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## A REVIEW ON THE ROLE OF NANOTECHNOLOGY IN ENHANCING ENVIRONMENTAL SUSTAINABILITY

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**Abstract:** Nanotechnology is one of the most essential technology applicable in all areas of science. Several physical and chemical methods were used for synthesizing and stabilizing nanomaterials. Many researchers and scientists have confirmed that these methods are not eco-friendly and are harmful to the environment and human health. Thus, many of them have moved to a modern nanoscience called “green nanotechnology”. The aim of green nanotechnology is to produce nanomaterials which will not cause damage to the environment. Also, the synthesized nanomaterials can be effectively used to tackle major environmental issues like energy crisis and pollution.

In this review, we have discussed the different biological sources for synthesis of nanomaterials. We have also discussed in detail the efficiencies of various nanomaterials in improving the quality of the environment. Largely, this review focuses on the fact that nanotechnology has a big role to play in enhancing environmental sustainability.

**Keywords:** Green Nanotechnology, Biomolecule, Quantum dots, Remediation, nZVI, Sensors

### 1. Introduction

Nanotechnology deals with the synthesis, development and application of nanoparticles [1]. They have complex structures composed of three layers: surface, shell and core layer. Surface layer can be functionalized using molecules like metal ions, surfactants and polymers.

Shell layer is a chemically different one from the core in all aspects. Finally, the core layer is the central portion of nanoparticle usually referred as nanoparticle itself [2, 3]. They can exist as aerosols, suspensions and emulsions; their properties are dependent on their size [4]. Their surface to volume ratio increases as their size decreases [5], hence they show variation

in characteristic color and properties with variation in shape and size [6]. Nanoparticles are dissimilar to their bulk and molecular counterpart as they possess enhanced structural, magnetic, electrical and optical properties and hence improved efficacy. Apart from these, they also exhibit unique properties such as particle aggregation, photoemission, catalytic activity, electrical and heat conductivity [1]. For the above reasons, nanoparticles can be used to replace their corresponding bulk materials. Replacing existing materials with nanomaterials will, not only reduce the cost, but also leave a reduced environmental burden.

Energy crisis, Pollution, Climate change and Health care are the major threats faced by the society. Many technologies have been developed to monitor and manage these issues. Nanotechnology is one among them, but with wider range of opportunities.

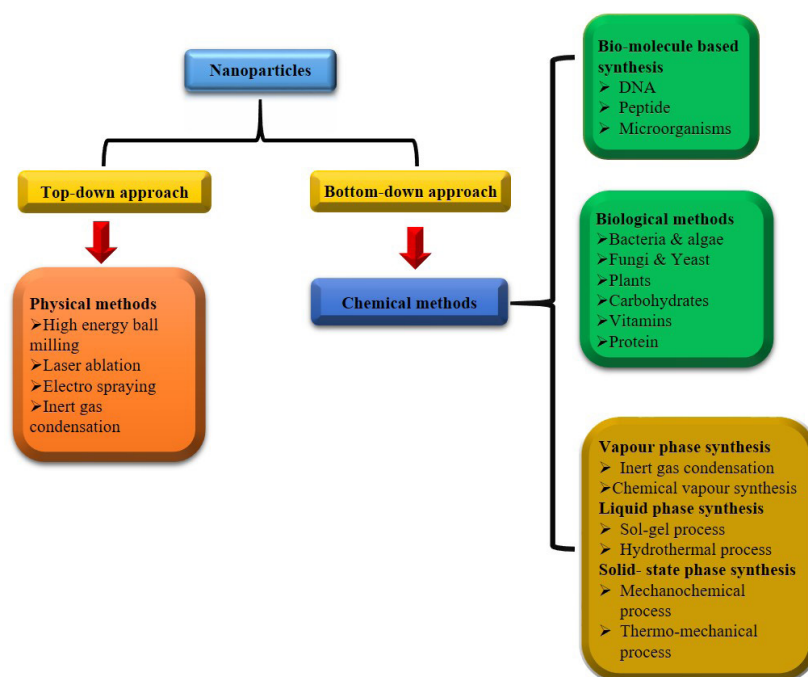
It is predicted that nanotechnology will play an important role in providing environment-friendly, cost effective and efficient methodologies for

solving energy crisis. Researchers are working on developing nanotechnology based solar panel/fuel-cell combination, methods for H<sub>2</sub> storage, CO<sub>2</sub> capture and energy conversion [7, 8].

Nanotechnology is also being used to improve air, water and soil quality, treat contaminants and also to mitigate pollution [9, 10]. Highly sensitive biosensors have been developed with the help of nanoscience to monitor pollution [11]. Nanomedicine involves the usage of biocompatible nanomaterials for the diagnosis, monitoring, control and treatment of various diseases. Several nanomaterials have been reported to possess antimicrobial and anticancer properties. Therefore, nanotechnology has a great role to play in enhancing environmental sustainability.

## 2. Synthesis of nanomaterials

The first step in nanotechnology is the synthesis of nanomaterials. There are two basic approaches to synthesize nanomaterials namely,



**Figure I: Classification of different methods in the synthesis of Nanoparticles**

top-down approach and bottom-up approach (Figure I) [12].

### 2.1. Top-down approach

In this approach, various physical methods are employed to prepare nanomaterials. Physical methods involve breaking down of bulk molecules into nanoparticles. It is widely employed to produce large quantities of nanomaterials [13]. Here various physical processes like crushing, milling and grinding are applied in accordance to the physical properties of the molecules. A few examples of physical methods along with their merits and demerits are illustrated in Table I.

### 2.2. Bottom-up approach

This approach employs chemical methods to prepare nanomaterials. In this approach inorganic and organic nanostructures are constructed atom by atom or molecule by molecule [14]. All these methods employ chemical synthesis, which can be divided into three phases. They are: vapour, liquid and solid state, and solid.

In vapour phase, conditions are created to enable vapor phase mixture or aerosol (supersaturated vapour) to form nanoparticle. Based on the methods used to achieve supersaturated vapor, there are several types of vapor phase synthesis such as inert gas condensation, chemical vapour synthesis etc.[15].

Liquid phase synthesis involves the usage of metal, inorganic or organic precursors and converting them into desired materials either in water or organic solvents. Sol-gel and hydrothermal processes are some examples for liquid phase synthesis [16, 17].

Solid-state chemical process involves the heating of non-volatile solids to produce

the desired nanomaterial. It consists of four major steps: diffusion, reaction, nucleation and growth [18-20]. Thermo-mechanical and mechanochemical methods are commonly used in solid-state chemical phase synthesis. The merits and demerits of these approaches are discussed in Table I.

### 2.3. Green Nanotechnology

Nanoparticles have the capacity to play a major role in environmental sustainability, but the process of synthesis of nanoparticles in large scale using chemical or physical methods were found to be harmful to the environment (table I). Therefore, nanotechnology which is supposed to sustain the environment will end up spoiling it. Due to this issue, scientists have come up with a new concept called Green Nanotechnology. The framework of green nanotechnology falls within green chemistry [30]. The 12 principles of green chemistry formulated by Paul Anastas and John Warner of EPA (Environmental Protection Agency) are “prevention of waste, atom economy, less hazardous chemical synthesis, safer chemical designing, use of safer solvents and auxiliaries design for energy efficiency, use of renewable feedbacks, reduction of derivatives, use of catalysis, design for degradation, real-time analysis for pollution prevention, and inherently safer chemistry for accident prevention [31]” These nanomaterials are used to enhance the quality of the environment through various applications.

#### 2.3.1. Biological synthesis

Biological synthesis has been successful in synthesizing metal nanoparticles. It involves the usage of a precursor material, reducing agent and capping agent. Organic compounds from plants and microorganisms are used as reducing and capping agents instead of harmful and toxic chemicals. The aqueous biological

**Table I. Details on types of synthesis, advantages and disadvantages of physical and chemical methods**

Type of physical and chemical methods	Types of synthesis	Advantages	Disadvantages
High energy ball milling*	-	Affordable. Can be combined with chemical treatments, to obtain desired product with minimal effort[21].	Noise pollution, Requires high amount of energy[21].
Laser ablation*	-	Nanoparticles in stable form without the usage of any capping or stabilizing agent can be synthesised[22].	High amount of energy is required. Low productivity[22].
Electro spraying*	-	Most efficient way to produce solid-lipid nanoparticles for drug delivery[23, 24].	Material loss to the surrounding resulting in lower yields. High amount of energy required [23, 24].
Inert gas condensation*	-	The size of the particles synthesized can be controlled effectively[17].	Time consuming hence not suited for industrial level production[17].
Chemical vapor synthesis <sup>#</sup>	Vapor phase synthesis	Multi-component nanoparticles can be formed by using multiple precursors[15,17,25,26].	Hazardous byproducts are formed. Some of the reactions entails high temperature [15,17,25,26].
Sol-gel process <sup>#</sup>	Liquid phase synthesis	Reactions can be carried out at low temperature[16, 17].	Organic solvents used are harmful[16, 17].
Hydrothermal process <sup>#</sup>	Liquid phase synthesis	Materials which cannot be synthesized using solid phase synthesis can be synthesized using this method[16, 17].	Involves high temperature and pressure. Fatal accidents may occur if not handled properly[16, 17].
Mechanochemical <sup>#</sup>	Solid state chemical synthesis	Materials with mean particle size as small as 4nm, showing low agglomeration and uniformity of crystal structure and morphology can be synthesized[18,19, 27-29].	High energy is consumed [18,19, 27-29].
Thermo-mechanical <sup>#</sup>	Solid state chemical synthesis	The reactions can be easily controlled[18,19, 27-29].	Requires high temperature[18,19, 27-29].

