

# Re-Configured Skeletal Nano-Material Matrixes

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**Abstract:** New-materials beat hereto technology gets hurdled by virtue of innate advance and unique features as employed for novel applications in S&T. Assorted composites are obtained through reconfigurations of their skeleton/matrix which appears as multi-phase matter and tenders manipulated new properties/functionalities via chosen amalgamations. Hence, it's meticulous to comprehend interactive materials for their skeletal reconfigurations to yield desired matrix alteration to cater needs of modern developments. Systematic and rational designing of nano-materials is fundamental as varied scaled reconfiguration permits recognition of characteristics functionalities being impracticable via conventional methods. Advanced bio-technology, physics, chemistry and nano-material engineering carry out skeletal reconfigurations to fabricate nanomaterials viz; decisive particles, species and devices at the atomic and molecular dimensions. Rational reconfigurations in material matrix reduce spatial dimension/captivity within crystallographic phases and usually alter innate features including mechanical, physical, chemical, thermal, optical and electrical-electronic properties.

Such reconfigured matrixes mostly restrain three nano-porous skeleton namely; 3D/zero dimensional (e.g., particle, grain; shell; capsule; ring; colloidal), 2D/one dimension (e.g., quasi crystal, nano-rod; filament; tubes; quantum wire) and 1D/two dimensional (e.g., disc; platelet; ultrathin film; super lattice; quantum well). Today, rational designing of smart nano-materials acquired via flexible matrix/skeletal reconfiguration are focussed for desired applications in advancement of science and technology. This chapter confer diverse re-configured skeletal-matrix to get nano-structures, devices and tools including respirocyte, nano-denderimer micelle, drug conjugate, carbon nanotube and quantum-dots owing special characteristic applications.

**Keywords:** Nano-material, nanotechnology, reconfiguration, 1D, 2D, 3D skeleton, metallo-organic frameworks, 2D carbon allotrope, graphyne.

## INTRODUCTION

Nano-technology envisages fabricating functionally materials through reconfigurations in their skeletal matrixes to offer integrated solutions for medical, biological and engineering model applications owing designing to fulfil the challenges [1]. The hierarchical structure alterations open/allow nano-material creations with comparable size to those occurred naturally. Consequently, advanced engineering and technological designing yield via skeletal reconfigurations and the resultant matrix more mimics certain intricate skeletons which are found in nature, in order to combine some advance viz; drug delivery, gene capture, tissue release, cell labelling, and scaffolds improvements [2].

## CLASSIFICATION OF NANO-MATERIALS

Nano-structure material found to condense in-toto or in part so as to yield assorted skeletal viz; particles, grains, crystallites, fibres, rods, layers attributed dimensions range from few to several nanometers. Long-range orderings in the structures are highly disturbed short-range orders verified multi-particle correlations via size and/or mutual atomic arrangement which govern macroscopic characteristics.

The classification of nano-structured materials was initiated by Gleiter in 1995 and elucidated by Skorokhod in 2000. The classification goes via dimensions of inherent structural elements as: zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) nanomaterials. Zero-dimensional comprises clusters/dispersions wherein nanoparticles get mutually isolated. One-dimensional include fibre/rod/tube of 100 nm to few microns. Two-dimensional involve films/coats owing some nm thickness. Three-dimensional materials embrace as powder, fiber, multilayers and polycrystalline owing 0D, 1D and 2D structural elements in close mutually contacting interfaces. While 3D nanostructure own merged bulky nano-polycrystals/grains of non-free surface with whole filled volumes. 3D packed nanomaterials possess interfaces while nano-powders own no-grain surfaces and really dissimilar agglomeration degree of same size compacts. Assorted 0D, 1D, 2D and 3D nano-materials as liquid/solid matrix/substrate as shown in Figure 1. Gleiter/Skorokhod classification scheme is taken for 0D, 1D, 2D and 3D structures excluding fullerenes, nanotubes and nanoflowers are not accounted (Pokropivny reported modified classification).

## Nano-Scale in Different Dimensions

There exists following four possible nano-scale dimension in fabrication of nano-material/structures as shown in below Figure 2:

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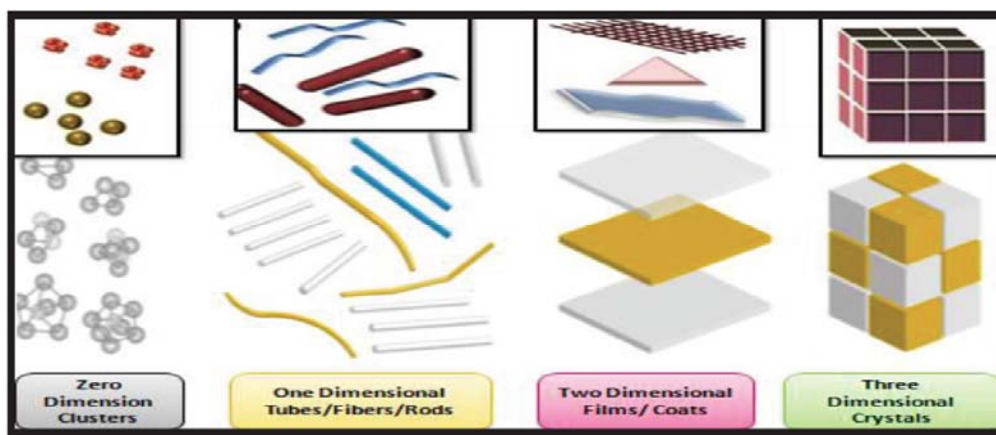


Figure 1: Assorted 0D, 1D, 2D & 3D nano-materials as liquid/ solid matrixes/substrates.

