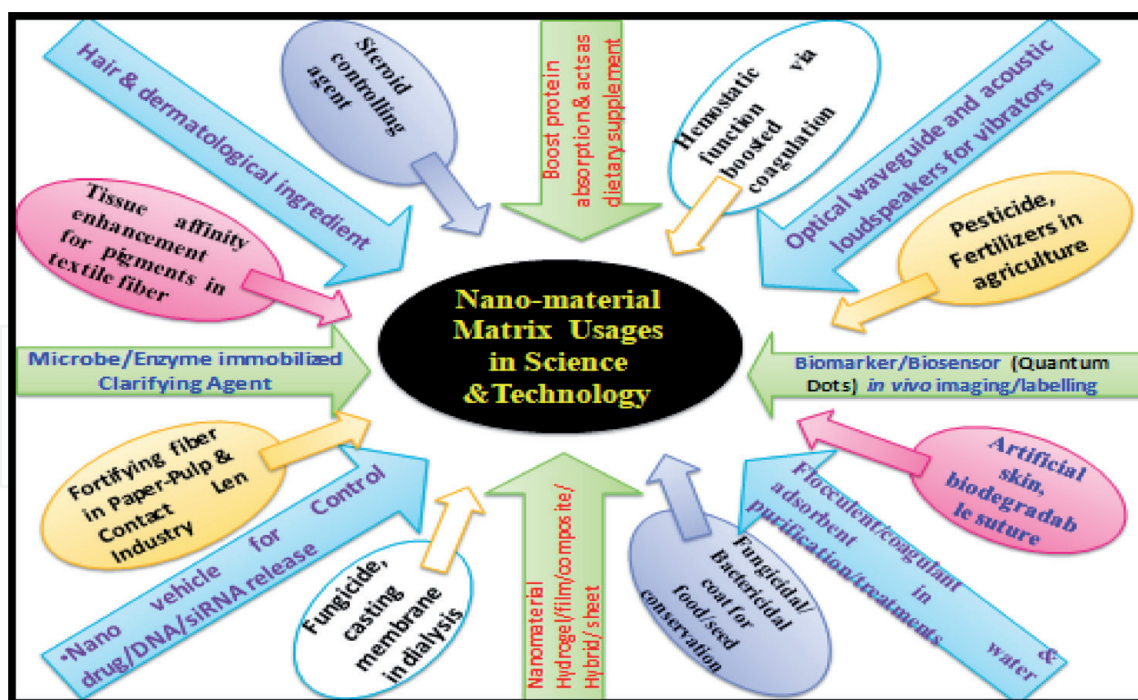


Figure 1.
 Assorted usage of nanomaterials in the field of science and technology.

drug development pharmaceuticals [1–7]. Assorted material reconfiguration yields products like liposomal and polymer-drug conjugates which carry active targets or perform controlled drug delivery as approved by the USA for clinical development [1–8]. Reconfigured nanostructured materials with requisite features achieved via surface modifications and/or coatings with improved biocompatibility and bioavailability as employed in orthopedics, tissue engineering and dental for encapsulation, bone replacements, prostheses, implants and scaffolds appear better than conventional counterparts [9, 10]. Reconfiguration alters raw-material matrixes at atomic/molecular scale as viable for augmented particular shape, size and functional alteration in the form of quantum dot, biosensor, bio-detector, biomarker, dendrimer, nanocarbon, fullerene and nano-array [11–14].

2.1 Nanoparticle taxonomy

Nanoparticles are categorized in three classes: 1D nanoparticles, e.g. thin film 1–100 nm or monolayer/manufactured surfaces used in solar cell technology, chemical/biological sensors, information storage systems, magneto-optic and optical device and fibre-optics [1, 15]; 2D nanoparticles, e.g. carbon nanotubes; and 3D nanoparticles like dendrimer, quantum dot and carbon-60/fullerene [1, 7, 8, 15]. Nanoparticles are characterized through their size/shape, morphology and surface charge, by means of sophisticated microscopic systems, viz. atomic force microscopy, scanning electron microscopy, transmission electron microscopy, etc. [15]. Varied size distribution, average particle diameter and charges of nanoparticles are found to affect physical stability besides in vivo distribution. Electron microscopy gives information about its surface morphology, size and overall shape. Stability and re-dispersibility of the polymer dispersion and in vivo performance get affected by surface charge of reconfigured nanoparticles. Such nanoparticles characterized by assorted methodology are revealed. Nanoparticle size portrayal can be evaluated by particle size distribution and morphology, while electron microscopy ascertains both the morphology and size. Application of nanoparticles in drug release and drug targeting can be conveniently determined by various tools. Size

of nanoparticle owns reflective consequence during the drug release applications. Small-size nanoparticles possess larger surface area and impart fast and significant drug release through drug carrying phenomenon as tiny particles get amassed during storage and dispersive transportation [16]. Thus the mutual compromise of upmost stability and pertaining small size is favored in reconfigured nanosize materials [1–16]. Surface charge and intensity parameters decide electrostatic interaction of reconfigured nanoparticles with biological milieu or bioactive samples.

2.2 Reconfigured nano-colloidal

The mixture of microscopically disperse insoluble particles which are suspended all over another substance is called as colloids. Colloid mixture cannot settle down easily and takes time appreciably [17, 18]. Nature of interaction of dispersive phase and its medium differentiate colloids as hydrophilic/reversible sols and hydrophobic irreversible sols. The stable colloidal form remains suspended in solution at equilibrium, and it's hindered by aggregation and sedimentation as driven by innate tendency of reduction in surface energy [17, 18]. Low interfacial tension stabilizes such colloidal. Rheological functions are valuable in reconfiguration of suspensions in nano-colloidal forms as low viscosity and high shear rates aid deagglomerated mixing which governs suspension flow. Such colloidal state parameters are reconfigured for their elevated particle size, shape/flexibility and surface chemical-electrical properties. The colloidal dispersion obtained through reconfigured alterations that own suitable particle and medium interfaces offers well-defined large surface area as the best to be utilized for emulsion/oil-water separations. Such rationally reconfigured interfaces tender facial capillarity, which is vulnerably essential for adsorption; for example, nanocarbon colloidal-based filters are used in purification of drinking water, beer/wine, decolorization of sugar, and gas masks [1].