\* Nanoparticles synthesized by physical methods; # Nanoparticles synthesized by chemical methods.

extract consists of a mixture of compounds such as phytochemicals, vitamins, carbohydrates, protein, polymers and natural surfactants. These compounds reduce the metal ions (precursor) into metal nuclei which serve as a template for nanocrystal growth. This process is known as nucleation or Oswald ripening. The capping agent terminates the growth by stabilizing the nanoparticle. Finally, the surfactant enhances dispersity of the synthesized nanoparticles [31-35]. Since all these organic compounds are soluble in water and other solvents, the nanoparticles can be easily washed and recovered after the reaction. In case of bacteria mediated biosynthesis, the mechanism is slightly different. The metal ions are captured onto the surface of the cell or inside the cell depending on the species of bacteria. The enzymes, such as, NADPH and NADH-dependent nitrate reductase in the cell, act as reducing agent [33,

36].

Some researchers have isolated organic compounds having reducing and capping properties and used them for the synthesis of nanomaterials. A few of them are discussed in table II. The most preferred biomaterial for synthesis is plant extract as it is cheap and easy to handle. Due to this reason majority of the green synthesis research is carried out using plants. Though green synthesis is advantageous in many ways, it is still in its budding stage and suffers from several drawbacks. The major drawback is low yield and so scaling up is quite challenging. However, because of its huge potential tons of efforts have been taken by scientists all around the world to overcome the challenges and in the upcoming years it would definitely hit the world's markets.

**Table II. Different plant, bacterial, fungal and algae-based biomaterials used for the synthesis of nanomaterials**

Name of the plants/bacteria/fungi/Algae	Biomaterials	Nanoparticle	Reference
<i>Citrus maxima</i>	Fruit extract	Au	[37]
<i>Carica papaya</i>	Leaf extract	TiO <sub>2</sub>	[38]
<i>Tamarindus indicus</i>	Fruit extract	Ag	[39]
<i>Lawsonia inermis</i>	Leaf extract	Cu	[40]
<i>Cynara scolymus</i>	Leaf extract	ZnO	[41]
<i>Stenotrophomonas maltophilia</i>	Keratinase	Ag	[42]
<i>Microbacterium marinilacus</i> and <i>Stenotrophomonas maltophilia</i>	Whole cell	Cu, Ag, Fe	[43]
<i>Porphyra zeoensis</i>	R-phycoerythrin	Ag	[44]
<i>Egrecia sp.</i>	Whole thallus	Au	[45]
<i>Beauveria bassiana</i>	Whole mycelium	Ag	[46]

## 2.4. Biomolecule based nanostructure

In biomolecule-based nanostructures, biomolecules are used as precursors during synthesis. These materials can be synthesized using environment friendly methods and hence they come under green nanotechnology. These nanostructures can be used to solve biocompatibility issues when nanomaterials are applied in medicine and can also be used as a substitute for nanoparticles in many other applications which are discussed in the forthcoming subheadings.

### 2.4.1. DNA Based nanomaterials

The bottom up construction of nanomaterials, using DNA or nucleic acid, is also known as DNA origami. Nandrain C. Seeman, in 2004, introduced the idea of using DNA for the construction of nanoscale structures [47]. This technique was introduced by Paul Rothemund in 2006, where two and three-dimensional shapes can be assembled using his principle. DNA nanostructure can be designed manually and also by using bioinformatic tools [48]. Several softwares have been developed to aide this process of folding the DNA. GIDEON and Nanoengineer I can be used to construct a 3D nanostructure. The most popular is caDNAno, which is semi-automatic and can be used to construct multi-layered 3D DNA origami. The latest is DAEDALUS, which is fully automatic [49]. DNA based nanomaterials can be constructed using a long single strand DNA (ssDNA) and short oligonucleotides. The structure is cross linked and it can be stabilized by short oligonucleotides or complimentary strands which are also known as the staple strands. Rothemund chose circular genomic DNA from the virus M13mp18 as the scaffold. He took 100-fold excess of 200-250 staple and mixed it with the scaffold and annealed from 95 °C to 20 °C in less than 2 hrs. When the sample was deposited on mica, only the folded DNA

structures stuck to the surface while the excess sample remained in the solution. These folded structures were viewed with the help of AFM (Atomic Force Microscopy) imaging [48]. Few applications of DNA based nanostructures are discussed in Table III.

### 2.4.2. Peptide based nanomaterials

Like DNA molecules, peptide can also be used as building blocks for constructing functional nanostructures. Nanostructure of required physical and chemical properties can be prepared by controlling the amino acid sequences [50]. Most amino acids are chiral in nature and exist in L-form. They have the same basic structure but possess a different R-group at the central carbon position. The peptides acquire different configurations depending on the R-groups present in each amino acid. One peptide chain can interact with another peptide chain non-covalently. Hence, these building blocks can be used to create supramolecular structures [51]. Ghadiri and co-workers developed a tubular nanostructure using peptides. The structure was formed in a proton triggered, self-assembly process. Numerous ring-shaped peptide subunits interact through an extensive network of hydrogen bonds to form the tubular nanostructure. Each ring consists of an eight-residue cyclic peptide with the following sequence: *cyclo* [ -(D-Ala-Glu-D-Ala-Gln)<sub>2</sub> ]. The ionization state of glutamic acid triggers the initiation of self-assembly in alkaline aqueous solution. Self-assembly of these subunits into tubular structure can be achieved by controlled acidification of the alkaline solution [52]. Few applications of peptide-based nanostructures are discussed in Table III.

### 2.4.3. Microorganism based nanomaterials

Biological systems have sophisticated nanoscopic and microscopic features which cannot be attained chemically. These

features can be exploited to create different nanostructures for various purposes. Zhou et al. [53] developed a bacterium-based controlled assembly of metal chalcogenide hollow nanostructures with enhanced light-harvesting and photocatalytic properties. They selected two bacterium species *Cocci* and *Bacillus*, along with two metal chalcogenide PbS and ZnS. The metal chalcogenide was synthesized and functionalized by sonochemical method. The functionalized metal was then coated on the cell surface and subjected to ultrasound, which lead to cell disruption and self-assembly of the nanoparticles. The developed nanostructures

were found to possess superior light-harvesting and photocatalytic properties than their solid counterparts.

Viral based nanomaterials are of two types: Viral Nanoparticles (VNP) and Virus-Like Nanoparticles (VLP). VLP are genome free counterparts of VNP. VNP can be produced in their natural host, generally plants. VLP can be produced from VNP by pH induced swelling followed by alkaline hydrolysis of the released nucleic acids. The produced VLP and VNP structure and physiochemical properties can be modified to suit the purpose it has to serve [54-

**Table III. Application of DNA, peptide and microorganism-based nanomaterials**

Types of Nanomaterials	Application	
DNA based	Drug delivery vehicle	Many cancer drugs, after intake, are often distributed nonspecifically, which lead to other complications. This can be prevented by using a drug delivery vehicle. DNA origami's ability to enhanced tumor passive targeting and long-lasting properties at the tumor region has been studied. In the study an anti-tumor drug, Doxorubicin was intercalated non-covalently into the nanostructure and tested for its efficiency <i>in-vivo</i> . The results proved its remarkable antitumor efficacy without any observable systemic toxicity[57].
	Single-molecule analysis	DNA origami structures formed can be addressed precisely. Each staple strand can serve as a point of attachment for other nanosized material. Hence, this method is suitable for the precise positioning of various compounds for the analysis of any chemical and biological processes[58]. DNA origami can be used to detect single nucleotide polymorphism by combining AFM with DNA origami, to provide a visual readout of the target nucleotides present in the probe sequence[59].
peptide-based	Biosensor	Peptide nanotubes have novel properties like molecular recognition and biomimetic mineralization which can be exploited to increase biosensor sensitivity[50]. Diphenylalanine nanotubes based biosensor for detecting hydrogen peroxide and NADH were found to possess short detection time, large current density and high stability [60].
	Template metallic nanowire	It is possible to coat metal nanoparticle on peptide nanotubes by designing the peptide molecule with specific binding motifs towards the nanoparticles[50]. Through electroless coating process, peptide nanotubes can be immobilized on Au surface and metalized by nickel[61].
Microorganism-based	Electronics	A hybrid bioelectric device was constructed with metal nanoparticles and live bacteria. The electrical property of the gold nanoparticle layer was controlled by actuating the peptidoglycan layer of the bacterium. An actuation of 8% in the peptidoglycan layer, induced by change in humidity from 20 to 0%, leads to more than a 40-fold increase in the tunneling current[62].
	Medicine	A vaccine against Human Papilloma Virus (HPV) was developed by producing a VLP from L1 protein present in HPV. It resembles HPV virions. Phase 11 clinical trial results revealed that HPV 16 L1 VLP vaccine were generally well tolerated, induced high-titers of serum antibodies to HPV 6, 11, 16 and 18[63].

