

# SELENIUM BASED NANOMATERIALS: STRUCTURES, SYNTHESIS METHODS AND APPLICATIONS

## Abstract

Nanotechnology has enabled production of new molecular and supramolecular assemblies in nano-scale range (1-100 nm). Moreover, it has found strong base amongst modern technologies as it caters to various sectors such as material science and technology, engineering and manufacturing, medicine, electronic devices, energy, environment, consumer products *etc.* Nanomaterials have remarkably different physical (magnetic, electronic, mechanical and optical), chemical and biological behaviour at nanoscale level than their bulk counterparts. By controlling their size, shape, surface morphology, crystal orientation *etc.*, novel nanomaterials with enhanced commercial value can be synthesized. In this context, selenium nanomaterials have gained significant attention recently from researchers and engineers worldwide. This has been attributed to its unique status as a metalloid with favourable physical, chemical and biological features. Nanoselenium in its various forms, have been found to possess superior advantages over bulk selenium and importantly, can be used in relatively higher concentrations. Thus, this chapter highlights the recent nanotechnological progress in the field of selenium-based nanotechnologies: structural evaluation, production strategies and their wide scope in various technological sectors in the form of next-generation nanomaterials. However, it is equally important that suitable *in vitro* and *in vivo* toxicity assessments are carried out before these technologies can be rolled out for practical applications.

**Keywords:** Nanotechnology, selenium, nanomaterials, supramolecular, next-generation nanomaterials

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## I. INTRODUCTION

Nanotechnology, in the modern sense, is a relatively newer field of science and technology than others like physics, engineering *etc* [1]. It encompasses controlled manipulation of matter on a near-atomic scale to produce new molecular and supramolecular assemblies with at least one dimension (1-D) ranging from 1 to 100 nanometers (nm) in size [2]. From a historical perspective, it was in 1959 that a renowned physicist, Richard Feynman sowed the seeds of “nanotechnology” for the first time in his talk, “*There's Plenty of Room at the Bottom*”, where, he hinted at the direct manipulation of atoms for synthesis of materials [3-4]. Yet the term, "nano-technology" was first used by Norio Taniguchi in 1974 and popularized by K. Eric Drexler through his 1986 book, “*Engines of Creation: The Coming Era of Nanotechnology*” [5]. Thus, modern nanotechnology emerged as a field of study in 1980s, primarily due to the inventions of scanning tunnelling microscope and atomic force microscope in 1981 which assisted in visualization and manipulation of individual atoms at the atomic scale [5]. Later on, discovery of fullerenes in 1985 by Harry Kroto, Richard Smalley, and Robert Curl (Nobel Prize in Chemistry, 1996) and carbon nanotubes (also known as graphene tubes or Bucky tubes) by Sumio Iijima in 1991 firmly established nanotechnology as a scientific, technological and research discipline [6-7].

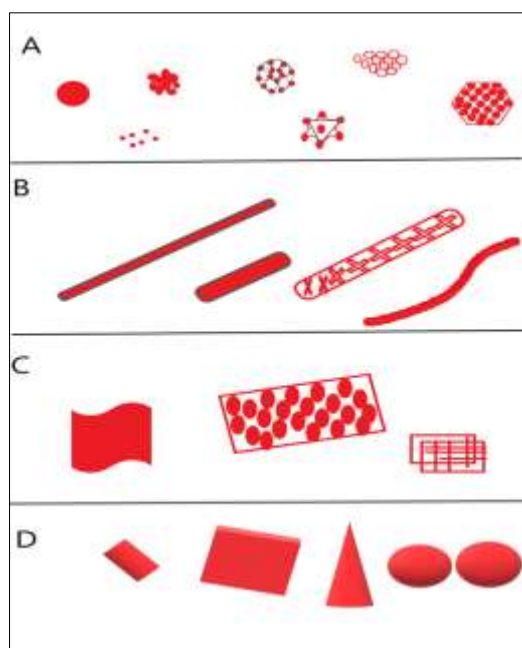
Over the years since then, nanotechnology has found strong base amongst modern technologies as it caters to various sectors such as material science and technology, engineering and manufacturing, medicine, electronic devices, energy, environment, consumer products *etc.* [2, 8]. Such a versatile applicability of nanomaterials derived through nanotechnology is related to their unique properties that affect their physical (magnetic, electronic, mechanical and optical), chemical and biological behaviour at nanoscale level [1, 9]. Thus, it is asserted that these properties of molecules or atoms are strikingly different and highly tunable in nano-dimensions as compared to their corresponding bulk-states [10]. For example, properties like higher surface area per unit volume and quantum effects of nanomaterials are due to their very small size which are difficult to observe in their bulk-material condition [9, 11]. Thus, by controlling their size, shape, surface morphology, crystal orientation *etc.*, novel nanomaterials with enhanced commercial value can be synthesized [12-13].