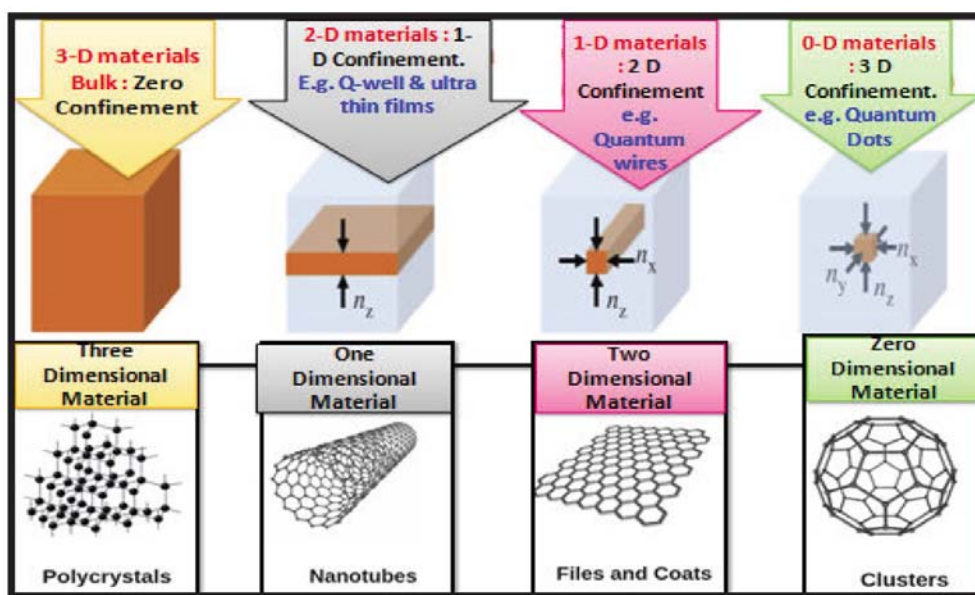


Figure 2: Possible nano-scale dimension in fabrication of nano-material/structures.

## 0-Dimension

Quantum dot is semiconductor nano-crystal owing tightly confine single to thousand of electrons or electron holes. Quantum dots are zero dimensional nano-structured carriers of electrons/electron holes which are spatially confine/restricts in all 3D. Quantum dots acts as artificial atoms that own stressed singularity with bound, discrete/quantize electronic energy states similar to inherent atoms/molecules. Several electron gets lodged in a single energy level which impart high power and low threshold character to these quantum dots being active component of semiconductor LASER and photodetectors.

## 1-Dimension

The one dimensional nanomaterials owing length of 100 nm to few microns and assembled as fibers, rods,

wires and tubes. Due to free longitudinal size these are termed as one-dimensional materials owing diameter of de Broglie wavelength of the electron. The quantum effects found dominated in such 1 dimensional nano-structure materials which impart attractive properties different than the bulk materials.

## 2-Dimensions

The nanostructures with thickness of atomic monolayer to few atomic layers are called as 2 dimensional materials. These 2D nano-materials possess high aspect ratio and their small size aids quantum detention of electrons.

## 3-Dimensions

The bulk materials are termed as 3 dimensional nanostructures. There occurs no restriction of carrier

confinement and carriers are liberal for movements in all possible three directions. Thus, property/characteristics nature remains same as that of the materials in such 3D nano-structured since energy levels are continuous while varied state density.

### Characteristics of Nano-Materials

Varied sizes, average particle diameter and charges can affect physical stability and *in-vivo* distributions of nanomaterials. Thus, characterised through its size/shape, morphology and surface charge, by means of sophisticated microscopic systems viz; atomic force microscopy, scanning electron microscopy and transmission electron microscopy [15]. Electron microscopy informed surface morphology and size/shapes both besides stability and re-dispersion surface charge of nanomaterials. Nanoparticle size is evaluated by means of particle size distribution and morphology studies. The mutual compromising upmost stability pertains with small size found to favour in re-configured materials [1-16]. The surface charges and intensity parameters also decide electrostatic interaction with biological milieu/bioactive sample to carry via such materials.

Nanoparticles are generally obtained through known three techniques viz dispersion of preformed polymers, ionic gelation (hydrophilic polymeric coacervation) and monomeric polymerization. In order to control of 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 nano-matrixes. Dispersive polymeric technique is well use to reconfigure biodegradable nano-particles via dispersion of biodegradable polymers like as poly-glycolide, polylactic acid; poly-cyanoacrylate, and polylactide-co-glycolide [5].

### Utility of Nano-Materials

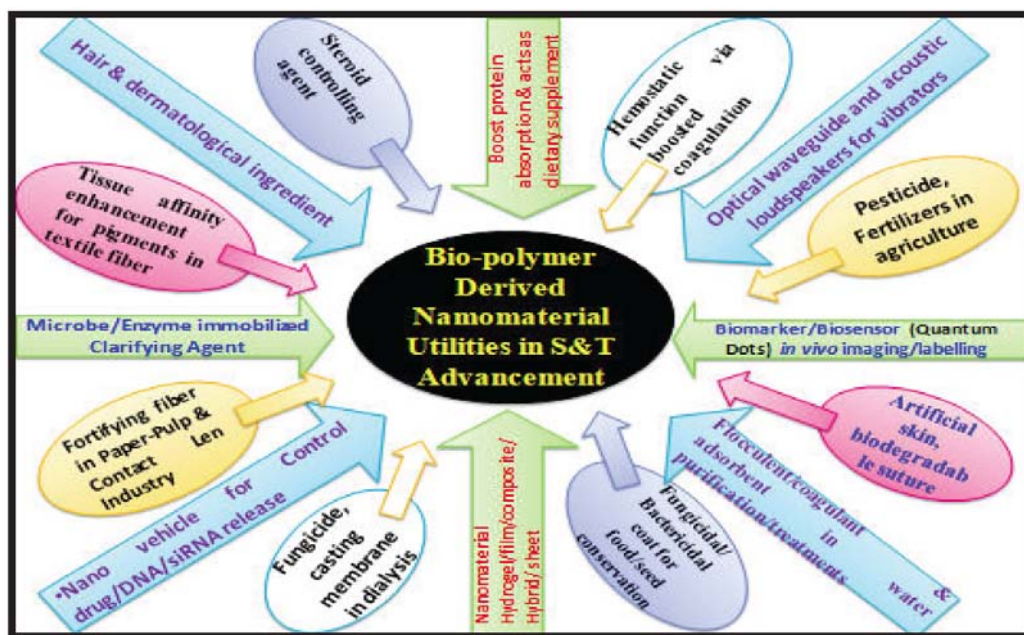
Advanced nanotechnology offers novel tool, opportunities, scopes in significant applications for diagnostic and therapeutic purpose. Rationally designed smart materials are well-established for drug delivery, diagnostics, treatment and prognostic of illness via re-configured/re-structured devices and tools. Pharmaceutical nanotechnology embracing nano-products own improved and requisite characteristics sub-domains viz; polymeric nanoparticle, magnetic/metallic nano-particles, biosensors, biomarkers, liposome, carbon nanotubes (CNT),