56]. Apart from that, some viruses like TMV (Tobacco Mosaic Virus), CCMV (Cowpea Chlorotic Mottle Virus), CPMV (Cowpea Mosaic virus) consist of a protein superstructure in their protein shell, due to which they can be used as precursors for the synthesis of functional nanomaterials [50]. Few applications of microorganism-based nanostructures are discussed in Table III.

### 3. Energy conversion and storage

The world's population keeps growing and developed countries keep expanding, therefore, the energy requirements keep increasing day by day. An adequate energy supply with minimal environmental adversities is the need of the hour, as the emissions from the Earth have started to cause environmental damages such as climate change. A large number of scientists are working to create a material that would increase the efficiency of the current energy source or create a new energy source that might be practical at industrial scale. This quest ended in nanotechnology. Nanomaterial's large surface area per unit volume makes it suitable for this purpose and the introduction of green nanotechnology made it even more desirable. Implementation of nanotechnology into renewable resources like solar, wind and hydro energy would possibly be the best way out from our dependence on the depleting non-renewable resources [64]. The following is an example of implementation of nanotechnology in solar energy.

#### 3.1. Quantum dots

Quantum dots (QD) were first discovered in 1980 by a Russian Physicist Alexey Ekimov in glass crystals [65, 66]. QD are semiconductor particles whose diameter ranges between 2nm to 10nm. They are really tiny particles and consist of only about 100 to few 1000 atoms. However, all nanoparticles with diameter below

10nm cannot be considered as QD. They are generally fluorescent unlike most nanoparticles. Once light is absorbed by the QD, the energy excites electrons and generates holes. They find each other due to coulomb's attraction and form electron-hole pair; this is known as an exciton. This exciton dimension is less than that of exciton Bohr radius. The energy required to separate the electron-hole is unique for each material [65]. According to the quantum theory these dots have well defined energy levels and are more like individual atoms than like a crystal hence, nicknamed as artificial atoms [67]. These properties make them differ from other nanoparticles.

Smaller QD required higher energy to excite electrons hence the light emitted have short wavelength and higher frequencies. On the other hand, bigger QD require lower energy, and so the light emitted is of longer wavelength with lower frequency. Therefore, they have lesser band gap than small quantum dot. The increase in excitation energy with decrease in particle size is called Quantum confinement [67, 68]. The colour of the light emitted by the quantum dot depends on the nature of its atoms. Different atoms give different colours as energy levels have different values i.e., they are quantized. The energy levels depend on the size of the quantum dot and not on the properties of the precursor materials. Hence, quantum dot of different sizes, prepared using the same material, emit light of different wavelength or colour. Small particles emit blue light whereas large particles emit red light [67].

The energy levels can be tuned by adjusting the size of the quantum dot. Size can be adjusted by controlling synthesis time and temperature. This can bring about changes in the band gap without making any alteration to the precursor material [69]. Like other nanoparticles, QD can be synthesised using various physical and chemical methods. In recent times the green



synthesis route which can produce QD having optical properties like high quantum yield, narrow fluorescence emission, broad absorption profile, and stability against photobleaching, has been developed. There are two types of green synthesis methods namely OCS (Organometallic Colloidal Synthesis) and ACS (Aqueous Colloidal Synthesis) [65, 70]. OCS is a traditional method which involves the usage of metal or chalcogenide precursor and solvents like tri-n-octyl phosphine oxide, trioctylphosphine, hexadecylamine etc. In green nanotechnology oleic acid, castor and olive oils are used instead of hazardous solvents [65]. In AQS, the solvent used is water. QD prepared using this method are generally hydrophilic, stable and small in hydrodynamic size [65, 71].

### 3.2. QD based solar cells

Solar cells are photovoltaic system which can convert light energy into electricity. Based on the photoactive materials solar cells are named as single/poly-crystalline silicon solar cells, CdTe solar cell, Cu (In, Ga) Se<sub>2</sub>, CIGS solar cell, dye sensitized solar cells, organic solar cell, and QDSolar Cells (QDSC). Except for Si solar cell, most devices are far from commercialization due to its low Power Conversion Efficiency (PCE), lack of long-term stability, and toxicity. On the other hand, Silicon Solar Cell also suffers from such a complication in manufacturing with high production cost and long energy payback time [72, 73]. Currently QDSC are highly lacking yet remain the most desired. Enormous amounts of research are going on and one can harvest its great potential in the forthcoming years. QD possess various characteristics which makes it ideal for solar cell application, few of them are:

- QD show well defined absorption and photoluminescence. They can absorb light in visible and near infrared red regions and generate multiple excitons. By adjusting the

size of the QD the band gaps can be tuned; this phenomenon can be used to extend the absorption range of the QD to near infrared region. Harvesting NIR (Near-Infrared) photons represents a great opportunity to increase the solar cell's efficiency. The tandem or multijunction solar cell can be constructed to absorb most part of the solar spectrum. It can be constructed at room temperature and at low cost. It consists of multiple layers of QD, each of different size and hence, can absorb photons at different wavelengths. Shockley and Queisser theoretically calculated the maximum efficiency of a solar cell to be only 31%, however, the advent of multijunction solar cell may increase the efficiency to 49% [73, 74].

- QD possess characters of extended hot carrier lifetime. Hot carriers are electrons or holes that attain high kinetic energy when accelerated by high electric field. Hence, they are also known as hot electrons. The excess energy of hot carriers relative to the band gap are generally wasted as heat through phonon (discrete quantum of vibration) emission. Phonon emission can be saved by directly extracting hot carriers from QD before they thermally relax into the band gap edge and become cool. This is possible due to phonon bottleneck effect, where, no long wavelength acoustic phonon modes can exist in nanosized crystals. This prevents relaxation by direct phonon emission between closely spaced stark levels [75]
- QD can generate multiple excitons from a single photon, if the photon absorbed possess energy higher than that of the semiconductor band. On the basis of thermodynamic calculation, 2 excitons can be generated by a single absorbed photon. Photon of energy at least twice the band gap energy can be used to generate multiple excitons to avoid energy loss. This phenomenon can increase

the efficiency up to 42% which represents ~35% improvement. By harvesting the hot electrons, the efficiency can be increased to 66% [76, 77]

- Semiconductor metal chalcogenides CdS, CdSe, PbS, PbSe, PbSSe, CuInS<sub>2</sub>, CuInSe<sub>2</sub>, CdSSe, CuInSe<sub>x</sub>S<sub>2-x</sub> are popular choices for QDSC. PbS and PbSe quantum dot are widely used in the photovoltaic cells. Important components of QDSC are photoanode, counter electrode, redox electrode or hole conductor. The photoanode is sensitized by the QD, the counter electrode is used to complete the circuit and allow charge to flow, the redox electrode helps to monitor the reaction, and hole conductor is simply a hole-transporting material [78]. As mentioned before, QDSC is highly lacking in many aspects and needs improvement in the areas mentioned below in order to develop a highly efficient solar cell.
- Improve in charge carrier transport by increasing the mobilities of electrons and holes and decreasing the charge carrier recombination.
- Though the relaxation rate is slower in QD than in bulk semiconductor, capturing hot electrons and generating multiple excitons from QD is challenging due to fast relaxation rate of charged carriers. A new technology to increase the hot carrier's lifetime and extraction of multiple electrons needs to be developed.
- Another challenge is scaling up of QD synthesis. For a good QDSC high quality PbS QD is required. PbS QD is synthesised by hot injection method. High quality PbS QD, so far, is successfully synthesised only at the laboratory level with no available technology to upscale the synthesis from the laboratory to industry level.
- Another issue is the toxicity of QD as it contains cadmium and lead. QD synthesised using nontoxic or less toxic alternatives could not yield satisfactory results [73]

#### 4. Nanotechnology in environmental remediation and pollution sensors

Through the advent of nanotechnology several cost-effective mechanisms were developed for environmental remediation and pollution monitoring. Remediation is removal or reduction of contaminants from air, water and soil to maintain and improve its quality, thereby, ensuring sustainability of the Earth and all its life forms [79, 80].

##### 4.1. Soil and groundwater remediation

The subsurface contamination can be treated by *in-situ* and *ex-situ* methods. The most popular one is using Permeable Reactive Barrier (PBR), an *in-situ* technique. PBR can be defined as “a permeable subsurface zone constructed of reactive materials to intercept, destroy or immobilize contamination.” Another version of PBR is PRTZ (Permeable, Reactive Treatment Zone), which is a geochemically altered subsurface zone where the aquifer material is manipulated to promote destruction or immobilization of the contaminants. The major function of PBR is to bring the contaminants in contact with the reactive materials responsible for decontamination (Figure II). There are various types of reactive materials and the most sought after one is nanoscale zerovalent iron (nZVI) [81].