Recently, “Next-generation nanomaterials” (NGNMs) have aroused significant attention in this field as these materials being the second and third generation nanomaterials, have found invaluable applications as (re)active nanomaterials and multifunctional nanosystems, respectively [14-15]. (Re)active nanomaterials respond specifically to various physical, chemical and/or biological stimuli (light, temperature, redox, pH, electromagnetic fields and gaseous signals, antigens, antibodies, *etc.*) due to which they are forming a part of high-end performance devices [16-17]. On the other side, multifunctional nanosystems are highly complex and hybrid systems consisting of stimuli-responsive nanoparticles and nanostructures, organised in several unique ways to generate unexpected qualities/interactions/synergism amongst its various components [18]. In other words, multifunctional nanosystems usually take form of miniaturized machines at nano-scale (e.g. micromotors, nanobots) which could carry out specific tasks like protein synthesis, plaque removal, photosynthesis, *etc.* [19-20]. There have been numerous exciting developments in the field of NGNMs resembling graphene and can be categorized into following four types: (1) carbon-based (examples-fullerene, single & multiwall carbon nanotube); (2) inorganic (metal-based: gold (Au), silver (Ag), copper (Cu), quantum dots *etc.*, and metal oxide-based:

silica ( $\text{SiO}_2$ ), iron oxide ( $\text{Fe}_3\text{O}_4$ ), zinc oxide ( $\text{ZnO}$ ) *etc.*); (3) organic-based (e.g. liposome, dendrimers, micelle *etc.*) and; (4) composite-based comprising complex structures obtained from any combination of other three types e.g. metal-organic frameworks [12, 21-22]. Herein, we restrict our discussion on only selected selenium-based next-generation nanomaterials/nano-assemblies in this chapter to highlight their structural, production, technical and economic aspects in various sectors.

## II. SELENIUM BASED NANOMATERIALS (SeNMs)-STRUCTURAL ASPECTS

Selenium (Se) is a chemical element with atomic number 34. It is regarded as a metalloid because its properties are intermediate to those of sulfur (non-metal) and tellurium (metal) which are present in the same group of the periodic table [23]. It occurs mainly in metal sulfide ores, where sulfur is replaced by selenium atoms occasionally [24]. Significantly, it possesses favourable physical, chemical and biological features which make it valuable for many roles such as antimicrobial, anticancer, antioxidant, superconductor, super adsorbent *etc.* [25-27]. In biological context, it has been found that trace amounts of selenium are essential for cellular functions in many animals, including humans (part of antioxidant enzymes), but are generally toxic if concentration rises above trace levels causing selenosis [28]. Thus, selenium possesses a very narrow therapeutic window in its natural forms. However, it has been widely used commercially in glassmaking, semiconductor, electronics and pigment industries [29].



**Figure 1:** A schematic diagram of various nanostructures formed under general classification. A) 0-Dimensional; B) 1-Dimensional; C) 2-Dimensional; and D) 3-Dimensional

No doubt, excess selenium content is of concern, yet it could be utilized to our utmost advantage when quantity is regulated. However, nanoselenium in its various forms, has superior advantages over bulk selenium and importantly, can be used in relatively higher concentrations [30-31]. Nowadays, nanotechnology has widened the scope of selenium

application immensely in various sectors in the form of next-generation nanomaterials [32-37].