Certain particle size reconfigurations have open influence on the bioavailability of active pharmaceutical ingredients and further effectively deliver intravenous lipid emulsion. Suspensions and colloidal dispersions own a range of sizes/shapes, and reduction of nanoparticle size can enhance surface area besides enlarging surface area/volume ratio. Shape is irrelevant, while surface area per mass of colloid scale nanoparticle owes a huge surface area resulting in superior adsorption achieved via interactive suspension rheology, coating and adhesion. Reconfigured nano-colloidal permits faster dissolution of active pharmaceutical ingredients and corresponding bioavailability in hydrophobic membrane porous species. The active pharmaceutical ingredients establish incompetent treatment due to critical factors like innate low bioavailability, elevated cost, and toxicity; thus, they seek nanotechnology reformulated and reconfigured colloidal matrixes to cater for the advanced pharmaceutical applications. Reconfigured interfaces of dispersive phase and their medium are negligible for colossal materials but dominant in colloidal being decisive in physicochemical alterations like surface chemistry and in toto system's reactivity [1, 3].

The colloidal size/shape for particle crystallization can be obtained through irregularity or asymmetric environment of nanoparticles determines its overall physicomachanical features as needed for intrinsic pharmaceutical applications. Colloidal sizes can exist as corpuscular like spherical/ellipsoid, laminar such as disc/plate and linear, viz. rod/needle. Globular proteins shape up with approximate spherically compact random coil configuration, while assorted active pharmaceutical ingredients occurs as rod/needle shape. Macromolecular bio-protein, polysaccharide and artificial polymer can be reconfigured as long thread/branch series colloidal owing to substantial mechanical potency and durability. The shape of colloidal can be reconfigured as large extended unidimensional strings up to rigid

dense random coils which get manipulated by many factors like solution temperature, pH and nature of salt/electrolytes. Liquid-liquid interfaces, colloidal dispersions, metal sols like gold nanoparticles, lyophobic colloidal dispersions including polymeric-embodied APIs and ionic solid surface charge govern unequal dissolution due to crystal lattice anisotropy [3].

Till date numerous “nanotechnology-based” colloids are reconfigured for environment, nano-medicine, healthcare and cosmetics. The use of ZnO/TiO₂ colloidal in creams attenuated UV-A/UV-B rays which induced sunburns and skin cancer; toothpastes own nano-hydroxyapatite to fill tooth cracks, and anti-aging products use nanocapsules. Nanosilver colloids are reconfigured for injury healing/wound dressings. Nanosize zirconia-based hydroxyapatite colloidal acts as bioactive ceramics for orthopedic weight-bearing implants owing to advantageous sintering. Traditional pharmaceutical have delivered precise therapeutic to its accurate targets without side effects by means of these reconfigured material-based nano-medicine. Colloidal stability is measured through its zeta potential gradient as a function of the outer Helmholtz plane and surface of shear which indirectly compute surface charges. Zeta potential in colloidal dispersions assesses storage stability as high potential either positive or negative certifies innate stability and avoids aggregation pivotal to evaluate surface hydrophobicity, encapsulation and surface coatings [1, 3, 17, 18].

2.3 Nano-colloidal analysis techniques

The establishment of colloidal surface hydrophobicity as achieved via sophisticated analytical techniques, viz. hydrophobic interaction chromatography, biphasic partitioning, and contact angle measurements. Rather X-ray photon correlation spectroscopy resolves surface hydrophobicity, which also aids in recognizing certain surface proactive functionalities [1, 3]. UV HPLC, ultracentrifugation, ultrafiltration, gel filtration, centrifugal ultrafiltration analyses and the extent of drug release parameter require its delivery being a vehicle-like role of reconfigured nanomaterials [3, 17, 18].

2.4 Nano-dendrimers

Dendrimer is a unique polymer owing to a quite manageable size/shape with compartmental zones consisting of hyper-branched and tree-like reconfigured skeletons. The convergent or divergent step growth polymerization approach is used in fabrication of dendrimer skeleton from its monomeric units. Regular-branched polymeric nanostructures of dendrimers' own size depend on its controllable branching quantification [3, 19]. The nanostructure dendrites right from core shape alterations to spherical arrangements can also impart cavities during synthesis polymerization and are achieved through numerous reconfigured alterations. Reconfigured dendrimers are effectively utilized in drug transport via its free ends that are involved in conjugation or attachment. End groups of dendrimers are tailored through interconnecting networks as per needful conditions which can transport loaded moiety/drug at desirable site to impart novel biomedical applications [1, 19]. Dendrimers have fine nanostructures and are also capable of surface functionalization; monodispersions with immense stability make it smart carrier for drugs. Drug moiety undergoes complexation and encapsulation in such dendrimers at its basic core, branches and surface skeletal units. Branch/end groups tailoring or grafting into biocompatible and high biopermeable species networking aid sustainable delivery of vaccine, cell, drug, gene and metal. Reconfigured dendrimers' own innate hollow arrangements with space/voids to include drug/bioactive samples through physic-chemical interactions help its control delivery

due to beneficial features like modulated target-specific delivery, feasibly defined molecular weight, good trap capacity, flexible surface functionalization and lowest polydispersity index. Poly(ethylene glycol), chitin, melamine, polyglutamic acid, poly-propylene imine, polyamidoamine and polyethyleneimine biodegradable skeletons are easily reconfigured into dendrimers via the above-mentioned synthetic methods. Dendrimer-based complexes act as nano-device's own potential utility in cancer chemotherapy as targeted drug therapy like tecto-dendrimers owing to every dendrimer unit exhibits assorted role, e.g. targeting, disease diagnosis, drug carrier and imaging [14]. Reconfigured dendrimers used in therapy avoid stimulated immune side effects. Drug/therapeutic dendrimers conjugate target cells and indicate useful advantageous features, viz. boron EGF-carrying PAMAM dendrimers, intra-tumoural injection and CED-doxorubicin-2,2 bis(hydroxymethyl)propanoic acid-derived dendrimers, showing in vitro/in vivo less toxicity in colon carcinoma cell treatment in rats [1, 3, 17, 18]. Cationic dendrimers showed more cytotoxicity, cell membrane instability and cell lysis than anionic dendrimer, PAMAM. Assorted nano-dendrimers' yield via block polymerization and chemical cross-linking is shown in **Figure 2**.