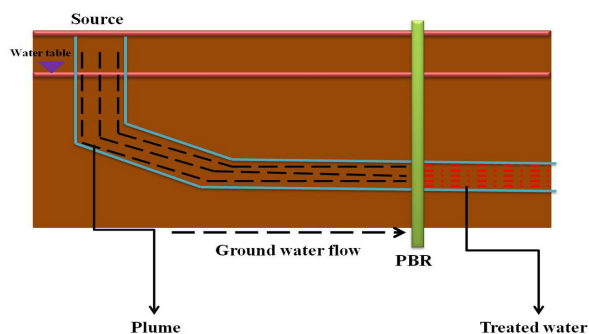


Figure II: Schematic illustration of PBR

Nanoscale materials are a major asset of clean-

ups due to two reasons:

- (i) Because of its size, it can penetrate easily into groundwater and soil
- (ii) They can be engineered to remain suspended in ground water.

Recent works reveal that iron nanoparticles can effectively degrade organic contaminants. Whereas, zerovalent iron (nZVI) particles can be used to degrade organic, inorganic as well as, dissolved metal contaminants. The basic reaction that takes place during decontamination is corrosion. nZVI is actually a reductant i.e. has the tendency to donate electrons and in turn be oxidized. The biggest disadvantage of using iron is that during the degradation process the particle itself gets oxidized and cannot be reused. However, nZVI is the most preferred reactive material [80, 82] and can be synthesised using top-down or bottom-up approach. The most common method is a top-down approach where an aqueous ferric solution is reduced by reducing agents like sodium borohydride or sodium hypophosphate [79]. There are various types of ZVI viz., granular ZVI, nanoscale ZVI and bimetallic ZVI. Nanoscale ZVI and bimetallic ZVI has diameter between 1 to 100nm. Bimetallic ZVI are nZVI with a second zerovalent material deposited on its surface. The size of granular ZVI ranges in microscale hence, nZVI has higher surface area and so they are estimated to be 10 to 1000 times more reactive than granular ZVI; their absorption capacity is also higher [83, 84]. nZVI can be used in two ways:

- (i) Injection of immobile nZVI to form a zone of iron nanoparticles adsorbed on the aquifer solid
- (ii) Injection of mobile nZVI to form a plume of iron nanoparticles that dissolve any contaminants that form a DNAPL (dense non-aqueous phase liquid) source in the aquifer [79].

After injection, the reactive material is made to come in contact with the contaminants for the decontamination process to commence which varies according to the nature of the contaminants. Organic compounds like chlorinated hydrocarbons get reduced by the nanoparticle, which in turn gets oxidized. The reduced compound undergoes dichlorination and transforms into another distinct compound e.g. tetrachloroethane gets reduced to ethane by nZVI [85]. The interaction between metal contamination and the nanoparticles can be reduction, adsorption, oxidation, reoxidation, co-precipitation or precipitation. Some metals like chromium can undergo more than one mechanism. It can undergo reduction, adsorption and co-precipitation.

**Reduction:**  $\text{Cr}^{6+}$  is a carcinogenic pollutant found in industrial waste sites, whereas  $\text{Cr}^{3+}$  is an essential nutrient but toxic at higher concentration.  $\text{Cr}^{6+}$  can be reduced into a less toxic form by nZVI and immobilize by precipitation as  $\text{Cr}(\text{OH})_3$  [84, 86]

**Adsorption:** Arsenic is a carcinogenic compound, present in the groundwater as  $\text{As}^{5+}$  or  $\text{As}^{3+}$ .  $\text{As}^{5+}$  is comparatively more toxic and soluble than  $\text{As}^{3+}$ . Both these compounds can be adsorbed onto the iron oxides on the outer layer of the iron nanoparticles. The adsorption can be because of the electrostatic interactions such as coulombic attraction or due to ion exchange or induced polarization, covalent bonding and Van der Waals forces [84, 87].

**Oxidation or Reoxidation:**  $\text{As}^{5+}$  can be converted into the lesser toxic form  $\text{As}^{3+}$  by oxidation. The rate of oxidation is low in neutral pH and high in alkaline and acidic solution [84, 87].

**Precipitation and co-precipitation:** Uranium is a common contaminant found in the nuclear waste sites. The Uranyl ions get adsorbed on the

particle surface, and reductive precipitation of less soluble  $U^{4+}$  occurs [84, 88]

## 4.2. Water remediation

The traditionally used techniques for remediating large volumes of water are carbon absorption, air stripping, oxidation through ozonation or chlorination, ultrafiltration, sedimentation and even activated charcoal absorption. Most of these techniques focus on removing solid contaminants and kill microorganisms, but still the hazardous ones remain dissolved in the water and cannot be removed by these methods. Hence, recent techniques revolve around converting harmful contaminants into harmless compounds. These techniques are often used in combination with the traditional methods to obtain best results. Nanotechnology is the most recent technology that can make water remediation easier and cheaper [82].

### 4.2.1. Nano absorbents

Zero valent iron can also be employed in a similar way as in groundwater to remediate waste water contaminated with organic, inorganic and metal contaminants. Apart from that other Nano absorbents such as titanium oxide and zinc oxide can also be used [89]. Guo et al. [90] reported that three-dimensional titanium dioxide nanostructure with a nanoparticle core and fabricated to have a needle like surface, effectively removed arsenic(V) and chromium(VI) from water and could be easily separated from water by sedimentation. The nanoparticle removed most of the ions in less than 1 hr and it showed maximum absorption capacity of 59.7 mg/g for arsenic (V) and 29.92 mg/g for chromium (VI). The effective removal of the ions by the nanoparticle was due to its large hydroxyl group density and high surface area. Dehaghi et al. [91] reported that chitosan-zinc oxide nanoparticle beads can remove permethrin pesticide from water. The

beads were found to be an excellent absorbent in the batch studies, as it removed 99% of permethrin from the 25 ml permethrin solution (0.1mg/L). The absorption and regeneration studies revealed that the beads could be reused with 56% regeneration after 3 cycles in on-line column. Hence, it could be effectively used in water treatment process.

### 4.2.2. Photocatalysis

These absorbents can also act as photocatalytic agents. Photocatalysis process includes two types of reactions, photoreduction and photooxidation. Semiconductor nanomaterials consist of a filled valence band and empty conducting band. When these materials absorb light energy, which is equal to or more than the semiconductor's band gap, an electron gets excited from valence band to conducting band creating an electron vacancy in the valence band. This vacancy is a positive charge called hole. Then, the electron gets transferred to the absorbed compound leading to a series of photooxidation and photoreduction process, which would eventually degrade the organic compound (Figure III) [92, 93]. Rajapriya et al. [41] reported that ZnO nanoparticle effectively degraded 93 % of methyl violet and 89.5% of malachite green within 120 minutes.

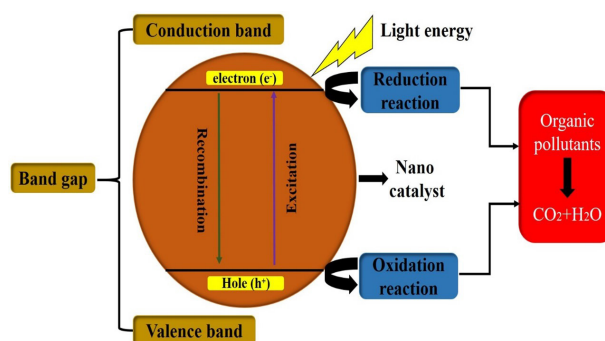


Figure III: Schematic representation of photocatalysis of a Nano-catalyst

### 4.2.3. Nanofilter

Nanofilter is a type of semipermeable membrane, whose pore size measures typically 1nm in diameter. They only allow solvent molecules and very low molecular weight solute molecules to pass through. When in contact with aqueous solutions, they possess specific charge due to disassociation of specific functional groups or adsorption of charged solutes, based on which they can reject certain ions and charged molecules. These filters were initially used only to remove salt and soften the water [94-96]. Recently, nanofilters are found to successfully remove organic contaminants of emerging concerns (CECs) such as arsenic, hormones and personal care product from water. [95-98]. Apart from CECs they can also act as potential barriers for pathogens as the size of viruses ranges from 10 to 100nm and the pore size of the filter is much smaller. Hence, they can be effectively used to convert domestic waste water into reusable form [99]. The properties of nanofilter is in-between Ultrafiltration and Reverse osmosis. Few advantages of nanofilters is that the operating pressure is much lower comparatively and exhibits low rejection of monovalent ions, high rejection of divalent ions and higher flux compared to RO membranes. [94-96]. The greatest disadvantage in using nanofilter membranes is membrane fouling. This can lead to flux decline, cost increase and membrane degradation [95].

Nanofilters incorporated with nanoparticles are gaining more interest. The incorporation can increase the membrane permeability, mechanical properties, hydrophilicity and selectivity in some cases. Titanium dioxide, zinc oxide, silica and silver are some of the commonly incorporated nanomaterials [96]. Bandehali et al. [100] developed a Polyether-imide based nanofiltration membranes incorporated with Glycidyl POSS-functionalized ZnO capable of removing heavy metal ions from water. These membranes showed significant separating performance and antifouling properties. Parvizian et al. [101]

developed a hybrid nanofiltration membrane by incorporating oleic acid-titanium oxide nanoparticles to polyethersulphone membrane. The incorporation of nanoparticles increased the flux recovery ratio (FRR%) to 83% that led to the improvement of the antifouling properties.