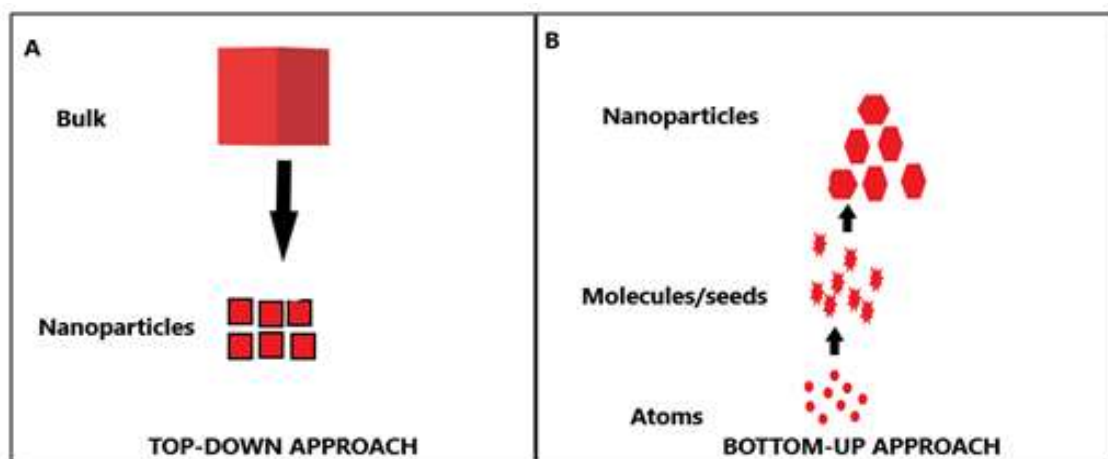
Since the discovery of graphene, several zero-dimensional (0-D), one-dimensional (1-D), two-dimensional (2-D) and three-dimensional (3-D) nanomaterials of selenium have been synthesised till date as outlined in Figure 1 below and described ahead [38-39]:

- Zero-dimensional (0-D) nanomaterial has all dimensions (x, y, z) at nanoscale ( $\leq 100$  nm). It includes nanospheres and nanoclusters (Figure 1A).
- One-dimensional (1-D) nanomaterial has two dimensions (x, y) at nanoscale and the other is more than 100 nm. This leads to formation of needle/rod shaped nanomaterials. It includes nanotubes, nanofibres, nanorods and nanowires (Fig.1B).
- Two-dimensional (2-D) nanomaterial possesses one dimension (x) at nanoscale and the other two outside the nano-range. These materials form plate-like shapes and include nanofilms, nanocoatings and nanolayers with nanometre thickness also (Fig.1C).
- Three-dimensional (3-D) nanomaterials do not have any dimension confined to the nanoscale. These materials have three arbitrary dimensions (x, y, z) above 100 nm. Generally, these form bulk nanomaterials comprising of multiple nanosize crystals arranged in different orientations e.g. dispersions of nanoparticles, multi-nanolayers (polycrystals), bundles of nanowires and nanotubes. In other words, 3-D nanomaterials are composed of 0-D, 1-D and/or 2-D structural elements in close contact with each other and form variable interfaces (Figure 1D).

### III. SYNTHESIS METHODOLOGIES

Broadly, two main approaches are used to create selenium nanomaterials depending on how the precursors (atoms, ions, molecules or bulk material) are manipulated (assembled or splitted) *viz.*, Top-down approach and bottom-up approach (Fig.2) [12, 41-43]. In top-down approach, solid bulk material (metal cube/plate *etc.*) is used to produce nano-sized structures using physical procedures (size-reduction or destructive methods). Examples of methods of top-down approach are sputtering, mechanical alloying, laser ablation, ball milling, nanolithography *etc.* Fig.3. One beneficial aspect of top-down approach is that huge quantities of nanomaterial can be obtained. However, it is difficult to control shape and size of nanostructures using this approach and requires enormous amount of energy to create high-pressure and high temperature conditions for synthesis. Thus, this approach is generally employed to synthesise nanostructured materials for bulk use [12, 41-43].

Alternatively, bottom-up approach entails self-assembly of the precursor elements (atoms, the molecules or the clusters) in the formation of varied nanostructures using mostly chemical or biological methods (constructive modes) (Fig.2 and 3). Generally, this approach utilizes wet-chemistry mechanisms such as reduction, sonochemical, sol-gel, co-precipitation reactions *etc.* This approach is advantageous for preparing far better controlled nanomaterials in terms of their homogeneous size, shape and physico-chemical properties. Moreover, it is comparatively less expensive. However, major limitation of this approach is the purification of the final products from the mother liquor which may contain toxic chemicals or organic solvents and reagents except green synthesis methods. Particularly, purified nanomaterials are essential for use in biomedical applications [12, 41-43].