quantum dots (QD), and dendrimers etc [3]. Nano-pharmaceutically reconfigured materials own vital utility in delivering therapeutic components at desired site in treatment of critical illness and crucial diseases. Re-configured matrixes are effective vulnerable drug delivery agents, targeting cell release, specific tissue liberation in biological samples. Size reduced targeted formulation and suitable drug delivery pathways designing are performed through intrinsic skeletal re-configurations yields varied nanostructures which displayed sole physicochemical/biological features. Rationally designed nano-particles own potential utility for such purpose imparting peculiar advantageous like less-toxicity, more release capacity, improved solubility, bioavailability and better drug formulations [3-4].

Nano-technologically achieved reconfigurations offer assorted nano-range matrixes owing augmented performance. There are certain notable rewards of reconfigurations in material skeleton attenuated in nano-size matrixes such as reduce fed/inconsistency, amplified surface area, improved solubility, better bioavailability, more dissolution, fewer doses and rapid therapeutic action [4-5]. Advance nanotechnology via electronic, physics and engineering can manipulate at atomic, molecular, and supra-molecular level altered designed products which functionality offered novel science and technologically improved applications in biophysics, molecular biology, medicine, immunology, cardiology, endocrinology, ophthalmology, oncology, pulmonology, brain-tumour targeting and gene/cell/tissue carriers advancements [1-6]. 1–100 nm thin films/monolayer surfaces, 2-D carbon nanotubes and 3-D dendrimer, quantum dots, carbon-60/fullerene are some of the frequently used nano-materials in solar cell technology, chemical/biological sensors, drug release and drug targeting, information storage systems, magneto-optic and fiber-optic devices [1,7,8, 15]. The assorted size nano-particles have reflective consequence during the drug releases as small nano-particles owing larger surface area so as to impart fast/significant drug release through tiny assembly [16].

Various bio-polymer reconfigured nano-material utilities in the advancement of S & T for getting materials, devices and matrix reveal novel substantial transformed nano-scale unique physic-chemical features for making molecular tools, improve diagnosis, treatments and prevention of diseases, traumatic hurts and pain-reliefs as shown in Figure 3:

Certain novel therapeutic and drug delivery systems are frame by use of re-configured nanoparticles in



**Figure 3:** Bio-polymer derived nano-material utilities in the advancement of S & T.

medicines which also extend its utility for remedial and diagnostic research. Varied advance nano-particulates like paramagnetic nano-particle, quantum dot, nano-shell and nanosome gets re-configured for cancer detection base on fluorescent material, contrast agent, targeting antibody besides molecular research which modernize and amend landscape of drug development pharmaceuticals [1-7]. Assorted materials reconfiguration yields products like liposomal and polymer–drug conjugates which carry active targets or perform controlled drug delivery as approved by USA for clinical development [1-8]. Re-configured nano-structured materials with requisite features achieved via surface modifications and/or coatings with improved biocompatibility and bio-availability as employed in orthopaedics, tissue-engineering and dental for encapsulation, bone replacements, prostheses, implants and scaffolds appears better than conventional counterparts [9-10]. Re-configuration 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].

### Reconfigured Nano-Colloidal

The mixture of microscopically disperse insoluble particles which are suspended all over another substance is called as colloids. Colloid mixture can't get settle down easily takes time appreciably [17]. Nature of interaction of dispersive phase and its

medium differentiate colloids as hydrophilic/reversible sols and hydrophobic irreversible sols. The stable colloidal 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]. Low interfacial tension stabilizes such colloidal. Rheological functions are valuable in reconfiguration of suspensions in nano-collidal forms as low viscosity and high shear rates aids de-agglomerated mixing which governs suspensions flow. Such colloidal state parameters are reconfigured for its elevated particle size, shape/flexibility, and surface chemical-electrical properties. Reconfigured colloidal dispersion own suitably interfaces amongst particles and the medium owing well-define large surfaces area which is best utilize for emulsion/oil-water separations. Rational reconfiguration yields interfaces that aids concern capillarity as essential for adsorption e.g., nano-carbon colloidal based filters are used in purification of drinking water, beer/wine, de-colorization of sugar, gas masks [1].

Particle size reconfiguration openly influences bioavailability of active pharmaceutical ingredients beside affects intravenous lipid emulsion safety. Suspensions and colloidal dispersions owns range of size/shape and reduction of nano-particle size can enhances surface area beside enlarges surface area/volume ratio. Shape is irrelevant while surface area per mass of colloid scale nano-particle owe huge surface area resulting superior adsorption achieved via interactive suspension rheology, coating and adhesion.

Re-configured nano-colloidal permits faster dissolution of active pharmaceutical ingredients and corresponding bioavailability in hydrophobic membrane porous species. Since low bioavailability of active pharmaceutical ingredients escort incompetent treatment, elevates cost and toxicity; thus constrain for nanotechnology to reformulate/re-configured colloidal matrix. Re-configured interfaces of dispersive phase and its medium are negligible for colossal materials but dominant in colloidal being decisive in physico-chemical alterations like surface chemistry and in-toto system's reactivity [1,3].

Nano-particle asymmetry is vital to determine overall physico-mechanical features of colloidal as shape account particle formation/crystallization. Colloidal sizes can exist as corpuscular like spherical/ellipsoid, lamellar 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 substantial mechanical potency and durability. Shape of colloidal can be re-configured as large extended uni-dimensional strings up to rigid dense random coils gets manipulated by many factors like solution temperature, pH, and nature of salt /electrolytes. Liquid-liquid interfaces, colloidal dispersions, metal sols like gold nano-particles, lyophobic colloidal dispersions including polymeric embodied API's, ionic solids surface charge govern unequal dissolution due to crystal lattices anisotropy [3].