### 4.3. Air remediation

The major pollutants in the atmosphere are carbon monoxide, chlorofluorocarbons, sulphur dioxide, hydrocarbons, heavy metals, VOC (Volatile Organic Compounds), dioxins, nitrogen oxides, sand particles and biological substances. These pollutants are emitted by various physical, chemical and biological sources. Similar to the previously mentioned environmental issues, nanotechnology is effectually employed for air remediation also. Akin to water remediation, nanoparticles can be used as adsorbents, catalysis and also in nanofilters [102].

#### 4.3.1. Nano adsorbents

Nano adsorbents have the same potential to remediate air pollutants as water pollutants. The mechanism of adsorption in air is similar as discussed before. The nano absorptive materials can be chemically modified in several ways to increase its adsorption capacity, a few of them are discussed in table IV.

#### 4.3.2. Nano-catalyst

Nano-catalyst can perform several different types of catalytic activity. Here the catalytic activity of interest is photocatalysis. It a very promising technique as it has huge potential to destroy contaminants in both water and air. The mechanism is also the same as in the photocatalysis process. As they are plasmonic-metal nanoparticles they can interact with the incident light through the excitation of localized surface plasmon resonance and gain

energy by the conduction electrons of the metal nanostructure [105]. Few nano-based photocatalytic apparatuses, for degradation of various air pollutants reported in the literature, are given in table IV.

Nano-based photocatalytic apparatus, including the ones mentioned above, are not available commercially as it is still under development. There are some commercial products coated with photocatalytic nanoparticles such as paints, glass, concrete etc., available in the markets. These products are manufactured specially to combat the ever-increasing air pollution. George et al. [111] conducted an investigation titled PhotoPAQ (Demonstration of Photocatalytic remediation process on Air Quality) to study the air quality improvement upon deployment of photocatalytic materials on the pavement, streets, buildings etc., and the

results revealed that this technology can convert harmful pollutants into less harmful reaction products. Sometimes these particles were found to produce harmful reaction products like formaldehyde. Hence, they recommend every researcher to test new nano-catalyst not only for their reactivity against pollutants but also for the formation of harmful reactive products [111].

#### 4.3.3. Nanofilters

In industries like food, pharma and biotechnology, it is important to control aerosol contamination. Most of the filters which are currently in use requires high maintenance due to fouling and some of it are not energy efficient. This led to the advent of nanofibers filtering media. Nanofibers can be synthesised using electrospinning technique. Due to the

**Table IV: Nano based apparatus for pollution remediation**

Pollutant	Nano apparatus	Examples
Mercury	Chemically modified nano absorptive materials	<u>Cysteine activated silica</u> : It is a chelating absorbent. Cysteine is the chelating agent and it has the ability to selectively remove the metal ions. The metal gets adsorbed and ionized onto the surface layer, which later leads to chelate formation (metal-ligand complex)[103].
Toluene	Chemically modified nano absorptive materials	<u>Nano-graphene modified by ionic liquid</u> : Both graphene and ionic liquid are very good absorbent. Nano-graphene modified by ionic liquid showed maximum adsorption than individual nano-graphene and ionic liquid[104].
VOC	Nano-based photocatalytic apparatus	Per fluorinated ionomeric coating with TiO <sub>2</sub> nano powder [106].
NO <sub>x</sub>	Nano-based photocatalytic apparatus	Nitrogen doped graphene QD/Graphitic C3N4 [107].
NO <sub>2</sub> , SO <sub>2</sub>	Nano-based photocatalytic apparatus	Ca (OH) <sub>2</sub> /TiO <sub>2</sub> photocatalytic coating for buildings [108].
Organochlorine pesticide	Nano-based photocatalytic apparatus	Nano-TiO <sub>2</sub> coated film [109].
Hg <sup>0</sup>	Nano-based photocatalytic apparatus	Coloured TiO <sub>2</sub> -sensitized Bi <sub>5</sub> O <sub>7</sub> I nanorods [110]
Size particulate matter	High efficiency nanofilter	<u>Gelatine nanofiber</u> : It was able to remove 99.3% of 0.3µm size particulate matter and 99.6% of 2.5µm size particulate matter[113]
<i>E.coli</i> and <i>staphylococcus aureus</i>	Antimicrobial nanofilter	<u>Polyacrylonitrile nanofiber incorporated with silver nanoparticles</u> : This membrane is capable of removing and killing <i>E.coli</i> and <i>staphylococcus aureus</i> in 30 minutes[114]
Incense smoke and Formaldehyde	Nano absorbent cum nanofilter	<u>ZIF-8@SiO composite nanofiber membrane</u> : It showed efficient removal of 99.96% of incense smoke and 79.53% absorption of formaldehyde[115]

recent advancement of this technique a lot of industries in countries like USA, South Korea, Germany and Japan have started to produce nanofiber filtering media. Table IV gives a brief explanation about few types of nanofiber filter media reported in the literature [112].

#### 4.4. Nanotechnology based sensors for pollution detection

Pollution detection is the first step for pollution remediation. Nanotechnology, is making a huge impact on pollutant degradation. Due to its unique optical property it has also been found helpful in pollution detection. High crystallinity, high integration density and low power consumption are the advantages of nano-based sensors. Several sensors based on nanostructures like nanoparticles, nanorods, nanotubes and nanowires have already been reported, but,

most of it has not been commercialized yet [116]. Nevertheless, its immense potential has attracted a lot of researchers and we can expect nano-based sensors to rule the markets in the forthcoming years. Carbon nanotubes and nanowires are the most commonly used nanostructures in sensors because of their high surface area and high detection sensitivity. Other nanostructures like metal oxide nanoparticles are also equally good but often suffers from degradation as it agglomerates when operated for longer time at high temperature. Conversely, metal-oxide-based nanowires are chemically stable. This might be due to the 1D structure of the nanowire [116, 117].

Carbon nanotube has a perfect cylindrical structure with an open or closed end. It is a 1D nano material therefore, one dimension of the material does not measure in nanoscale. It

**Table V: Sensors for pollutants detection and its working principle**

Sensor	Pollutant	Working principle
Carbon nanotube based ionizing gas chamber with different electrodes to detect different pollutants <sup>#</sup>	NO and SO <sub>2</sub> in air	Every gas has a distinct ionization characteristic. The sensor identifies the unknown gas with this unique breakdown voltage. The concentration of the gas is determined by monitoring self-sustained discharge current i.e. how long the current flow is maintained [121].
MWCT electrode <sup>#</sup>	Zinc, cadmium and lead in water	The detection is done based on the reduction of the metal ions onto the multiwall carbon nanotube [122]
Amperometric acetylcholinesterase sensor based on Fe <sub>3</sub> O <sub>4</sub> nanoparticle/ MWCT modified ITO-coated glass <sup>#</sup>	Malathion, chlorpyrifos, monocrotophos, endosulfan in food and soil	The phosphate group in the pesticide gets covalently bond to the active side of the enzyme acetylcholinesterase which in turn gets immobilized onto Fe <sub>3</sub> O <sub>4</sub> nanoparticle/ MWCT modified ITO-coated glass. Hence the amount of enzyme immobilized is directly proportional to the pesticide present in the sample [123].
Porous Si nanowire <sup>*</sup>	NO <sub>x</sub> in air	Upon adsorption of NO, the electron carrier and conductance of the nanowire increases due to the strong electron-donating power of NO molecule [125].
M13 Bacteriophage-templated Au nanowire <sup>*</sup>	Hg (II) in water	Au-Hg amalgam is formed which is sensed colorimetrically [126].
Copper nanowire electrochemical sensor <sup>*</sup>	Herbicide trifluralin in soil	Addition of copper nanowire to the matrix of carbon past electrode results in high electrocatalytic activity towards the oxidation of trifluralin at pH 4.0 in aqueous solution, which is measured voltammetrically [127]

\* Nanowire based sensors; # Carbon nanotube sensors

is made up of layers of graphene, one layer in single wall nanotube (SWNT) and more than one layer in multiwall nanotube (MWNT). The carbon network of the layer resembles a honey comb. Due to their 1D structure they have excellent electrical and optical properties [118, 119]. Carbon nanotube especially SWNT shows large alteration in its electrical resistance and optical properties in response to environmental changes, which is controlled by the absorption of the target onto the surface of the nanotube, therefore, the detection and sensitivity of the sensor can be modified by addition of functional groups. Hence, they prove to be potential candidates for the development of low temperature and ambient pressure sensors [119, 120]. The table V lists out few Carbon nanotube sensors for detecting pollutants.

Nanowires are 2D nanomaterial, that means two dimensions of this nanomaterial are not in nanoscale. Just like carbon nanotubes, they also exhibit unique chemical and electronic properties making them conceivable for sensor applications. Nanowire based chemical and biological sensors were found to be more sensitive and consumes less energy than the conventional sensors. The working principle of nanowire sensor is similar to that of carbon nanotubes [124].