**Figure 2:** Two general approaches employed for the production of selenium nanomaterials:  
A) Top-down B) Bottom-Up

Some of the methods are described briefly ahead [12, 41-43]:

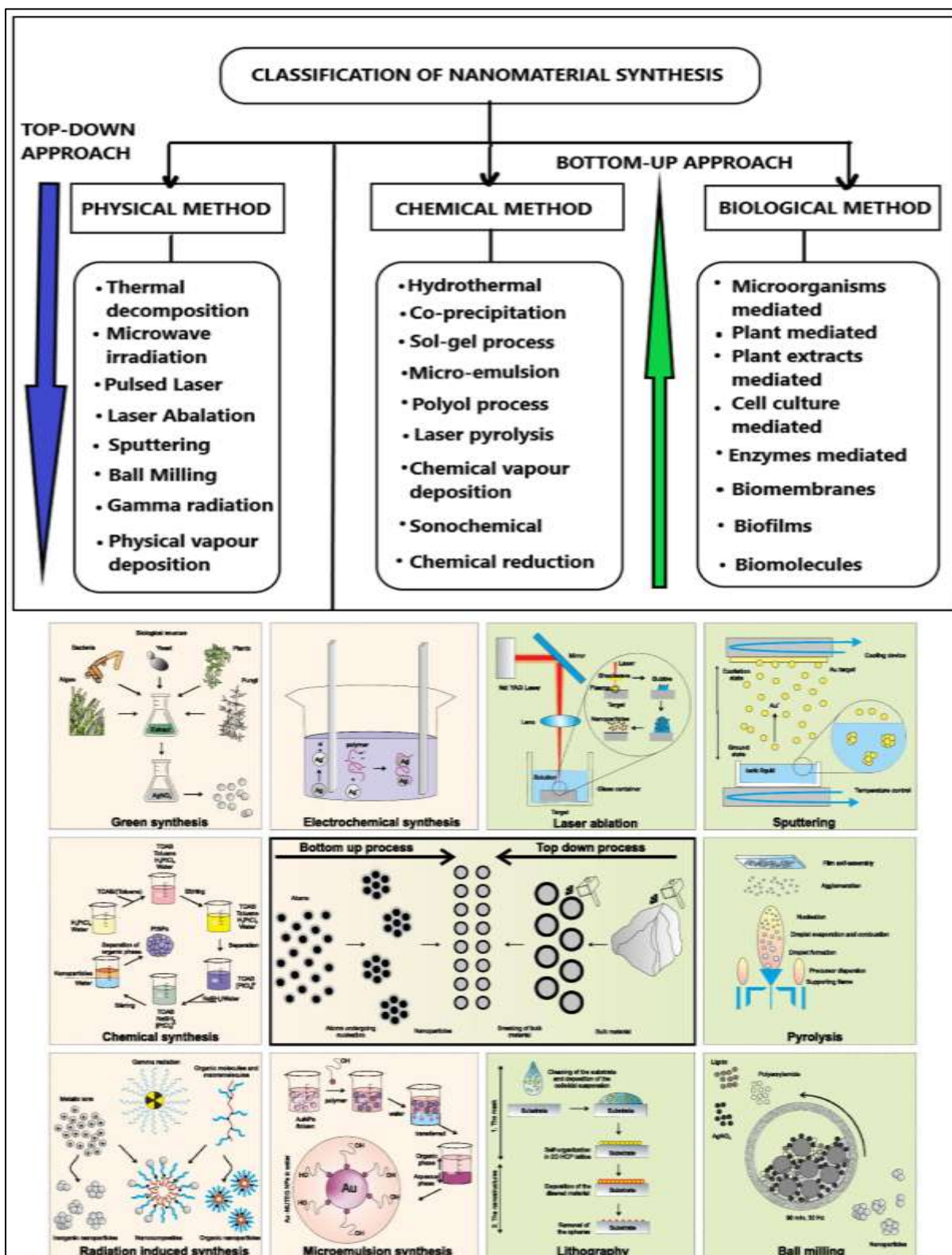
### 1. Top-Down Approach

- **Laser Ablation:** In this method, a laser beam is made to fall on a metal target (usually a metal plate/ solid block) to form low-flux plasma plume which is then converted finally into nanoparticles by evaporation or sublimation. Thus, by employing this method, high yields of metal nanoparticles are produced which may find applications in biomedical field as purification is relatively simple and devoid of any harsh chemical reagents.
- **Sputtering:** Sputtering is basically physical vapour deposition in which the nanoparticles are formed as a thin layer deposition over the substrate following collision of metal ions. It is further followed by annealing process. This method is highly efficient in forming differently sized and shaped 2-D nanomaterials, which are controlled by factors such as substrate type, layer thickness, annealing conditions etc.
- **Pyrolysis:** It is an endothermic decomposition process whereby chemical bonds of the target compound are broken down using thermal energy. This leads to formation of nanoparticles lying in the resulting ash. Pure nanoparticles can be recovered thereafter when the solid ash is processed further. This method is used generally for the production of noble metal nanoparticles. However, excessive energy is required to carry out the process.
- **Ball Milling:** In this method, bulk material is broken down into micro-/nano structures using direct forces of abrasion, vibration etc. One specific example is mechanical milling in which kinetic energy of roller balls is transferred to the bulk powder to produce very small sized grains or nanoparticles powder. Other types of mills are vibratory, tumbler, shaker, attrition and planetary. Shape and size of nanoparticles can be controlled by adjusting the working parameters of mills like media, atmosphere, time, intensity and temperature employed.