Till date numerous "nanotechnology-based" colloids are reconfigured for environment, nano-medicine, healthcare and cosmetics. The use of ZnO/TiO<sub>2</sub> colloidal in creams attenuated UV-A/B rays induced sunburns and skin cancer; toothpastes own nano-hydroxyapatite to fill tooth cracks and anti-aging products uses nano-capsules. Nanosilver colloids are reconfigured for injury healing/wound dressings. Nanosize zirconia based hydroxyapatite colloidal acts as bioactive ceramics for orthopedic weight-bearing implants owing advantageous sintering. Traditional pharmaceutical have delivered precise therapeutic to its accurate targets without side effects by means of these re-configured material based nano-medicine. Colloidal stability is measured through its zeta potential gradient as a function 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 avoid aggregation pivotal to evaluate surface hydro-phobicity, encapsulation and surface coatings [1,3,17].

### Nano-Colloidal Analysis Techniques

Certain sophisticated analytical tools like hydrophobic interaction chromatography, biphasic partitioning, adsorption, contact angle measurements found to establish surface hydrophobicity of colloids. While, X-ray photon correlation spectroscopy resolves surface hydrophobicity and aids recognition of surface proactive functionality [1]. UV HPLC, ultracentrifugation, ultra filtration, gel filtration, centrifugal ultra-filtration analyses extent of drug release parameter require its delivery being a vehicle like role of reconfigured nano-matereials [3, 17].

### Nano-Dendrimers

Dendrimer is unique polymer owing 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, 18]. Dendrimeric nanostructure reconfiguration occurs through numerous branches from core in shape of spheric arrangement which imparts cavities while its synthesis polymerisation. Reconfigured dendrimers are effectively utilized in drug transport via its free ends that's 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 [1,18]. Dendrimers have fine nanostructures and also capable of surface functionalization, mono-dispersions 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's aids sustainable delivery of vaccine, cell, drug, gene and metal. Reconfigured dendrimers own innate hollow arrangements with space/voids to include drug/bioactive samples through physico-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 poly-dispersity index. Poly(ethylene glycol), chitin, melamine, poly-glutamic acid, poly-propyleneimine, polyamidoamine, polyethyleneimine biodegradable skeletons are easily reconfigured into dendrimers via above mention synthetic methods. Dendrimer based complexes acts as nano-device own potential utility in cancer chemotherapy as targeted drug therapy like tectodendrimers owing every dendrimer unit exhibits assorted role e.g., targeting, disease diagnosis, drug career and imaging [104]. Re-configured dendrimers used in therapy avoids stimulated immune side-effects. Drug/therapeutic dendrimers conjugate target cells and indicate useful advantages features viz; boron EGF-carrying PAMAM dendrimers, intra-tumoral injection, CED-doxorubicin-2,2 bis (hydroxymethyl) propanoic acid derived dendrimers shown *in vitro/vivo* less toxicity in colon carcinoma cells treatment in rats [1, 3, 17]. 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 linkings shown in Figure 4:

#### Nanocrystal and Nanosuspension

Aggregated structures formed through the combination of various particles in crystalline form coated with surfactant combinations which impart static and electrostatic surface stabilization. Such nanocrystal and nano-suspension aggregated materials lessen bioavailability and absorption issues due to its resolve formulation. Nano-crystal size permits safe and effective passage via capillaries. Re-configured solid lipid nano-particles owe discrete reward of unique carrier systems over liposomes and polymeric nano-particles due to solid lipid matrix owing 1  $\mu\text{m}$  diameter

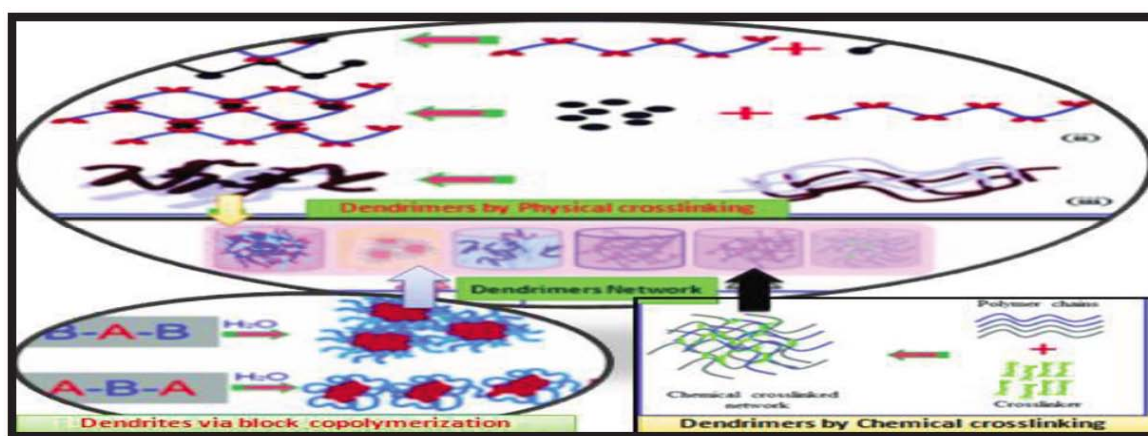
where drug gets easily incorporated. Such nano-particle/nano-systems for clinical are obtained by high pressure homogenization that uses varied surfactants to avoid aggregation and imparts dispersion stability. Reconfigured cationic solid lipid collidal nano-particles are prepared and used for liposomal transfection agents besides gene transferring dominant for *in vitro* [1,3, 15-17].

#### Silicon-Based Nano-Materials

Silicon-based nano-structures 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 usage of sodium silicate as a precursor. Such reconfigured silicon-derived materials can offer effective delivery of drugs like porous silicon embedded platinum is applied for many usages like antitumor drug release and career for antibody, antibiotic, enzyme and DNA. These materials also act as good semiconductors and thus preferred in micro-electromechanical usage [1-3].