## Conclusion

In this review we discussed in detailed about various methods of nanomaterial synthesis i.e. physical, chemical and biological. Physical and chemical techniques are not environmentally friendly hence, manufacturing nanoparticles in large scale using those techniques will lead to environmental damages. But synthesising nanomaterials is indispensable as it is the technology of the future. Therefore, a new technology called the green nanotechnology was introduced. Green nanotechnology deals with environmentally friendly synthesis of

nanomaterials. It involves the usage of plants, animals and other organic compounds for the synthesis of nanoparticles. This type of synthesis is called green synthesis or biological synthesis. Green synthesis is still in its initial stages and due to various reasons, industrial scale synthesis is not successful till date. However, it has the potential to prosper and soon, with the culminative efforts from scientist around the globe it will be successful at industrial level. Green nanotechnology also includes biomolecule-based nanomaterials. They were initially used only in medicine now it has expanded to various other fields. We have brief about few commonly used biomolecules namely DNA, peptides and microorganisms. Each biomolecule-based nanomaterial has a different synthesis method and we have explained a few of them.

The last part of the review explains how nanotechnology deals with the two major environmental issues, energy crisis and pollution. In this part we have introduced few types of nanomaterials like QD, nZVI, metal nanoparticles, nanofilter, nanofiber, carbon nanotube and nanowire. QD can be used in solar cells and QDSC was found to be more efficient than commercial solar cells. nZVI can be utilized for the remediation of waste water and groundwater. Metal nanoparticles can be used as a nano absorbent and nanocatalyst in air and water treatment. They also can be incorporated into nanofilters to increase its efficiency. Nanofilter membranes can be used for both air and water treatment. Nanofibers can be used to synthesise nanofilters with antifouling properties. Finally, carbon nanotubes and nanowires can be used in sensors to detect pollutants. Therefore, nanotechnology has a big role to play in medicine, conversion and storage of energy, degradation and sensing of pollutants. In all these fields it has proven its potential to perform better than the existing technology. Hence, nanotechnology will



definitely overcome its shortcomings in the upcoming years and acquire a bigger and better role in enhancing environmental sustainability.

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### References:

- I Khan, K Saeed and I Khan, Nanoparticles: Properties, applications and toxicities, *Arabian Journal of Chemistry* 12(7), 2019, 908-31.
- JB Hall, MA Dobrovolskaia, AK Patri and SE McNeil, Characterization of nanoparticles for therapeutics, 2007.
- RJ Nick and JR Linton, Particles including nanoparticles, uses thereof, and methods, 2016.
- J Rockenberger, L Tröger, A Kornowski, T Vossmeier, A Eychmüller, J Feldhaus, and H Weller, EXAFS studies on the size dependence of structural and dynamic properties of CdS nanoparticles. *The Journal of Physical Chemistry B*, 101(14), 1997, 2691-701.
- T Theivasanthi and M Alagar, Studies of copper nanoparticles effects on micro-organisms, *arXiv preprint arXiv*, 2011, 11101372.
- E Hao, GC Schatz and JT Hupp, Synthesis and optical properties of anisotropic metal nanoparticles, *Journal of Fluorescence*, 14(4), 2004, 331-41.
- SS Mao, S Shen and L Guo, Nanomaterials for renewable hydrogen production, storage and utilization, *Progress in Natural Science: Materials International*, 22(6), 2012, 522-34.
- E Serrano, G Rus and J Garcia-Martinez, Nanotechnology for sustainable energy, *Renewable and Sustainable Energy Reviews*, 13(9), 2009, 2373-84.
- IS Yunus, Harwin, A Kurniawan, D Adityawarman and A Indarto, Nanotechnologies in water and air pollution treatment, *Environmental Technology Reviews*, 1(1), 2012, 136-48.
- FD Guerra, MF Attia, DC Whitehead and F Alexis, Nanotechnology for environmental remediation: materials and applications, *Molecules*, 23(7), 2018, 1760.
- MR Willner and PJ Vikesland, Nanomaterial enabled sensors for environmental contaminants, *Journal of nanobiotechnology*, 16(1), 2018, 1-16.
- BH McNaughton, V Stoica, JN Anker, R Clarke and R Kopelman, Fabrication of uniform half-shell magnetic nanoparticles and microspheres with applications as magnetically modulated optical nanoprobe, 2005, *arXiv preprint cond-mat/0506418*.
- T Tsuzuki, Commercial scale production of inorganic nanoparticles, *International journal of nanotechnology*, 6(5-6), 2006, 567-78.
- K Sobolev and MF Gutiérrez, How nanotechnology can change the concrete world, *American Ceramic Society Bulletin*, 84(10), 2005.
- MT Swihart, Vapor-phase synthesis of nanoparticles, *Current Opinion in Colloid & Interface Science*, 8(1), 2003, 127-33.
- CJ Brinker and G Scherer, *Sol-gel sciences, The Processing and the Chemistry of Sol-Gel Processing*, 1990.
- AV Rane, K Kanny, V Abitha, S Thomas, Methods for synthesis of nanoparticles and fabrication of nanocomposites, *Synthesis of inorganic nanomaterials: Elsevier*, p. 121-39, 2018.
- D-H Li, S-F He, J Chen, C-y Jiang C-y, C Yang and editors, *Solid-state Chemical Reaction Synthesis and Characterization of Lanthanum Tartrate Nanocrystallites Under Ultrasonication Spectra*, IOP Conference Series: Materials Science and Engineering, IOP Publishing, 2017.
- X He, Z Peng, N Yu, J Han and C Wu, Poly (sodium 4-styrenesulfonate) modified carbon nanoparticles by a thermo-mechanical technique and its reinforcement in natural rubber latex, *Composites science and technology*, 68(14), 2008, 3027-32.
- D Li, S He, J Chen, C Jiang, C Yang and editors, *Solid-state chemical reaction synthesis and characterization of lanthanum tartrate nanocrystallites under ultrasonication spectra*, IOP Conf Ser Mater Sci Eng, 2017.
- CC Piras, S Fernández-Prieto, WM De Borggraeve, Ball milling: a green technology for the preparation and functionalisation of nanocellulose derivatives, *Nanoscale Advances*, 1(3), 2019, 937-47.
- MC Sportelli, M Izzi, A Volpe, M Clemente, RA Picca, A Ancona, PM Lugarà, G Palazzo, and N Cioffi, The pros and cons of the use of laser ablation synthesis for the production of silver nano-antimicrobials, *Antibiotics*, 7(3), 2018, 67.
- X Wu, RD Oleschuk and NM Cann, Characterization of microstructured fibre emitters: in pursuit of improved nano electrospray ionization performance, *Analyst*, 137(18), 2012, 4150-61.
- DN Nguyen, C Clasen and G Van den Mooter, Pharmaceutical applications of electrospraying, *Journal of pharmaceutical sciences*, 105(9), 2016, 2601-20.
- J Creighton and P Ho, Introduction to chemical vapor deposition (CVD), *Chemical vapor deposition*, 2, 2001, 1-22.
- B Buesser and SE Pratsinis, Design of nanomaterial synthesis by aerosol processes, *Annual review of chemical and biomolecular engineering*, 3, 2012, 103-27.
- T Tsuzuki and PG McCormick, *Mechanochemical*