- **Lithography:** This procedure involves either of these processes viz., depositing, etching, writing, printing, micropatterning *etc.* of nanostructures on other substrates using optical rays, electron beams, ion beams or x-rays much like a printing process. This methodology is most suitable for generation of microarrays, biosensors *etc.*

## 2. Bottom-Up Approach

- **Electrochemical Synthesis:** In this method, a pure metal sheet forms the anode and from it, metal ions are dissolved in the electrolyte. Then the metal ions are reduced in the form of nanoparticles on the cathode as a part of electrochemical cell apparatus. Thus, this methodology is capable of synthesising metallic nanoparticles and nanocomposites. The efficiency of this technique relies on various factors such as the purity and concentration of the metal, nature of the reducing agent and the stabilizer employed, choice of the electrolyte, pH and temperature.
- **Green Synthesis:** These methods are better alternatives to chemical ones as biomedical applications of nanomaterials are based on their non-toxicity. Thus, eco-sensitive methods are utilized for synthesis of nanoparticles under a common “Green synthesis” umbrella term. These techniques involve application of plants and plants extracts; microbes like bacteria, fungi, actinomycetes, yeast, algae; purified enzymes and biopolymers like starch, cellulose, pectin, agarose *etc.* in the production of nanoparticles which are eco-friendly. This methodology results in safer and economically relevant nanomaterials devoid of harsh chemicals.
- **Chemical Reduction:** As the name implies, this method involves the reduction of metal ions (e.g.  $\text{Ag}^+$ ,  $\text{Se}^{4+}$ ,  $\text{Au}^{3+}$ ) from their ionic salts using various chemical reducing agents (citric acid, ascorbic acid, sodium borohydride *etc.*) in the presence of a stabilizing agent (e.g. polyvinyl pyrrolidone) under favourable reaction conditions (pH, temperature, concentration *etc.*) to form stable nanoparticles (Silver nanoparticles (AgNPs), selenium nanoparticles (SeNPs), Gold nanoparticles (AuNPs) *etc.*). This technique is popular as it is simple, cheaper and reliable to produce almost all kinds of metallic nanoparticles easily.
- **Irradiation Mediated:** In this method, ionizing radiations like X-rays, ultra-violet light, gamma radiation are used for the production of metal nanoparticles. As these radiations fall on aqueous solution of metal salts, reducing and stabilizing agents, there is formation of nanoparticles due to radiation-mediated radiolysis of water molecules and consequent production of transient reactive intermediates acting as strong reducing or oxidizing agents. Thus, this method is highly efficient to produce fully reduced and highly pure nanoparticles.
- **Microemulsion:** This is a very effective method for the production of conjugated nanoparticles and nanocomposites. In this method, two immiscible solvents (e.g. metal salt aqueous solution/organic solvent) in the presence of a surfactant are simply mixed using either low-energy (magnetically stirred) or high-energy input (ultrasonicator probe). By adjusting the concentration of precursor solutions and surfactants, speed of stirring, pH, temperature *etc.*, size and shape of the nanostructures can be better controlled. The nanoparticles formed are characterized by ultra-low interfacial tension, large interfacial area and high thermodynamic stability.



**Figure 3:** Schematic representation of various nanomaterial synthesis methods: top panel shows a general classification; bottom panel shows different methods of nanomaterial synthesis pictorially under broad approaches: top-down (images with the green background) and bottom-up (images with pale yellow background) {lower panel image was adapted from [41]}.

Conclusively, it can be observed that each of the different methodologies suffer from one or two drawbacks. The choice of synthesis method is dependent on several factors such as intended application, quantity requirement, cost, material requirements, availability of resources and above all, environmental impact [44-45]. Moreover, scalability of the production processes to large-scale synthesis of nanomaterials is still challenging [46]. Hence, more research and effective techniques are needed to generate nanomaterials at large-scale with desired properties.