2.5 Nanocrystal and nanosuspension

Aggregated structures are formed through the combination of various particles in crystalline form coated with surfactant combinations which impart static and electrostatic surface stabilization. Such nanocrystal and nanosuspension aggregated materials lessen bioavailability and absorption issues due to its resolved formulation. Nanocrystal size permits safe and effective passage via the capillaries. Reconfigured solid lipid nanoparticles owe discrete reward of unique carrier systems over liposomes and polymeric nanoparticles due to solid lipid matrix owing to 1 μm diameter where drug gets easily incorporated. Such nanoparticle/nanosystems for clinical usage are obtained by high-pressure homogenization that uses varied surfactants to avoid aggregation and imparts dispersion stability. Reconfigured cationic solid lipid colloidal nanoparticles are prepared and used for liposomal transfection agents besides gene transferring dominant for in vitro [1, 3, 15–18].

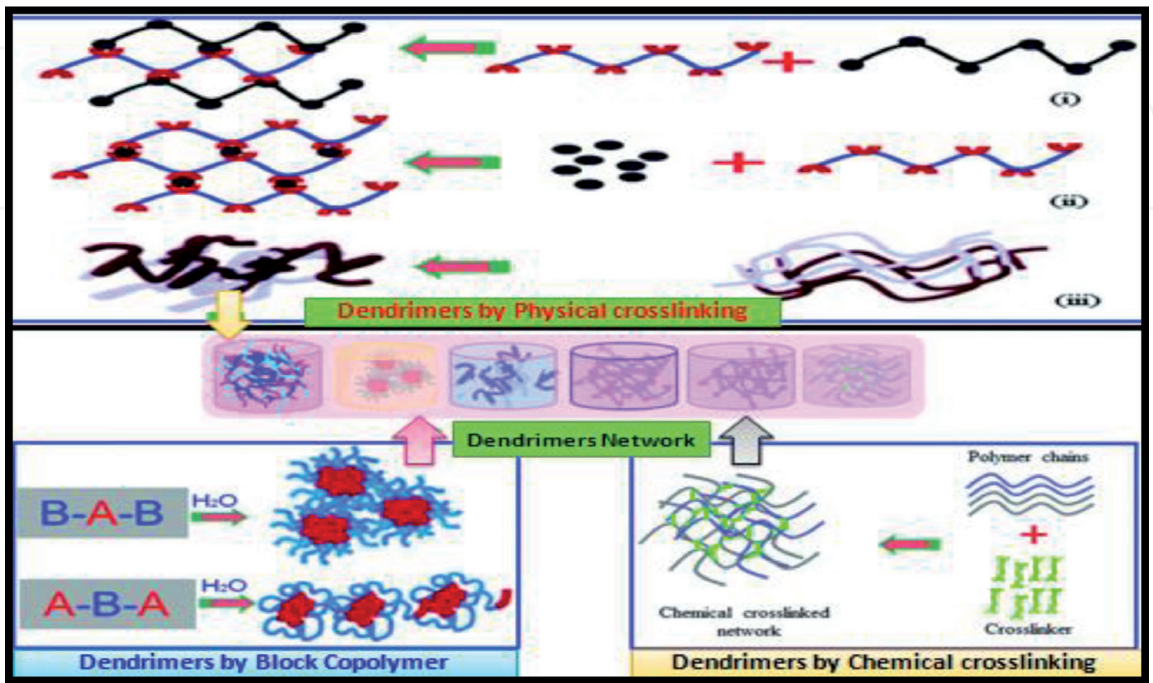


Figure 2.
Nano-dendrimer synthetic route: block polymerization and chemical cross-linking.

2.6 Silicon-based nanomaterials

Silicon-based nanostructures are reconfigured by means of assorted techniques including etching, photolithography and deposition. Materials like porous silicon, silica and silicon dioxide are facile to reconfigure as the calcified nanopores, nanoparticles and nanoneedles. Assorted porous hollow silica nanoparticle suspensions owing sacrificial nanoscale templates mostly involved the usage of sodium silicate as a precursor. Such reconfigured silicon-derived materials can offer effective delivery of drugs like porous silicon-embedded platinum which is applied for many usages like antitumour drug release and carrier for antibody, antibiotic, enzyme and DNA. These materials also act as good semiconductors and thus preferred in micro-electromechanical usage [1–3].