- synthesis of nanoparticles, Journal of materials science, 39(16-17), 2004, 5143-6.
28. BP Nenavathu, AK Rao, A Goyal, A Kapoor and RK Dutta, Synthesis, characterization and enhanced photocatalytic degradation efficiency of Se doped ZnO nanoparticles using trypan blue as a model dye, Applied Catalysis A: General, 459, 2013, 106-13.
  29. K Ravichandran, PK Praseetha, T Arun and S Gobalakrishnan, Synthesis of nanocomposites, Synthesis of Inorganic Nanomaterials: Elsevier, p. 141-68, 2018.
  30. D Nath and P Banerjee, Green nanotechnology—a new hope for medical biology, Environmental toxicology and pharmacology, 36(3), 2013, 997-1014.
  31. Sharma D, Kanchi S, Bisetty K. Biogenic synthesis of nanoparticles: A review. Arabian journal of chemistry. 2019;12(8):3576-600.
  32. A Singh, PK Gautam, A Verma, V Singh, PM Shivapriya, S Shivalkar, AK Sahoo and SK Samanta, Green synthesis of metallic nanoparticles as effective alternatives to treat antibiotics resistant bacterial infections: A review, Biotechnology Reports, 25, 2020, e00427.
  33. J Singh, T Dutta, K-H Kim, M Rawat, P Samddar and P Kumar, 'Green'synthesis of metals and their oxide nanoparticles: applications for environmental remediation, Journal of nanobiotechnology, 16(1), 2018, 84.
  34. Y Yamashita, R Miyahara and K Sakamoto, Emulsion and emulsification technology, Cosmetic Science and Technology, 2017, 13.
  35. NT Thanh, N Maclean and S Mahiddine, Mechanisms of nucleation and growth of nanoparticles in solution, Chemical reviews, 114(15), 2014, 7610-30.
  36. K Kalishwaralal, V Deepak, S Ramkumarpandian, H Nellaiah, G Sangiliyandi, Extracellular biosynthesis of silver nanoparticles by the culture supernatant of *Bacillus licheniformis*, Materials letters, 62(29), 2008, 4411-3.
  37. J Yu, D Xu, HN Guan, C Wang, and LK Huang, Facile one-step green synthesis of gold nanoparticles using Citrus maxima aqueous extracts and its catalytic activity, Materials Letters, 166, 2016, 110-2.
  38. H Kaur, S Kaur, J Singh, M Rawat and S Kumar, Expanding horizon: green synthesis of TiO<sub>2</sub> nanoparticles using Carica papaya leaves for photocatalysis application, Materials Research Express, 6(9), 2019, 095034.
  39. N Jayaprakash, JJ Vijaya, K Kaviyarasu, K Kombaiyah, LJ Kennedy, RJ Ramalingam RJMurugan A. Munusamy, and Hamad A. Al-Lohedan, Green synthesis of Ag nanoparticles using Tamarind fruit extract for the antibacterial studies, Journal of Photochemistry and Photobiology B: Biology, 169, 2017, 178-85.
  40. K Cheirmadurai, S Biswas, R Murali and P Thanikaivelan, Green synthesis of copper nanoparticles and conducting nanobiocomposites using plant and animal sources, RSC Advances, 4(37), 2014, 19507-11.
  41. M Rajapriya, SA Sharmili, R Baskar, R Balaji, NS. Alharbi, S Kadaikunnan, JM Khaled, KF Alanzi, and B Vaseeharan, Synthesis and Characterization of Zinc Oxide Nanoparticles Using Cynara scolymus Leaves: Enhanced Hemolytic, Antimicrobial, Antiproliferative, and Photocatalytic Activity, Journal of Cluster Science, 2019, 1-11.
  42. EY Jang, YJ Son, SY Park, JY Yoo, YN Cho, SY Jeong, S Liu, and HJ Son, Improved biosynthesis of silver nanoparticles using keratinase from *Stenotrophomonas maltophilia* R13: reaction optimization, structural characterization, and biomedical activity, Bioprocess and biosystems engineering, 41(3), 2018, 381-93.
  43. P Mukherjee, *Stenotrophomonas* and *Microbacterium*: Mediated Biogenesis of Copper, Silver and Iron Nanoparticles—Proteomic Insights and Antibacterial Properties Versus Biofilm Formation, Journal of Cluster Science, 28(1), 2017, 331-58.
  44. Y Xu, Y Hou, Y Wang, Y Wang, T Li, C Song, N Wei, and Q Wang, Sensitive and selective detection of Cu<sup>2+</sup> ions based on fluorescent Ag nanoparticles synthesized by R-phycoerythrin from marine algae *Porphyra yezoensis*, Ecotoxicology and environmental safety, 168, 2019, 356-62.
  45. JA Colin, I Pech-Pech, M Oviedo, SA Águila, JM Romo-Herrera and OE Contreras, Gold nanoparticles synthesis assisted by marine algae extract: Biomolecules shells from a green chemistry approach, Chemical Physics Letters, 708, 2018, 210-5.
  46. S Tyagi, PK Tyagi, D Gola, N Chauhan and RK Bharti, Extracellular synthesis of silver nanoparticles using entomopathogenic fungus: characterization and antibacterial potential, SN Applied Sciences, 1(12), 2019, 1545.
  47. NC Seeman, Nucleic acid junctions and lattices. Journal of theoretical biology, 99(2), 1982, 237-47.
  48. PW Rothmund. Folding DNA to create nanoscale shapes and patterns, Nature, 440(7082), 2006, 297-302.
  49. A Udomprasert and T Kangsamaksin, DNA origami applications in cancer therapy, Cancer science, 108(8), 2017, 1535-43.
  50. L Wang, Y Sun, Z Li, A Wu and G Wei, Bottom-up synthesis and sensor applications of biomimetic nanostructures, Materials, 9(1), 2016, 53.
  51. RV Ulijn and AM Smith, Designing peptide based nanomaterials, Chemical Society Reviews, 37(4), 2008, 664-75.
  52. MR Ghadiri, JR Granja, RA Milligan, DE McRee and N Khazanovich, Self-assembling organic nanotubes based on a cyclic peptide architecture, Nature, 366(6453), 1993, 324-7.
  53. H Zhou, T Fan, T Han, X Li, J Ding, D Zhang, Q Guo and H Ogawa, Bacteria-based controlled assembly of metal chalcogenide hollow nanostructures with enhanced light-harvesting and photocatalytic properties, Nanotechnology,

- 20(8), 2009, 085603.
54. I Yildiz, S Shukla and NF Steinmetz, Applications of viral nanoparticles in medicine, *Current opinion in biotechnology*, 22(6), 2011, 901-8.
  55. A Schneemann and MJ Young, Viral assembly using heterologous expression systems and cell extracts, *Advances in protein chemistry*, 64, 2003, 1-36.
  56. A Mueller, A Kadri, H Jeske and C Wege, In vitro assembly of tobacco mosaic virus coat protein variants derived from fission yeast expression clones or plants, *Journal of virological methods*, 166(1-2), 2010, 77-85.
  57. Q Zhang, Q Jiang, N Li, L Dai, Q Liu, L Song, J Wang, Y Li, J Tian, B Ding and Y Du, DNA origami as an in vivo drug delivery vehicle for cancer therapy, *ACS nano*, 8(7), 2014, 6633-43.
  58. A Rajendran, M Endo and H Sugiyama, Single-molecule analysis using DNA origami, *Angewandte Chemie International Edition*, 51(4), 2012, 874-90.
  59. HK Subramanian, B Chakraborty, R Sha and Seeman NC, The label-free unambiguous detection and symbolic display of single nucleotide polymorphisms on DNA origami, *Nano letter*, 11(2), 2011, 910-3.
  60. M Yemini, M Reches, E Gazit and J Rishpon, Peptide nanotube-modified electrodes for enzyme- biosensor applications, *Analytical Chemistry*, 77(16), 2005, 5155-9.
  61. Matsui H, Gologan B, Pan S, Douberly Jr G. Controlled immobilization of peptide nanotube-templated metallic wires on Au surfaces. *The European Physical Journal D-Atomic, Molecular, Optical and Plasma Physics*. 2001;16(1):403-6.
  62. V Berry and RF Saraf, Self-assembly of nanoparticles on live bacterium: an avenue to fabricate electronic devices, *Angewandte Chemie International Edition*, 44(41), 2005, 6668-73.
  63. LL Villa, RL Costa, CA Petta, RP Andrade, KA Ault, AR Giuliano, CMWheeler, LA Koutsky, C Malm, M Lehtinen and FE Skjeldestad, Prophylactic quadrivalent human papillomavirus (types 6, 11, 16, and 18) L1 virus-like particle vaccine in young women: a randomised double-blind placebo-controlled multicentre phase II efficacy trial. *The lancet oncology*. 2005;6(5):271-8.
  64. KW Guo, Green nanotechnology of trends in future energy: a review, *International journal of energy research*, 36(1), 2012, 1-17.
  65. CM Bonilla and VV Kouznetsov, Green” QD: Basics, green synthesis and nanotechnological applications, *Green Nanotechnology-Overview and Further Prospects*, 2016, 174-92.
  66. A Ekimov and AL Efros and AA Onuschenko, *Solid State Commun*, 56, 1985, 921.
  67. AM Bagher, QD applications. *Sensors & Transducers*, 198(3), 2016, 37.
  68. X Xue, W Ji, Z Mao, H Mao, Y Wang, X Wang, W Ruan, B Zhao and JR Lombardi, Raman investigation of nanosized TiO<sub>2</sub>: effect of crystallite size and quantum confinement, *The Journal of Physical Chemistry C*, 116(15), 2012, 8792-7.
  69. O Sublemontier, H Kintz, F Lacour, X Paquez, V Maurice, Y Leconte, D Porterat, N Herlin-Boime and C Reynaud, *Synthesis and on-line size Control of Silicon QD, KONA Powder and Particle Journal*, 29, 2011, 236-50.
  70. SM Farkhani and A Valizadeh, Three synthesis methods of CdX (X= Se, S or Te) QD, *IET nanobiotechnology*, 8(2), 2014, 59-76.
  71. C Chen, X He, L Gao and N Ma, Cation exchange-based facile aqueous synthesis of small, stable, and nontoxic near-infrared Ag<sub>2</sub>Te/ZnS core/shell QD emitting in the second biological window, *ACS Applied Materials & Interfaces*, 5(3), 2013, 1149-55.
  72. P Hersch and K Zweibel, *Basic photovoltaic principles and methods*, Solar Energy Research Inst., Golden, CO (USA), 1982.
  73. MR Kim and D Ma, Quantum-dot-based solar cells: recent advances, strategies, and challenges, *The journal of physical chemistry letters*, 6(1), 2015, 85-99.
  74. EH Sargent, Infrared photovoltaics made by solution processing. *Nature Photonics*, 3(6), 2009, 325-31.
  75. JJ Van Hest, GA Blab, HC Gerritsen, C de Mello Donega and A Meijerink, The role of a phonon bottleneck in relaxation processes for Ln-doped NaYF<sub>4</sub> nanocrystals, *The Journal of Physical Chemistry C*, 122(7), 2018, 3985-93.
  76. M Hanna and A Nozik, Solar conversion efficiency of photovoltaic and photoelectrolysis cells with carrier multiplication absorbers, *Journal of Applied Physics*, 100(7), 2006, 074510.
  77. RT Ross and AJ Nozik, Efficiency of hot-carrier solar energy converters, *Journal of Applied Physics*, 53(5), 1982, 3813-8.
  78. K Honeychurch, *Printed thick-film biosensors, Printed Films: Elsevier*, 2012, p. 366-409.
  79. B Nowack, Pollution prevention and treatment using nanotechnology. *Nanotechnology*, 2, 2008, 1-15.
  80. P Mehndiratta, A Jain, S Srivastava and N Gupta, *Environmental pollution and nanotechnology, Environment and Pollution*, 2(2), 2013, 49.
  81. PG Tratnyek, MM Scherer, TL Johnson and LJ Matheson, Permeable reactive barriers of iron and other zero-valent metals, *Environmental Science and Pollution Control Series*, 2003, 371-422.
  82. P Bhawana and M Fulekar *Nanotechnology: remediation technologies to clean up the environmental pollutants, Research Journal of Chemical Sciences* \_\_\_\_\_ ISSN, 2231, 2012, 606X.
  83. JAdusei-Gyamfi and V Acha V, Carriers for nano zerovalent iron (nZVI): synthesis, application and efficiency, *RSC advances*, 6(93), 2016, 91025-44.