#### Nano-Micelles

Polymeric miceller assemblies are reconfigured through amphiphilic block copolymers which impart nano-sopic supra-molecular core-shells as aggregates in solutions. In such micellers, the reconfigured components get ordered as spherical owing hydrophobic core-shells that are water secured due to hydrophilicity. Many components owing hydrophobic and hydrophilic portions are reconfigured like Amphiphilic AB or ABA kind of block copolymeric units



**Figure 4:** Nano-dendrimer synthetic route: Block polymerization & chemical cross linking.

yield polymeric micelles as nanoscopic supra-molecular core-shells as aggregates in solutions [1-3]. Nano-science technology has reconfigured assorted supramolecular architectures as a result of self-assembly 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 acts as 'smart drug carriers' due to binding of specific ligand onto proactive surfaces which aids targeted/formulates stimuli-sensitivity found devoid in their counterparts. Self-assembly in block/graft copolymers occurred in selective solvents spontaneously reconfigured as supra-molecular assemblies owing cylindrical and vesicular core-shells of 10–100 nm shape/size nano-materials 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. Reconfigured polymeric micelles appear to be novel vehicle for carrying sparingly soluble i.e., hydrophobic drugs, since external shell are hydrophilic and its nano-size assists prolong residency in blood besides gather in tumor-specific zone due to more permeation/ retention. 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 [3, 18].

### Biopolymeric Nano-Particles

Nano-array of polymers 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, non-immunogenic and appear extra-stable to volatile pharmaceutical agents besides offer low-cost fabrication at large scale/multitude methodology. Bio-polymeric derived reconfigured nano-materials appears to be biocompatible and biodegradable as anticipated for tissue engineering

scaffolds and drug/gene release/carrer besides novel vaccination approach [1-3, 18]. Certain natural polymers like chitosan, gelatin, and sodium alginate owing non-toxic profile gets easily re-configured in situ with man-made polyesters viz; poly-caprolactone, poly-cyanoacrylate, poly-lactide-co-glycolide, poly-lactide and poly-lactid acid to yield resultant matrixes advocated under advance nano-biotechnology. These bio-polymer derived nanoparticles offers 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 re-configured as vesicular systems like nano-capsules and matrix systems like nano-spheres. Reconfigured nano-capsules owe innate cavities that can detain assorted bio-moiety including drugs, genes and cells enclosed by polymeric membrane while nano-spheres bio-moiety get diffused all over its polymer matrix. Polymeric nano-particles adopt as globular vesicular nano-capsules wherein polymeric membrane can dissolve, entrap, attach/encapsulate foreign moiety throughout its reconfigured core-matrix/skeleton. Polymeric background are chosen which own ability of modifications so that resultant nanoparticles can acts as ideal carrier/vehicle for delivery of assorted species viz; drugs, vaccine, cells, contraceptive and antibiotic. Re-configured polymeric nano-particles acts an attractive modules for intracellular and site specific delivery besides engage in fabricating smart scaffolds/templates in advance tissue engineering [19-22].

### Nano-Graphynes

Carbon owing versatile Dirac cones and hexagonal networking are called as graphyne which exists as  $\alpha$ ,  $\beta$ , and  $\gamma$  forms. Graphyne are carbon allotropes owing carbon triple bonds, shown versatile Dirac cones which plays extraordinary role in atomic/electronic structural materials [1, 23]. Such carbon triple bonding adapts hopping template elements with undo signs yields Dirac cone with perverse chirality in re-configured  $\alpha$ ,  $\beta$  and  $\gamma$  graphynes which impart momentum shift of energy gaps besides offer chemi-sorption of adatoms via sublattice symmetry loss. Unique characteristics of such 2-D carbon nano-materials can be reconfigured as graphyne and stacking graphdiyne found to stimulate innovative and fascinating utilities in advance electronics. Atomically specific 2-D graphdiyne and graphyne matrix reconfiguration is awaited challenge for material scientists. Technique of on-surface synthesis in ultrahigh vacuum yields graphyne that's can be further feedstock for making comprehensive

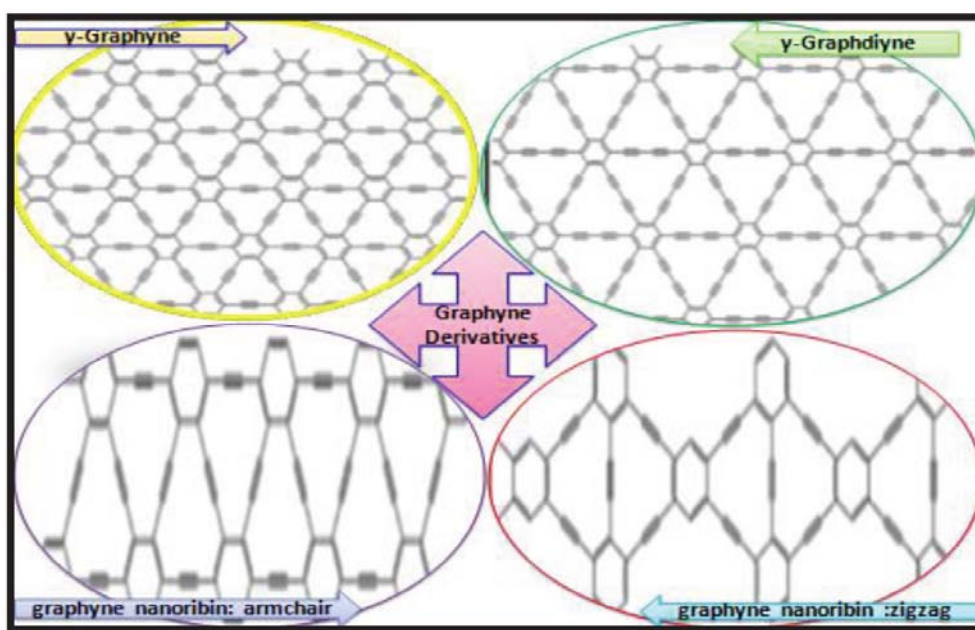
graphynes in particular atomically precise graphdiyne nano-wires. In past decades, low-dimension carbon materials viz; fullerenes, carbon nanotubes, and graphene have ever fascinated scientific and technological focuss. Amid two-dimensional carbon allotropes called graphyne is deliberately pioneered via morphological reconfiguration as porous nano-strips or nano-ribbons which own innate bandgap as competitive/superior as graphene. Graphynes is also tentative artificial carbon allotropes owing intervallic acetylene bondings with blend  $sp^n$  hybridization where  $1 < n < 2$ . Thus based on  $sp/sp^2$  hybridized carbon, such graphynes are catagorized as  $\alpha$ ,  $\beta$ , and  $\gamma$  and named as graphyne, graphdiyne, and  $n$ -graphyne where  $n > 2$ , as per acetylene units [1, 23]. The schematic representation of graphyne and graphdiyne matrixes is shown in below Figure 5.