2.7 Nano-micelles

Polymeric micelle assemblies are reconfigured through amphiphilic block copolymers which impart nanoscopic supramolecular core shells as aggregates in solutions. In such micelles, the reconfigured components get ordered as spheroidal owing to hydrophobic core shells that are water secured due to hydrophilicity. Many components owing to hydrophobic and hydrophilic portions are reconfigured like amphiphilic AB, or ABA kind of block copolymeric units yield polymeric micelles as nanoscopic supramolecular core shells as aggregates in solutions [1–3]. Nanoscience technology has reconfigured assorted supramolecular architectures as a result of self-assemblage of amphiphilic block polymers through hydrophobic/hydrophilic effects, electrostatic interactions, hydrogen bonding and metal complexation which proffer sharp structures and precise functionalities for their usages in biomedical purpose. Such polymeric micelles fascinated special attention in drug/gene release by virtue of outstanding biocompatibility, less toxicity, more blood circulation and enhanced solubility in its innate micellar core shells. Polymeric micelles act as ‘smart drug carriers’ due to binding of specific ligand onto proactive surfaces which aids targeted/formulated stimuli sensitivity found devoid in their counterparts. Self-assemblage in block/graft copolymers occurs in selective solvents spontaneously reconfigured as supramolecular assemblies owing to cylindric and vesicular core shells of 10–100 nm shape/size nanomaterials called polymeric micelles. Spherical reconfigured core-shell size/morphology gets crucially varied with chemical structures and compositions of constituent block copolymers besides exhibited elevated thermodynamic/kinetic stabilities over surfactant micelles. Polymeric micelle yields through advanced reconfigurations own an external hydrophilic nanoshell that assists in prolonged residency in blood, besides gathering in tumor-specific zone due to more permeation, and thus acts as a novel vehicle for sparingly soluble (hydrophobic) drugs. Polymeric micelles have shown adaptability to various ligands which aids active targeted delivery by virtue of better solubility and improved pharmacokinetics besides no adverse effects. Great interest is generated by these micelles in technological advancements due to remarkably stable and bendable physicochemical features exhibited with various stimuli [1–3, 19].

2.8 Biopolymeric nanoparticles

Nano-array of polymer-based nano-conjugates obtained from different natural sources own modern functions besides specific and targeted drug delivery. The natural polymeric reconfigured nanoparticles are biocompatible, less toxic across many bio-membranes against various pH and non-immunogenic and appear to be extra stable to volatile pharmaceutical agents besides offering low-cost fabrication at

large-scale/multitude methodology. Biopolymeric reconfigured nanomaterials are biodegradable as anticipated for tissue engineering scaffolds and drug/gene release/carrier besides novel vaccination approach [3, 19]. Certain natural polymers like chitosan, gelatin and sodium alginate owing to nontoxic profile get easily reconfigured in situ with man-made polyesters, viz. polycaprolactone, polycyanoacrylate, poly (lactide-co-glycolide), polylactide and polylactic acid, to yield resultant matrixes advocated under advance nano-biotechnology. These bio-polymer-derived nanoparticle offers to develop utility over usual oral/intravenous mode of drug delivery with more competence and efficiency. Certain polymeric nanostructures possess homogeneously dispersed template which can be reconfigured as vesicular systems like nanocapsules and matrix systems like nanospheres. Reconfigured nanocapsules owe innate cavities that can detain assorted biomoiety including drugs, genes and cells enclosed by polymeric membrane, while nanospheres biomoiety get diffused all over its polymer matrix. Polymeric nanoparticles adopt as globular vesicular nanocapsules wherein polymeric membrane can dissolve, entrap and attach/encapsulate foreign moiety throughout its reconfigured core-matrix/skeleton. Polymeric background is chosen which owns ability of modifications so that resultant nanoparticles can act as ideal carrier/vehicle for delivery of assorted species, viz. drugs, vaccine, contraceptive and antibiotic. Reconfigured polymeric nanoparticles act as an attractive module for intracellular and site-specific delivery besides engaging in fabricating smart scaffolds/templates in advance tissue engineering [20–23].

2.9 Nano-graphynes

Carbon owing to versatile Dirac cones and hexagonal networking is called as graphyne which exists as α , β and γ forms. Theorized allotrope of carbon called graphyne is found to own carbon-carbon triple bonds pertaining versatile Dirac cones, which aid to perform an astonishing role in reconfigured atomic/electronic structural materials [1, 24]. Such carbon triple bonding adapts hopping template elements with undo signs which yields Dirac cone with perverse chirality in reconfigured α , β and γ graphynes which impart momentum shift of energy gaps besides offering chemisorption of adatoms via sublattice symmetry loss. Unique characteristics of such 2D carbon nanomaterials can be reconfigured as graphyne and stacking graphdiyne found to stimulate innovative and fascinating utilities in advance electronics. Atomically specific 2D graphdiyne and graphyne matrix reconfiguration is an awaited challenge for material scientists. Technique of on-surface synthesis in ultra-high vacuum yields graphyne that can be further feedstock for making comprehensive graphynes in particular atomically precise graphdiyne nanowires. In the past decades, low-dimension carbon materials, viz. fullerenes, carbon nanotubes and graphene, have ever-fascinated scientific and technological focus. Amid two-dimensional carbon, allotropes called graphene are deliberately pioneered via morphological reconfiguration as porous nano-strips or nanoribbons which own innate bandgap as competitive/superior as graphene. Graphynes are also tentative artificial carbon allotropes owing to intervallic acetylene bondings with blend sp^n hybridization where $1 < n < 2$. Thus based on sp/sp^2 hybridized carbon, such graphynes are categorized as α , β and γ and named as graphyne, graphdiyne and n -graphyne where $n > 2$, as per acetylene units [1, 24].

Reconfiguration of single layer, i.e. 2D carbon allotrope graphyne, is still an exigent task, since hardly any natural crystalline substances contain stacked graphynes as inclusive in auxiliary nanostructures like nanotubes, nanoribbons, quantum dots and junctions. The graphyne's innate C-C triple bonding is facile for advanced reconfigurations via attachment of hydrogen/halogen without disturbing innate two-dimensional hexagonal planarity; such reconfiguration tunes energy gap factor

at the Dirac point [3, 24]. These graphynes' synthesis is achieved through realistic and choosy functional polymerization owing to diligence precision up to atomic scale, e.g. dehydrobenzoannulenes onto catalytic copper foil via acetylenic cross-coupling resolved core-graphyne subunits. Dehydrobenzoannulene can also be reconfigured in assorted morphologies including single-layer graphdiyne, tubes, wires and walls which thrust significant utilities in catalysis and energy field.