#### IV. FIELDS OF APPLICATION

Nanomaterials find applications in various sectors *viz.*, electronics, energy storage, materials science, medicine, diagnosis *etc.* Selenium based next-generation nanomaterials have also been developed to work in these sectors and a few such representative examples have been summarized in Table-1 for quick reference [47-76].

- 1. Applications in Electronics and Energy Sectors:** Selenium based nanomaterials (Se-doped nanostructured Te/PEDOT:PSS composite, Silver ion irradiated Se nanowires, Selenium-enriched CoSe nanotubes *etc.*) are used to fabricate tiny transistors, supercapacitors and other electronic components at the nanoscale for faster, lighter and more efficient electronic devices like smart watches, data storage devices, optoelectronic devices (for medical imaging and communication applications), thermoelectric appliances *etc.* In addition, efficient energy-storage devices are also manufactured using selenium nanomaterials, for example, NiSe<sub>2</sub>@NGCF fibres were developed for sodium-ion batteries. Similarly, photo-voltaic technologies and photo-detectors have also been constructed using selenium nanomaterials.
- 2. Applications in Material Chemistry:** Novel and improved commercially relevant materials with enhanced physico-chemical properties have been created using selenium based nanomaterials. For examples, metal-organic framework-derived selenium-doped cobalt Sulfide@Graphene nanofoam and selenium-doped metal organic framework MOF CoS<sub>2</sub> hollow spheres; cobalt pyrite (CoS<sub>2</sub>, CoSe<sub>2</sub>) can be applied as efficient electrocatalysts. Generally, these are formed as complex nanocomposites and can have varied applications in chemical sciences as nano-coatings, chemical sensors, electrodes, photocatalysis *etc.* Such nanomaterials are stronger, corrosion-resistant and more durable than traditional materials.
- 3. Applications in Diagnostic and Biomedical Sectors:** Nanoselenium and its various composites have found immense applications in diagnostic and biomedical sectors. For examples, selenium and nitrogen co-doped carbon dots (SeN-CDs) have been tested as electrochemiluminescence (ECL) based biosensor to detect microRNA-221 (miRNA-221) sensitively in biological samples. Also, nanocomposite selenium-gold-chitosan (Se-Au-CS), selenium nanowires modified with nano-silver, selenium-doped calcium phosphate (Se-CaP) biomineral *etc.* have been evaluated therapeutically against many multi-drug resistant infections and cancer models. Not only this, selenium based nanomaterials have also been tested for developing: antimicrobial coatings for active food packaging; medical implants and matrix for wound repair; adjuvants; multi-intensified photodynamic- and immuno-therapy modules; and radioprotective agents. Thus, selenium nanoparticles can be used to deliver drugs directly to cancer cells, thereby reducing the various side effects associated with traditional chemotherapy. They can also be used to



create contrast agents for imaging techniques such as MRI and CT scans, allowing for earlier and more accurate diagnosis of diseases besides production of nano-sensors.

In the nutshell, an analysis of the Table-1, shows that selenium based nanomaterials are finding significant space in the nanotechnology based applications in almost every sector in recent times. This potential is expectedly going to expand further in coming years.

## V. FUTURE PROSPECTS AND CHALLENGES

Nanotechnology is indeed an expanding research area today which involves synthesis, designing and improvisation of structures, devices and systems with novel properties and functions at nano-scale (1–100 nm). Thus, nanotechnology has the potential to solve many of the upcoming crises in human life and his environment like climate change, pollution, energy deficit, multidrug resistant diseases *etc.* by providing efficient technologies in nano-domain *i.e.*, biosensors, chelators, drug delivery systems, catalysts, nanobots, energy storage devices *etc.* Selenium based nanomaterials have the potential to complement the already popular carbon based nanotechnologies by contributing more energy efficient, lighter and faster nanostructures for integration. The most important challenge facing the nanotechnology sector is the probable environmental impact of the nanomaterials contained in them and waste generated therein. Hence, it is important that suitable *in vitro* and *in vivo* toxicity assessments are carried out before these technologies can be rolled out for practical applications.