Reconfiguration of single layer i.e., 2-D carbon allotrope graphyne is still an exigent task, since hardly any natural crystalline substances contain stacked graphynes as inclusive in auxiliary nanostructures like nano-tubes, nano-ribbons, quantum-dots and junctions. Since, graphyne's C-C triple bonding is reconfigured via attachment of hydrogen/halogen without disturbing innate 2-dimensional hexagonal planarity. Such reconfiguration tunes energy gap factor at the Dirac point. These graphynes synthesis are achieved through realistic and choosy functional polymerization owing diligence precision upto atomic scale e.g., dehydrobenzoannulenes onto catalytic copper foil via acetylenic cross-coupling resolute 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.

### Graphdiyne Nano-Wires

Nanoscale graphdiyne derived templates are developed via Glaser reaction/acetylenic homocoupling to yield targeted  $\pi$ -conjugated 2D-nanomaterials which further can be reconfigured as  $sp$ -hybridized nanostructure matrixes [1-3, 23]. Certain terminal alkynes like 1,3,5-triethynyl-benzene acts as convergent tritopic precursors in reconfiguring graphdiyne based porous matrix via mild thermal annealing. Discriminating butadiyne inspirts elementally incarcerate graphdiyne reconfiguration in the form of nanoribbons and  $m$ - $n$  nanowires, where  $m$  is phenyl rings and  $n$  is alkynes through recurring backbone Figure 5. If side functionality is established in such graphdiyne further improves its quality in extended polymerize nanowires as anticipated for molecular electronic parameters. Graphdiyne nano-wires in vacuum own energy gap of  $\approx 1.6$  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 nano-wires proffer notable automatic strength and elasticity if acetylene bondings get well-conserved and offer constant chemical characteristics. Superior grade graphdiyne



**Figure 5:** Schematic representation of graphyne and graphdiyne matrixes.



nano-wires 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  $\pi$ -conjugated 2D-nanomaterials like graphyne and graphdiyne derivatives. Adatoms and atoms citted onto top layer of metal surfaces are vital for proactive surface activities viz; adsorption molded once molecular deposition while various metal induce distinguished catalytic surface activities. On-surface acetylenic glaciar 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 cyclo-trimerization depending on the symmetry of precursors like, if three terminal alkynes get mutually coupled to form benzene. Lower mobility species gets easily detained onto metal which resulted side reactions in concurrence to alkynes cyclotrimerization. Ortho functional groups restrain tangential terminal alkyne contacts which results butadiyne linkages via weak supramolecular interactions amid nanowires can influence neighboring molecular alignments. Anisotropic motif in asymmetric 1,2,4-cyclotrimerizations over symmetric 1,3,5-cyclotrimerization onto gold surfaces are preferred to get H-shape oligomer and intrigue alkyne-gold interactions. Graphyne and graphdiyne derivatives are advantageous than mere graphene for innate electronic features [1-3, 22]. 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 form hexagonal planes on gold bridging mutual acetylenes. Hexaethynylbenzene is mostly used for getting reconfigured single layer stacking of graphyne/graphdiyne via acetylenic couplings. Advances on-surface synthetic protocols are developed for graphyne/graphdiyne based atomic precise nano-wires, quasi-1D nano-ribbons and 2-D networkings's. Porous structural reconfigurations of 2D materials are noteworthy for innate electronic and mechanical usages [1,3].

### Reconfigured Metallo–Organic Matrixes

Recently carbon based from metal–organic frameworks is more demanding due to innate

advantageous electron conductivity and extra porosity seek in diverse field. Thus morphology of carbon materials gets improved through altering its chemical/physical characteristics via optimized compositing with metal-organic materials. Such carbon re-configured metal–organic frameworks appear nontoxic and offer brilliant electrical conductivity as in contrast to other energy storage materials. This make carbon based metal–organic re-configured frameworks superior to most of the energy storage materials offer promising functions in demand for energy storage/conversion and to address confronts in lithium/lithium–sulphur/sodium battery, metal oxide /sulphide-carbon based super-capacitors and for electro-catalytic 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 solvo-thermal or hydrothermal techniques yields carbon based metal–organic-frameworks [24]. Carbon reconfigured through metal-organic porous coordination polymers resulted 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 m<sup>2</sup>/g 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<sub>2</sub> gas. Iron, Zirconium and Lanthanum metal doped-NH<sub>2</sub> reconfigured frameworks are obtained via solvothermal process followed by pyrolysis yields nano-carbon matrixes which are used for biosensor activity [1,3, 24].

### Reconfigured Carbon Nano-Cages

Carbon nanocages can be reconfigured as electrode viz; hollow nano-cobalt sulfide intervein graphitic carbon nanocages offers superior lithium storage capacity along with stable performance. Porous ZnO-carbon nanocage are reconfigured through pyrolysis of hollow MOF-5 at owes high specific surface areas besides hollow morphology [1,3]. Porous Co-Zn-NH<sub>2</sub>-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 offers superior capacities of 1000 mA h/g than that of graphite templates, thus gain waiteage 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 improved sodium storage simultaneously. Hollow NiO/Ni nanocrystal reconfigured onto graphene shell imparts good storage capacity and cycle stability [1,3-22-24].

Carbon matrix gets reconfigured with nitrogen-doping in  $Co_3O_4$  based metal organic hybrid/framework imparts unique features like high electronic conductivity, superb definite capacity and superior cycled constancy. Many bimetallic Ni-Co-organic frameworks owing hierarchical hollow crossbreed occurs 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 constant reversible capacity after long-term 200 cycles. Titanium-derived metal organic hybrid crystal yield via carbon -coated rutile materials are used for anode making in sodium ion battery upto 2000 cycles. Graphene- Titanium-oxide enfolds metal organic hybrid/composite owing porous skeleton conveyed great capacity retention up to 5000 cycles as anode usage for sodium ion battery [1].