2.10 Reconfigured graphdiyne nanowire

Nanoscale graphdiyne-derived templates are developed via Glaser reaction/ acetylenic homocoupling to yield targeted π -conjugated 2D nanomaterials which further can be reconfigured as sp-hybridized nanostructure matrixes [3, 24]. Certain terminal alkynes like 1,3,5-triethynyl-benzene act as convergent tritopic precursors in reconfiguring graphdiyne-based porous matrix via mild thermal annealing. Discriminating butadiyne inspires elementally incarcerated graphdiyne reconfiguration in the form of nanoribbons and m - n nanowires, where m is phenyl rings and n is alkynes through the recurring backbone (**Figure 3**). Once side functionality gets established in the graphdiyne moiety, it improves its quality in extended polymerize nanowires, which are best utilized in augmentation of molecular electronic parameters. Graphdiyne nanowires in vacuum own an energy gap of ≈ 1.6 eV; further statistical twisting of phenylene indicated fine changes in electronics due to cosine highest valence band and lowest conduction band viable for nonlinear electronic transportations like Bloch oscillations appropriate in high-frequency tools. Graphdiyne nanowires proffer notable automatic strength and elasticity if acetylene bondings get well conserved and offer constant chemical characteristics. Superior grade graphdiyne nanowires are prepared using butadiyne precursor through assorted tactics, viz. thermal processing, substrate selectivity, molecular designing, surface templating and metal-organic bonding creations. Raw feedstock selection is crucial in reconfiguration of π -conjugated 2D nanomaterials like graphyne and graphdiyne derivatives. An atom that lies on a surface of crystal acts as the reverse of a surface vacancy and is called as adatom, and it can be cited/reconfigured onto the top layer of metal surfaces, which impart proactive shell seeking the best adsorption molded molecular deposition and distinguished catalytic properties. On-surface acetylenic glacial coupling using silver metal is suitable to get acetylenic linkages in resultant graphyne and graphdiyne derivatives. Copper and gold both are primal metal for alkyne homocoupling with ditopic 1,4-diethynylbenzene as its over-reactivity gives extra reactions. Gold displayed surprising cyclotrimerization depending on the symmetry of precursors like if three terminal alkynes get mutually coupled to form benzene.

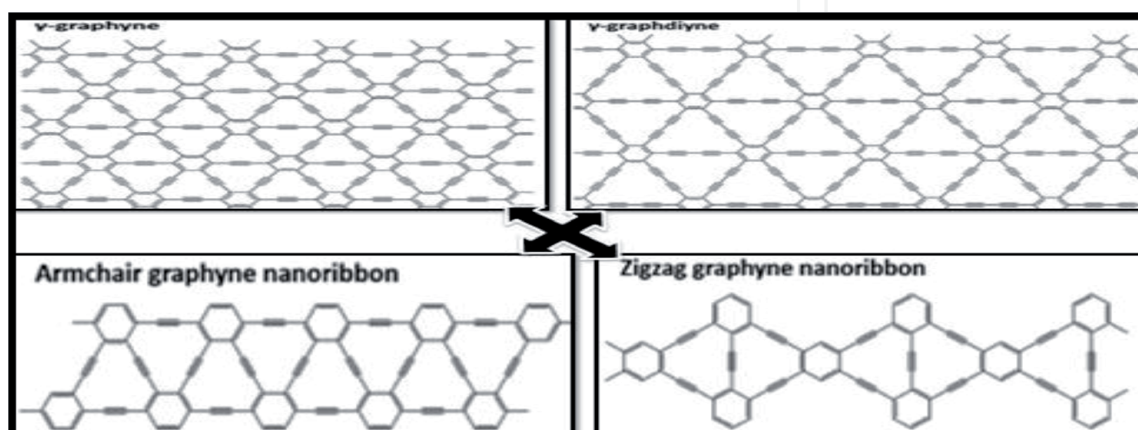


Figure 3.
 Schematic representation of graphyne and graphdiyne matrixes.

Lower-mobility species gets easily detained onto metal which resulted in side reactions in concurrence to alkynes' cyclotrimerization. Ortho functional groups restrain tangential terminal alkyne contacts which results in butadiyne linkages via weak supramolecular interactions amid nanowires that can influence neighboring molecular alignments. Anisotropic motif in asymmetric 1,2,4-cyclotrimerizations over symmetric 1,3,5-cyclotrimerization onto gold surfaces is preferred to get H-shaped oligomer and intrigue alkyne-gold interactions. Graphyne and graphdiyne derivatives are advantageous than mere graphene for innate electronic features [1, 3, 23]. On-surface acetylenic couplings can expand graphyne and graphdiyne networkings which correspondingly distinguish in intrinsic physic-chemical characters. Linear expansion of graphyne and graphdiyne into 2D graphyne and graphdiyne derivatives is still exorbitant, so strategic halide usages avoid influence of hydrogen abstraction forming hexagonal planes on gold bridging mutual acetylenes. Hexaethynylbenzene is mostly used for getting reconfigured single-layer stacking of graphyne/graphdiyne via acetylenic couplings. Advance on-surface synthetic protocols are developed for graphyne-/graphdiyne-based atomic precise nanowires, quasi-1D nanoribbons and 2D networkings. Porous structural reconfigurations of 2D materials are noteworthy for innate electronic and mechanical usages [1, 3].