**Table 1: Table presents the summarized account of various selenium based nanomaterials (representative) reported in recent times to highlight their wide applications in different sectors**

S. No.	Name of nanocomposite	Structure/configuration	Synthesis Methodology	Application	References
<b>A. APPLICATIONS IN ELECTRONIC AND ENERGY SECTORS</b>					
1	NiSe <sub>2</sub> @NGCF	1-D pea-shaped: NiSe <sub>2</sub> nanoparticles encapsulated in N-doped graphitic carbon fibres	Chemical process: by inducing the growth of tubular graphitic carbon fibers on the surface of Ni(0) catalyst formed <i>in-situ</i> : adsorption of Ni <sup>2+</sup> ions onto ZIF-8 templates in an aqueous solution, followed by carbonization and selenization processes	Sodium-ion batteries, energy storage systems (ESSs)	[47]
2	Se-doped nanostructured Te/PEDOT:PSS composite	1-D Largely nanowire shape	Solution synthesis method: Two methods employed: first simultaneous addition method; second sequential addition method; each followed by stirring at 90 °C, then cooling to room temperature and centrifugation	Thermoelectric device	[48]
3	Silicon layers hyperdoped with selenium	2-D: layered structures	Se implantation followed by pulsed laser annealing	Enhanced IR absorption /thermoelectric	[49]
4	Amorphous thin films (ATFs) of pure selenium; and nano-additives	2-D: Thin films	Melt-quench procedure followed by physical vaporization deposition (thermal evaporation) in a high vacuum	Optoelectronics	[50]

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	[Graphene, Multiwalled Carbon Nanotubes (MWCNTs), and Silver nanoparticles (AgNPs)] doped Se thin films				
5	Silver ion irradiated Se nanowires	1-D nanostructure: Selenium nanowires	Template-assisted electrodeposition: irradiation of synthesized Se nanowires with 120 MeV Ag <sup>9+</sup> (RADIATION)	Optoelectronics	[51]
6	$\gamma$ - In <sub>2</sub> Se <sub>3</sub>	2-D layered nanostructures: Single-phase quasi-spherical $\gamma$ -In <sub>2</sub> Se <sub>3</sub> nanostructures	Simple one-pot method	Photovoltaic technology and/or photo-response application	[52]
7	Hybrid Selenium-PEDOT:PSS junction	2-D composite films: uneven protruded surface, which is attributed to the presence of selenium particles inside the PEDOT:PSS layer	Facile sonication assisted mechanical mixing and drop-casting technique	High performance flexible photodetectors/ opto-electronic	[53]
8	SnSe <sub>2</sub> hierarchical nanostructures	3-D flower-like	Solution based method and the nanostructure is sintered into pellets by spark plasma sintering (SPS) (MICROPATTERNING)	Thermoelectric	[54]
9	ZnS <sub>x</sub> Se <sub>1-x</sub> solid solution in a dielectric template of porous anodic aluminum oxide (AAO),	Quasi-zero-dimensional nanostructures	Simple method of vacuum thermal evaporation	Dielectric confinement of the excitons	[55]

10	Selenium-enriched CoSe nanotube	1-D: nanotubes with porous nature	One-pot facile synthesis: a chemical bath deposition (CBD) procedure	Supercapacitor application	[56]
<b>B. APPLICATIONS IN MATERIAL CHEMISTRY</b>					
11	Selenium-doped metal organic framework MOF CoS <sub>2</sub> hollow spheres; cobalt pyrite (CoS <sub>2</sub> , CoSe <sub>2</sub> )	3-D: Hollow structure in which hollow primary spheres form a 500–600 nm framework. As synthesized ZIF-67 hollow spheres were sulfurated/ selenylated to produce Se-doped MOF CoS <sub>2</sub> hollow spheres	Normal melt diffusion method: two-step procedure that involves a solution technique and a sulfuration-selenization reaction	High-performance electrocatalysts	[57]
12	Glassy Se using AgNPs nanocomposites	1-D: nanowires	Melt-quench route	Nanomaterials	[58]
13	Selenium (0) nano rods	1-D rods	Wet chemical route	Selective hydrogen peroxide spectrometric sensor	[59]
14	rGO-Se nanocomposite	2-D: hexagonal structure of particles; sheets of rGO are nearly transparent and the dark-color indicating that the Se NPs with a well crystalline are entirely encapsulated by the rGO sheets and grown together with hexagonal morphology	Simple hydrothermal approach	Acetone gas sensors	[60]