Transition metal sulphide base carbon hybrid like  $Ni_3S_2/Co_9S_8/N-C$  gifted hollow-spheric skeleton obtained via carbonization-sulfurization of binary Ni-Co-metal organic framework are used in fabrication of electrode for sodium ion battery. Extra-fine nano-metal sulfide hollow porosity blends ultrathin N-doped organic carbon resulted hybrids having brilliant electrochemical function with competent capacity up to 100 cycles. Bimetallic zinc-antimony sulphide blens organic carbon core-double shell polyhedron frameworks exhibits unique electrochemical functions like consistant cycling stability and elevated coulombic efficiency besides precise capacity. Ultrathin/nano-molybdenum sulphide coated onto flexible N-C/carbon cloth nano-array hybrid /sheet own good electrochemical performanance as an anode upto 1000 cycles for sodium ion battery. Such admirable electrochemical functiongs 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 in such bimetallic organic frameworks [1-3,22].

Organic/carbonaceous nitrogen-doped metal porous frameworks gets reconfigured for making sodium ion battery electrodes residing unique features like fair capability, cycling stability, high electrical conductivity and elevated ion storage ability. Inorganic sulphur /phosphorus reconfigured with metal organic template aids to fabricate S/P-doped meso-carbon anodes which practically reported 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 gets reconfigured through 3D reduced graphene oxide anchored Phosporous-nickel foam owing Cobalt core-shell of phosphorous-carbon polyhedron which overall improved cycling stability and benefited damage relaxation during charging-discharging in resultant battery electrode performance. These reconfigured materials holds 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 galvano-static 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. Substantial metal organic frameworks owing greatest recycling, prolonged cycle electrical capacity, top capacitance as desired in advance battery electrode fabrication achieved via adjusting morphologies; reactive conditions and control carbonized reconfigurations in feedstock materials. Doping of nitrogen/sulphur further raised charge redistribution, electron delocalization and reversible capacity in resultant batteries that's superior to other counterparts. Rather metallic insertion in carbon frameworks yields copious and consistent porosity in ultrafine nano-skeletons as beneficially immobilized N/S in organic templates. Similar, sodium-ion battery electrodes are re-configured via phosphorous/nitrogen added 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].

Nano-carbon re-configured metal-organic frameworks are superior to fabricate electrode with

improved electrochemical performance in super-capacitors 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 prolong capacity up to 10000 galvanostatic cycles. Reconfigured hierarchical carbon-coated tungstic anhydride-Li-HSC porous anode and N-C hollow polyhedraon based cathodes exhibited soaring power density and high retained capacity up to 3000 operating cycles [19-25].

Splendid "brick-and-mortar" type squash-in nano-porous matrixes can be reconfigured owing dope metal as 'mortar' and abide organic framework as 'brick' to be used for electrode in next-generation energy/power storage battery. Remarkably re-configured novel nano-carbon metal oxide sheets/core-shell composite gets casted as asymmetric super-capacitor anodes owing longer cycle stability, high energy density, and huge energy density in aqueous electrolytes with upmost 10 000 cycles capacitance retention superior to other counterparts. Nano-carbon surfaces reconfigured onto bimetallic framework yields hybrid and flexible asymmetric super-capacitors via control carbonization and coexisting N-doping establishes nano-architecture with huge surface area and better capacitance than nano-carbon. Unique one dimensional hollow structure of N-dope-organic framework re-configured bi-metals imparted good power storage capacity and electrochemical performance up to 10000. Metal oxides derived super-capacitors conveyed superior power density and electrochemical stability than carbonaceous polymeric matrix. Flexible hybrid super-capacitors developed from N-C doped niobium oxide quantum dots performed as superior electrochemical electrodes owing maximum energy/power density and cyclic stability even up to 5000 cycles [26]. Porous manganese tetroxide reconfigured N-doped graphene by means of polystyrene template yields ordered porous composite owing brilliant electrochemical capacitance and cyclic stability up to 2000 cycles in aqueous electrolyte solutions. Ruthenium oxide reconfigured nano-carbon scaffolds shown outstanding electrochemical performance as super-capacitors owing capacitance retentions in lithium ion battery. Assorted hierarchical nano-porous organic carbon based skeletons are developed for its innate higher capacitance and cyclic stability even up to 140000 cycles than bulk amalgamated electrodes. Thus, reconfigurations of material indeed have breakthrough many challenging discovery of advanced anode/cathode materials in development of high-performance

batteries owing 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;  $\text{LiMn}_2$ , olivine  $\text{LiFe-PO}_4$ ,  $\text{LiCoO}_2$ , and  $\text{Li-Ni/Co/MnO}_2$  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  $\text{Li}_2\text{MnO}_3$  conveyed electro-chemical 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 although reconfiguration of novel electro-chemicals [25-26]. Sulphur and oxygen based bimetallic organic framework derived cathodes are intensely re-configured for innate superior theoretical capacity over usual metal oxide electrodes. Science and technology of developing such highly performed cathode/anode derived via assorted as reconfigured materials is still difficult task due to sizable challenge involved in designing progressive high-performance materials based electrodes. 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 re-configured material matrixes convey exceptional features like facile mount skeleton, high specific surface area and storage capacity besides hierarchically porosity contributed in innate onset potential electrochemical performances.

### Environmental Applications of MOF

Many metal-organic framework (MOF) matrixes are reconfigured to impart special features like huge specific surface area, adaptable porosity and constitutional uniformity, unlock metal sites besides certain facile physic-chemical variation [1] can be even utilized for better adsorption of dyes, gases and environmental pollutants as mentioned in following Table 1.