2.11 Reconfigured metal-organic frameworks

Recently carbon based from metal-organic frameworks is more demanding due to innate advantageous electron conductivity and extra porosity sought in diverse fields. Thus morphology of carbon materials gets improved through altering its chemical/physical characteristics via optimized compositing with metal-organic materials. Such carbon-reconfigured metal-organic frameworks appear nontoxic and offer brilliant electrical conductivity in contrast to other energy storage materials. This makes carbon-based metal-organic reconfigured frameworks superior to most of the energy storage materials offering promising functions in demand for energy storage/conversion and addressing confronts in lithium/lithium-sulfur/sodium battery, metal-oxide/sulphide-carbon-based supercapacitors and electrocatalytic oxygen/hydrogen reduction/evolution reactions besides water-wastewater treatment techniques. Ultrasensitive biosensors are reconfigured through carbonaceous skeleton via N/S doping to get electrodes for in vitro monitoring of uric acid and ascorbic acid released from living cells. Direct physical/chemical carbonization of organic templates with assorted species like zeolites, meso-silica via solvothermal or hydrothermal techniques yields carbon-based metal-organic frameworks [25]. Carbon reconfigured through metal-organic porous coordination polymers resulted in crystalline porosity due to episodic metal ion/metal clusters with organic ligand networkings. Metal-organic reconfigured carbon matrix/framework sustains assorted reward like extra porosity with tuneable sizes and very high up to $10,000 \text{ m}^2 \text{ g}^{-1}$ surface area as anticipated for adsorption, energy/gas storage/conversion, oil-water separation, catalysis, markers/sensors and solid-phase extraction. Rationally hierarchical porous nitrogen-doped carbon frameworks are developed through zinc and nitrogen templates which are used for elevated storage and adsorption capacity for CO_2 gas. Iron, zirconium and lanthanum metal-doped- NH_2 reconfigured frameworks are obtained via solvothermal process followed by pyrolysis, yielding nanocarbon matrixes which are used for biosensor activity [1, 3, 25].

2.12 Reconfigured carbon nanocages

Reconfigured nanocarbon cages can act as electrode; for example, hollow nanocobalt sulfide intervening graphitic nanocage offers superior lithium storage

capacity along with stable performance in advanced batteries. Porous ZnO-carbon nanocage is reconfigured through pyrolysis of hollow MOF-5 owing to high specific surface areas besides hollow morphology [1, 3]. Porous Co-Zn-NH₂-doped carbon polyhedral nanocage effectively acts as anode in lithium-ion batteries. Transition metal oxides of M_xO_y types derived from Mn, Fe, Ni, Co and Sn offer superior capacities of 1000 mA h g⁻¹ than that of graphite templates and thus gain weightage as anodes in sodium-ion batteries. However, transition metal oxides of M_xO_y types can be reconfigured in carbon materials so as to proffer elevated surface area and improve sodium storage simultaneously. Hollow NiO/Ni nanocrystal reconfigured onto graphene shell imparts good storage capacity and cycle stability [1, 3–25].

Carbon matrix gets reconfigured with nitrogen doping in Co₃O₄-based metal-organic hybrid/framework imparting unique features like high electronic conductivity, superb definite capacity and superior cycled constancy. Many bimetallic Ni-Co-organic frameworks owing to hierarchical hollow crossbreed occur via generic template-free strategy to fabricate anode electrode for sodium-ion battery. Hollow nano-skeleton of such organic framework/hybrids reconfigured entirely novel electrodes' utility owing to constant reversible capacity after long-term 200 cycles. Titanium-derived metal-organic hybrid crystal yield via carbon-coated rutile materials is used for anode making in sodium-ion battery up to 2000 cycles. Graphene-titanium oxide reconfigured metal-organic hybrids/composites can act as anode found to exhibit huge porosity and great retention capacity up to 5000 cycles for sodium-ion battery usage [11, 24].

Transition metal sulphide-based carbon hybrid like Ni₃S₂/Co₉S₈/N-C-gifted hollow-spheric skeleton obtained via carbonization-sulfurization of binary Ni-Co metal-organic framework is used in fabrication of electrode for sodium-ion battery. Ultra-fine hollow porosity is achieved in nanometal sulfide blended ultrathin N-doped organic carbon hybrids, which delivered brilliant electrochemical function with competent capacity up to 100 cycles. Bimetallic zinc antimony sulphide which blends organic carbon core-double shell polyhedron frameworks exhibits unique electrochemical functions like consistent cycling stability and elevated coulombic efficiency besides precise capacity. Ultrathin/nano-molybdenum sulphide coated onto flexible N-C/carbon cloth nano-array hybrid/sheet owns good electrochemical performance as an anode up to 1000 cycles for sodium-ion battery. Such admirable electrochemical functions are accredited to unique two-dimensional features viable for curtail ionic diffusion which overall extend Na⁺ insertion. The N-doping in organic carbon yields porosity in resultant nanowall which imparts advance conductivity and sustainable integrity of such bimetallic organic frameworks [1–3, 23].

Organic/carbonaceous nitrogen-doped metal porous frameworks get reconfigured for making sodium-ion battery electrodes' residing unique features like fair capability, cycling stability, high electrical conductivity and elevated ion storage ability. Inorganic sulfur/phosphorus reconfigured with metal-organic template aids to fabricate S/P-doped meso-carbon anodes which are practically reported to prolong cycle constancy, elevated energy density and wonderful rate capacity for sodium-ion battery. Amorphous red phosphorus reconfigured into micro-porous carbon-nitrogen matrix shows high Na⁺ storage performance and reversible capacity up to 1000 cycles for sodium-ion battery. Certain nano-sheets get reconfigured through 3D reduced graphene oxide-anchored phosphorus-nickel foam owing to cobalt core shell of phosphorus-carbon polyhedron which overall improved cycling stability and benefited damage relaxation during charging-discharging in resultant battery electrode performance. These reconfigured materials hold sole metal-organic framework as electrode which showed astonishing and superior electrochemical outputs like high power density, reversible capacity, brilliant stability, huge cycling stability, elevated rate capacity and galvanostatic charge-discharge

contour. Assorted homogeneous-dispersed hierarchical 1-/2-/3-D porous micro-/nano-layer cathode matrixes are reconfigured with nitrogen-doped organic frameworks through melting-diffusion and infiltration techniques. Extensive metal-organic frameworks are obtained via adjusting morphology, reactive conditions, and control carbonized reconfigurations in feedstock materials and are found to proffer characteristic features like greatest recycling, prolonged cycle electrical capacity, and top capacitance as desired in advance battery electrode fabrication [3, 25]. Doping of nitrogen/sulfur further raised charge redistribution, electron delocalization and reversible capacity in resultant batteries that are superior to other counterparts. Metallic insertion in carbon frameworks yields copious and consistent porosity in ultrafine nano-skeletons as beneficially immobilized N/S in organic templates. Similarly, sodium-ion battery electrodes are reconfigured via phosphorus/nitrogen added to carbon scaffolds so as to deliver superior electrochemical functions and impart high theoretical sodium-storage capacity due to Na-P synergistic effect devoid in its contemporary [1–3].