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15	Copper selenide (Cu <sub>2</sub> Se) nanostructures	2-D: film	Hydrothermal method	Activate the peroxymonosulfate (PMS) and electrocatalytic hydrogen evolution (HER)	[61]
16	Iron diselenide (FeSe <sub>2</sub> ) nanomaterial	0-D, 1-D and 2-D microgranular particles to nano-stick to nanoflakes	Wet chemical strategy	Stable catalysts for the detoxification of aqueous organic dye pollutants /detoxification	[62]
17	Metal-organic framework-derived selenium-doped cobalt Sulfide@Graphene nanofoam	2-D: nanofoam	<i>in-situ</i> recrystallization	Oxygen electrocatalysis	[63]
18	Transition metal dichalcogenides	2-D layered materials: sandwich structure (X-M-X), where two chalcogene atomic layers sandwiched hexagonally packed transition metal atomic layer	Physical process: hydrothermal/solvother-mal method, CVD method and molecular beam epitaxy (MBE)	Catalysis, adsorbent in sample preparation techniques, electronic applications, hydrogen production processes and energy storage	[64]
19	SnSe and SnSe <sub>1-x</sub> S <sub>x</sub> nanostructures with different concentrations of sulfur	2-D: layer / agglomerate	co-precipitation method	Photovoltaic and photocatalytic	[65]
20	<i>p</i> -type trigonal selenium nanowires (SeNWs), Se NW/AA and Se NW/Au	1-D nanowires	Chemical reduction method and electron and proton co-doping	Piezo-phototronic effect; <i>p</i> -type piezoelectric materials/ Semiconductor, photocatalysis	[66]

<b>C. APPLICATIONS IN DIAGNOSTIC AND BIOMEDICAL SECTORS</b>					
21	Selenium and nitrogen co-doped carbon dots (SeN-CDs)	0-D/2-D and 3-D: DOTS or spherical particles, monolayer structure	Hydrothermal method: heteroatom doping	Electrochemiluminescence (ECL), BIOSENSOR to detect microRNA-221 (miRNA-221) sensitively	[67]
22	Nanocomposite selenium-gold-chitosan (Se-Au-CS)	0-D and 2-D: Polyhedral shapes, rectangular and square shape, although structurally the XRD analysis revealed hexagonal crystal structures	Sonochemical method: reducing agent: ascorbic acid and ultrasound wave with the power of Q500 sonicator	Medical, anti-angiogenesis effects, Anti-oxidant effects	[68]
23	Ag doped Au-CdS <sub>1-y</sub> Se <sub>y</sub> plasmonic metal-semiconductor	3-D: yolk-shell nanostructures	Hydrothermal reaction: Sulfur or selenium precursor (SP/ SeP) were obtained;  Ultrasound and autoclaving to temp 160 °C followed by cooling: seed growth strategy to get Au NRs;  cation exchange reaction for final phases	Multi-intensified photodynamic- and immuno-therapy against drug resistant bacteria	[69]
24	Nano-elemental selenium particle (chondroitin sulfate A-selenium nanoparticle, CSA-SeNP)	3-D: spherical	<i>in-situ</i> reduction and supramolecular self-assembly of Na <sub>2</sub> SeO <sub>3</sub>	Cartilage repair	[70]
25	TiO <sub>2</sub> /ZnO/Ag hybrid nanostructures	2-D: hybrid nano engineered coat/layer	nano engineered synthesis by layer by layer technique	Antimicrobial coating	[71]

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26	Selenium nanowires modified with nano-silver (AgNPs: AgNPs modified ruthenium-selenium nanowires)	1-D nanowires	Hydrothermal synthesis	Clinical application as multiple antibiotic adjuvants deal with resistant bacterial infections	[72]
27	Selenium-doped calcium phosphate (Se-CaP) biomineral	3-D: microspheres	Microwave assisted hydrothermal reaction	Functional drug delivery system; therapy against multidrug resistant (MDR) bone tumors	[73]
28	Selenium nanoparticles	0-D OR 2-D polygonal-like nanostructure	Green method combined with Rapid solvothermal process using <i>Moringa oleifera</i> leaf extract as a reducing agent	Antibacterial activity, for active food packaging applications	[74]
29	Selenium nanostructures: sodium selenite and green tea extract (Se-GT) and Na <sub>2</sub> SeO <sub>3</sub> plus bovine serum albumin (Se-BSA)	0-D and 1-D : hexagonal crystal system and nanotubes	Green route: sodium selenite and green tea extract combined with mild heating (70 °C with stationary incubation)	Radioprotection, radiosensitizing action and antioxidant property	[75]
30	Ciprofloxacin loaded selenium-lipid nanoparticle (CxLSENP)	3-D: spherical shape	Hot-melt dispersion/ microemulsion procedure	Treatment of chronic lung infection; antimicrobial property	[76]

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