Varied materials are reconfigured for adsorption purpose e.g., 3-D two fold zinc doped porous carbons derived scaffolds resulted nano-porosity and elevated surface area carry out five fold higer adsorption of dyes

**Table 1: Metallo-Organic Reconfigured Carbon Frameworks/Matrixes for Adsorptions**

Metal in organic frameworks	Example	(BET) surface area [m <sup>2</sup> g <sup>-1</sup> ]	Pore volume [cm <sup>3</sup> g <sup>-1</sup> ]/d	Absorption capacity
Iron metal	Fe <sub>3</sub> O <sub>4</sub> -Carbon	439	0.80 nm	–
Zinc metal	hierarchical carbon- C1000	524	0.80 nm	59.20 cm <sup>3</sup> /g for CO <sub>2</sub>
Zeolitic matrix	magnetic organic/carbon	62	0.20 nm	58 000 mg/g for silicone oil
ZIF-8	Iron dope carbon	606	5 nm	Reflection loss 29 dB
Nickel metal	Nickel doped carbon	110	1.80 nm	Reflection loss 51.8 dB
ZIF-8	PCDM-1200	1855	—	320 mg/g for IBP
Nickel or Zinc metal	Ni-phthalocyanine -carbon nano-tube	999	0.9 nm	396 mg/g, 900 mg/g & 270 mg/g for dyes Rhodamine-B, Malachite green and Methyl orange respectively
MIL-100/ Cr-MCN	Nano-chromium oxide doped mesoporous carbon nitride	1294	0.4 nm	17 mmol/g for CO <sub>2</sub> & 22 mmol/g for H <sub>2</sub> gas

and ibuprofen and diclofenac contaminated water than commercial activated carbon. Ionic liquid reconfigured Porous carbon endows superior nitrogen content offers superior absorption of pollutants in aqueous/nonaqueous solvents. Magnetic carbon sponge reconfigured zeolitic imidazolate framework-67 carry out excellent work in separations of buoyant oil from water, oil from emulsions and achieve environmental catalysis besides execute catalytic H<sub>2</sub> generation. Extremely dispersive nano-chromium oxide can be reconfigured in mesoporous carbon nitrides to yield MIL-100(Cr) templates owing greater specific surface area which aids huge CO<sub>2</sub> adsorption capacity quite higher than counterparts [1-3,27-30].

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

sensitive Bi<sup>3+</sup> adsorption from water. All such reconfigured metal oxide carbon 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 bonding capacity and great hydrophobic environments [1-3].

### **Metallo-Organic Frameworks (MOF) for Biological Utility**

The outstanding properties of reconfigured MOF matrixes are used for sensing or absorption of assorted biological species like genes, cells, tissues, drugs, selective single-stranded DNA and quench label fluorescent dyes. Magnetic porous nano-carbon scaffolds are reconfigured via thermolytic iron oxides yield MIL-88A matrix that proclaimed sensing platform forms double-stranded DNA with target DNA and aid release of single stranded DNA probes (1 × 10<sup>-9</sup> M detection range) onto adsorptive surface. Iridium-MOF-8 scaffolds acts as hybrid electrochemical sensing/detection of anesthetic lidocaine (0.20 × 10<sup>-12</sup> M to 8 × 10<sup>-9</sup> M). N-link glycan-metal organic based frameworks obtained through pyrolysis can remove zinc ions from soils and complex biological samples.

### **Prospective Challenges in Metallo-Organic Frameworks (MOF)**

Advanced material's re-configured practices yield assorted skeletons including scaffolds, templates and matrixes that caters prevailing demands as anticipated

for certain prominent applications viz; ion batteries, high-performance energy-power storage, physico-chemical adsorptions, chemo-sensors and bio-markers in today's modern S&T [1,28-30]. Re-configuration in materials skeleton can proffer advancement over conventional materials by virtue of enormous specific surface area, tuneable porosity, and simplistic skeletal features. Smartly re-configured materials appear through assorted facile methodologies and structural alterations offers momentum in various disciplines viz batteries, super-capacitors, electro-catalysts and water treatments. Yet, lies certain key perspective challenges/problems need to be solved as below:

- Computer aided modelling and simulation needs to correlate material's microstructure and corresponding macroscopic properties quantitatively so as to yield impetus in re-configured nano-material utilities.
- Integrated modelled, simulated and visualized designing/alterations/reconfiguration of nanomaterials like graphene, nanotubes, and MOFs is needed as such modelling can edit adaptively without affecting the validity on the physical level. Pilot calculation for nanomaterials energy is to be realized via study of theory of surface fitting.
- Integrated framework of nano-materials modelling, simulation, and visualization needs to be intended and employed, since experimental/practical outcomes validated such approaches as feasible and effective.
- Synthetic practices in re-configured matrixes works on sophisticated techniques like high-temperature calcinations and effective polymerization to annihilate ordered skeleton and control flexible porosity and ordered morphology its innate activity.
- Re-configured matrixes based on Metal organic frameworks (MOF) relied on material synthesis and characterization, but research is to be concentrated for optimizing mechanistic performance.
- Methodical interfacial interactions among metal organic frameworks (MOF) and its doped components might offer superior optimized synthesis protocol.
- Tactical improvements are needed for doping polymeric adhesives in MOF that can manage functionalized carriers for operating strategy so as to boost electrochemical performance and

can cater industrial applicability at an affordable cost/economy.

- Smartly commendable MOF can be re-configured owing flexible skeletons, state of the art composition, and morphology so as to derive outstanding performances.
- Meticulous theoretical and practical computational investigative simulations can be impetus for ground-breaking reconfiguration in order to fabricate advanced scaffolds, templates and matrixes through assorted MOF permutations and combinations.
- Rational designing/alterations in material matrixes needs to control structural, functional, and performance characteristics of re-configured nano-materials.

## SUMMARY

Such advanced matrixes appears to be truly applied 0D, 1D, 2D &3D nano-materials that are successfully accounted, besides reconfigured via corresponding skeletal/matrix alterations derived for beneficial myriad utilities in modernization of S&T. The re-configured nano-material skeletons/matrixes showed varied physicochemical features as coherent with environmental conditions, diverse elements, united constituents and corresponding organic supports so as to commune intricate/mixed chemical characteristics. Each of such re-configured modules holds crucial prominence and found to execute vital role in its harmonized and proffer synergistic recitals. Usually, re-configured nano-matrixes obtain expedient qualities viz; hierarchical and flexible porosity, better mechanical stability besides eminent electrical and thermal conductivity. Certain inherent potential features of re-configured nano-matrixes are intensively utilized for assorted applications including batteries, super-capacitors, electro-catalysis and fabricating membranes for water purification and treatment techniques. Copious noteworthy improvements are done due to re-configuration of matrixes can offer attenuated performance modern utilities which persuades new breakthroughs for futuristic nano-materials in modernisation of S&T.

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