Nanocarbon-reconfigured metal-organic frameworks are superior to fabricate electrode with improved electrochemical performance in supercapacitors, e.g. zinc-organic scaffolds. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -derived hybrid super-capacitor yields Li-type anode and double-layered cathode electrochemical capacitance with duly great energy density and prolongs capacity up to 10,000 galvanostatic cycles. Reconfigured hierarchical carbon-coated tungstic anhydride-Li-HSC porous anode and N–C hollow polyhedron-based cathodes exhibited soaring power density and high-retained capacity up to 3000 operating cycles [20–26].

Splendid ‘brick-and-mortar’-type squash-in nanoporous matrixes can be reconfigured owing to dope metal as ‘mortar’ and abide organic framework as ‘brick’ to be used for electrode in next-generation energy/power storage battery. Remarkably reconfigured novel nanocarbon metal-oxide sheets/core-shell composite gets casted as asymmetric supercapacitor anodes owing to longer cycle stability, high energy density and huge energy density in aqueous electrolytes with upmost 10,000 cycle capacitance retention superior to other counterparts. Nanocarbons reconfigured onto bimetals yield hybrid via control carbonization, and coexisting N-doping architecture imparts huge surface area and better capacitance (than nanocarbon) to be used to fabricate flexible asymmetric advanced supercapacitors [3]. Unique one-dimensional hollow structure of N-dope-organic framework-reconfigured bimetals imparted good power storage capacity and electrochemical performance up to 10,000. Metal oxides derived from supercapacitors conveyed superior power density and electrochemical stability than carbonaceous polymeric matrix. Flexible hybrid supercapacitors developed from N–C-doped niobium-oxide quantum dots performed as superior electrochemical electrodes owing to maximum energy/power density and cyclic stability even up to 5000 cycles [27]. Porous manganese tetroxide reconfigured N-doped graphene by means of polystyrene template yields ordered porous composite owing to brilliant electrochemical capacitance and cyclic stability up to 2000 cycles in aqueous electrolyte solutions. Ruthenium oxide reconfigured nanocarbon scaffolds have shown outstanding electrochemical performance as supercapacitors owing to capacitance retention in lithium-ion battery. Assorted hierarchical nanoporous organic carbon-based skeletons are developed for its innate higher capacitance and cyclic stability even up to 140,000 cycles than bulk amalgamated electrodes. Thus, reconfigurations of material indeed have to break through many challenging discoveries of advanced anode/cathode materials in the development of high-performance batteries owing to good volumetric/gravimetric energy density and its allied futuristic functioning for electrification of vehicles besides grid power storage.

Noteworthy R&D is performed to discover high volumetric/gravimetric energy density electrodes through reconfiguration of material’s matrix for getting innate

electro-voltaic functions. Certain layered mixed metal oxides, viz. LiMn_2 , olivine LiFe-PO_4 , LiCoO_2 and Li-Ni/Co/MnO_2 , are reconfigured to fabricate electrodes for lithium-ion cell. Strategies are being developed for optional high-energy cathodes with preserved substantial stability, rate capability and its cycle life. High-energy cathodes made from Li_2MnO_3 conveyed electrochemical steadiness with improved specific capacity and corresponding volumetric/gravimetric energy density. Li-ion batteries offer prospective high volumetric/gravimetric power density of its cells achieved through reconfiguration of novel electrochemicals [26, 27]. Sulfur- and oxygen-based bimetallic organic framework-derived cathodes are intensely reconfigured for innate superior theoretical capacity over usual metal-oxide electrodes. The designing and development of progressive high-performance material-based electrodes derived via assorted reconfigured materials are still a difficult task/challengeable due to their innate size constraint. Lithium-ion battery needs prospective high-power electrodes as derived via various reconfigured matrixes including Si-alloy, metal-oxide frameworks and graphene carbons for electro-vehicles and grid power storage. Certain reconfigured material matrixes convey exceptional features like facile mount skeleton, high specific surface area and storage capacity besides hierarchical porosity contributed in innate onset potential electrochemical performances.

2.13 Environmental applications of MOF

Assorted metal-organic frameworks (MOF) are reconfigured to impart special valid features like huge specific surface area, adaptable porosity, and constitutional uniformity and to unlock metal sites although certain facile physic-chemical variations are anticipated in advanced S&T applications [3, 19] can be even utilized for better adsorption of dyes, gases and environmental pollutants as mentioned in **Table 1**.

Diverse materials are reconfigured to be used as adsorbents for mitigation of water pollution; for example, 3D twofold zinc-doped carbon porous scaffolds owing to elevated surface area conveyed five-fold higher sorption capacity for dyes and drugs like ibuprofen/diclofenac contaminated water over commercial-activated carbon [3]. Magnetic carbon sponges are reconfigured in zeolitic imidazolate framework-67 to carry out excellent separations of buoyant oil from water and oil from emulsions and executed excellent catalysis in H_2 gas generation [25, 27]. Extremely dispersive nano-chromium oxide can be reconfigured in mesoporous carbon nitrides to yield MIL-100(Cr) templates owing to greater specific surface area which aids huge CO_2 adsorption capacity quite higher than its counterparts [1–3, 28].

Specially reconfigured nickel oxide/poly-carbon nitride interlinked with tree-like chains/branches owing to unique features like nano-flower/leafy planes, huge surface area and hirsute dendrite core shells; superior porosity can impart superior and control/choosy arsenate anionic diffusion besides efficient As^{+3} to As^{+5} oxidative conversion in contaminated water. Porous nano-spherical scaffolds holding iron-EDTA ligands owe exclusive chelating sites that afford huge anionic adsorption capacity of 307 and 407 mg g^{-1} for As (V) and Cr (VI), respectively. Metal-organic frameworks are used to reconfigure many fluorescent sensors/markers like super-porous chemosensors owing to zirconium-based hydrophobic fluorescent probes developed to check ultratrace (0.1–2000 ppb level) Zn^{2+} ions from water. Ratiometric fluorescent sensor containing UiO-66-zirconium matrix is used for selective Zn^{2+} detection from water. Hydrophobic fluorescent probes reconfigured with rhodamine ethylene-diamine salicylaldehyde are developed for sensitive Bi^{3+} adsorption from water. All such reconfigured metal-oxide carbon

Metal in organic frameworks	Example	Brunauer-Emmett-Teller (BET) surface area [m ² g ⁻¹]	Pore volume [cm ³ g ⁻¹]/d	Absorption utility
Iron	Fe ₃ O ₄ -carbon	439	–/0.80 nm	—
Zinc	Hierarchical carbon-C1000	524	–/0.80 nm	59.20 cm ³ g ⁻¹ for CO ₂
Zeolitic imidazolate framework-67	Magnetic carbon sponges	62	0.20/–	58,000 mg g ⁻¹ for silicone oil
ZIF-8	Iron-doped carbon	606	–/5 nm	Reflection loss of 29.50 dB
Ni-based MOF	Nickel-doped carbon	110	–/1.80 mm	Reflection loss of 51.80 dB
ZIF-8	PCDM-800 nanoporous carbons	885	–/–	–
ZIF-8	PCDM-1000/1200	1855	–/–	320 mg g ⁻¹ for IBP
Nickel/zinc	Ni-phthalocyanine-carbon nanotubes	999	0.90/–	395 mg g ⁻¹ , 898 mg g ⁻¹ and 271 mg g ⁻¹ Rhodamine-B, malachite green and for methyl orange, respectively
Materials of Institut Lavoisier MIL-100 (chromium)	Cr-MCN nano-chromium oxide-mesoporous carbon nitrides	1294	0.40/–	16.8 mmol g ⁻¹ for CO ₂ and 22.5 mmol g ⁻¹ for hydrogen gas

Table 1.
Metal-organic framework-reconfigured carbon materials for adsorptions.

frameworks own wide utility in water treatment techniques like selective and sensitive adsorption/detection of pollutants from water/wastewaters. These reconfigured matrixes, scaffolds and templates own magnificent adsorption profile due to remarkable features, viz. huge surface area H-donor/ π - π bonding capacity and great hydrophobic environments [1–3].

2.14 Biological applications of MOF

The outstanding properties of reconfigured MOF matrixes are used for sensing or absorption of assorted biological species like genes, cells, tissues, drugs and selective single-stranded DNA and quenching label fluorescent dyes. Magnetic nanocarbon porous scaffolds are reconfigured via thermolytic iron oxides MIL-88A matrix to proclaim sensing platform for double-stranded DNA with target DNA and aids in the release of single-stranded DNA probes (1×10^{-9} m detection range) onto adsorptive surface in DNA hybridize sensor electrochemical impedance detection [3, 4]. Iridium-MOF-8 scaffolds act as hybrid electrochemical sensing/detection of anesthetic lidocaine (0.20×10^{-12} – 8×10^{-9} M). N-link glycan-metal organic-based frameworks obtained through pyrolysis can remove zinc ions from soils and complex biological samples.

Challenging areas in MOF.

These reconfigured scaffolds, templates and matrixes yield advanced materials which fulfill existing needs like high-performance energy-power storage, adsorption and chemosensor/marker utilities in today's modern science and technology [1]. Reconfigured materials offer superior benefits over traditional porous materials due to huge specific surface area, tuneable porosity and facile skeletal functions. Such innovative materials emerge through reconfigured synthetic methods and material structures, and analogous outputs really trust reciprocated improvement in various disciplines including batteries, supercapacitors, electro-catalysts and water treatment techniques. Yet, few perspective challenges and key problems as presented below are to be solved:

- Synthetic protocols involved in reconfiguration of metal-organic frameworks need to be explored for applicability at high-temperature calcinations and to aid ordered annihilation and impart huge porosity besides carrying out effective polymerization.
- Metal-organic framework-reconfigured matrixes still rely on material synthesis and its characterization, but R&D mechanistic performance is yet to be done. Methodical perceptions of interfacial interactions amid metal-organic frameworks and its doped components might offer superior optimized synthesis protocol.
- Strategic reconfiguration augmented MOF-doped polymeric adhesives, and control functionalized carriers are to be analyzed for its cost and operating strategy so as to boost electrochemical performance to meet industrial applicability.
- Meritorious MOFs need to be reconfigured as per adaptable structures, composition and morphology for its excellent performances.
- Experimental and theoretical computational simulations can give momentum for innovative reconfiguration as applicably predicted to fabricate advanced scaffolds, templates and matrixes via MOF.
- Rational design is to be done to strictly control structural, functional and performance-based aspects of metal-organic reconfigured materials.

3. Summary

Innovative and truly applied nanomaterials can be reconfigured through corresponding skeletal/matrix alterations which are successfully accounted in the past decades. Matrix reconfigurations in nanomaterial skeleton found to vary with environmental conditions, diverse elements, allied constituents and corresponding organic supports communicate intricate besides mixed chemical characteristics. Each of such modules owns crucial status, plays a vital role in its reconfigurations and harmonizes mutual deficiency besides proffered synergistic recitals. Usually, reconfigured nanomaterials acquired expedient features like hierarchical porosity, superior mechanical stability and elevated electrical/thermal conductivity. Due to their promising features, reconfigured nanomaterials are intensively used for many purposes including batteries, supercapacitors, electro-catalysis and water

treatment techniques. Abundant notable advancements are attenuated performance utility which persuades novel breakthroughs in reconfiguration of futuristic nanomaterials.

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