84. D O'Carroll, B Sleep, M Krol, H Boparai and C Kocur, Nanoscale zero valent iron and bimetallic particles for contaminated site remediation, *Advances in Water Resources*. 51, 2013, 104-22.
85. XQ Li, DW Elliott and WX Zhang, Zero-valent iron nanoparticles for abatement of environmental pollutants: materials and engineering aspects, *Critical reviews in solid state and materials sciences*, 31(4), 2006, 111-22.
86. X-q Li, J Cao and W-x Zhang, Stoichiometry of Cr (VI) immobilization using nanoscale zerovalent iron (nZVI): a study with high-resolution X-ray photoelectron spectroscopy (HR-XPS), *Industrial & Engineering Chemistry Research*, 47(7), 2008, 2131-9.
87. NE Korte and Q Fernando, A review of arsenic (III) in groundwater, *Critical Reviews in Environmental Science and Technology*, 21(1), 1991, 1-39.
88. Dickinson M, Scott TB. The application of zero-valent iron nanoparticles for the remediation of a uranium-contaminated waste effluent. *Journal of Hazardous Materials*. 2010;178(1-3):171-9.
89. B Choudhary, K Majumdar and S Deb, An overview of application of Nanotechnology in Environmental Restoration.
90. J Guo, X Cai, Y Li, R Zhai, S Zhou and P Na, The preparation and characterization of a three-dimensional titanium dioxide nanostructure with high surface hydroxyl group density and high performance in water treatment, *Chemical engineering journal*, 221, 2013, 342-52.
91. SM Dehaghi, B Rahmanifar, AM Moradi and PA Azar, Removal of permethrin pesticide from water by chitosan-zinc oxide nanoparticles composite as an adsorbent, *Journal of Saudi Chemical Society*, 18(4), 2014, 348-55.
92. EM Samsudin, SN Goh, TY Wu, TT Ling, SBA Hamid and JC Juan, Evaluation on the photocatalytic degradation activity of reactive blue 4 using pure anatase nano-TiO<sub>2</sub>, *Sains Malaysiana*, 44(7), 2015, 1011-9.
93. R Mohamed, D McKinney and W Sigmund, Enhanced nano-catalysts, *Materials Science and Engineering: R: Reports*, 73(1), 2012, 1-13.
94. WR Bowen and H Mukhtar, Characterisation and prediction of separation performance of nanofiltration membranes, *Journal of membrane science*, 112(2), 1996, 263-74.
95. Xue X-y, Cheng R, Shi L, Ma Z, Zheng X. Nanomaterials for water pollution monitoring and remediation. *Environmental chemistry letters*. 2017;15(1):23-7.
96. AW Mohammad, Y Teow, W Ang, Y Chung, D Oatley-Radcliffe and N Hilal, Nanofiltration membranes review: Recent advances and future prospects, *Desalination*, 356, 2015, 226-54.
97. AI Schäfer, I Akanyeti and AJ Semião, Micropollutant sorption to membrane polymers: a review of mechanisms for estrogens, *Advances in Colloid and Interface Science*, 164(1-2), 2011, 100-17.
98. M Sen, A Manna and P Pal, Removal of arsenic from contaminated groundwater by membrane-integrated hybrid treatment system, *Journal of Membrane Science*, 354(1-2), 2010, 108-13.
99. M Park and SA Snyder, Attenuation of contaminants of emerging concerns by nanofiltration membrane: rejection mechanism and application in water reuse. *Contaminants of Emerging Concern in Water and Wastewater: Elsevier*; 2020. p. 177-206.
100. S Bandehali, A Moghadassi, F Parviziyan, J Shen and SM Hosseini, Glycidyl POSS-functionalized ZnO nanoparticles incorporated polyether-imide based nanofiltration membranes for heavy metal ions removal from water, *Korean Journal of Chemical Engineering*, 37(2), 2020, 263-73.
101. F Parviziyan, F Ansari and S Bandehali, Oleic acid-functionalized TiO<sub>2</sub> nanoparticles for fabrication of PES-based nanofiltration membranes, *Chemical Engineering Research and Design*, 2020.
102. EF Mohamed, Nanotechnology: future of environmental air pollution control. *Environmental Management and Sustainable Development*, 2017, 6(2).
103. MA Abu-Daibes and NG Pinto, Synthesis and characterization of a nano-structured sorbent for the direct removal of mercury vapor from flue gases by chelation, *Chemical Engineering Science*, 60(7), 2005, 1901-10.
104. H Shir Khanloo, M Osanloo and O Qurban-Dadras, Nobel method for toluene removal from air based on ionic liquid modified nano-graphen, *International Journal of Occupational Hygiene*, 6(1), 2014, 1-5.
105. S Peiris, J McMurtrie and H-Y Zhu, Metal nanoparticle photocatalysts: emerging processes for green organic synthesis, *Catalysis Science & Technology*, 6(2), 2016, 320-38.
106. M Sansotera, SGM Kheyli, A Baggioli, CL Bianchi, MP Pedferri, MV Diamanti and W Navarrini, Absorption and photocatalytic degradation of VOCs by perfluorinated ionomeric coating with TiO<sub>2</sub> nanopowders for air purification, *Chemical Engineering Journal*, 361, 2019, 885-96.
107. K Yu, Nitrogen Doped Graphene QD/Graphitic C<sub>3</sub>N<sub>4</sub> Composites for Photocatalytic NO<sub>x</sub> Degradation, 2019.
108. M Nuño, GL Pesce, CR Bowen, P Xenophontos and RJ Ball, Environmental performance of nano-structured Ca (OH) <sub>2</sub>/TiO<sub>2</sub> photocatalytic coatings for buildings, *Building and Environment*, 92, 2015, 734-42.
109. B Yu, J Zeng, L Gong, M Zhang, L Zhang and X Chen, Investigation of the photocatalytic degradation of organochlorine pesticides on a nano-TiO<sub>2</sub> coated film, *Talanta*, 72(5), 2007, 1667-74.
110. H Cheng, J Wu, F Tian, Q Liu, X Qi, Q Li, W Pan, Z Li and J Wei, Visible-light photocatalytic oxidation of gas-phase Hg<sup>0</sup> by colored TiO<sub>2</sub> nanoparticle-sensitized Bi<sub>5</sub>O<sub>7</sub>I nanorods: enhanced interfacial charge transfer based on

- heterojunction, *Chemical Engineering Journal*, 360, 2019, 951-63.
111. C George, A Beeldens, F Barmpas, JF Doussin, G Manganelli, H Herrmann, J Kleffmann, Mellouki A, Impact of photocatalytic remediation of pollutants on urban air quality, *Frontiers of Environmental Science & Engineering*, 10(5), 2016, 2.
  112. RS Barhate and S Ramakrishna, Nanofibrous filtering media: filtration problems and solutions from tiny materials, *Journal of membrane science*, 296(1-2), 2007, 1-8.
  113. H Souzandeh, Y Wang and W-H Zhong, "Green" nanofilters: fine nanofibers of natural protein for high efficiency filtration of particulate pollutants and toxic gases, *RSC advances*, 6(107), 2016, 105948-56.
  114. L Zhang, J Luo, TJ Menkhaus, H Varadaraju, Y Sun and H Fong, Antimicrobial nano-fibrous membranes developed from electrospun polyacrylonitrile nanofibers, *Journal of membrane science*, 369(1-2), 2011, 499-505.
  115. Q Zhu, X Tang, S Feng, Z Zhong, J Yao, Z Yao, ZIF-8@SiO<sub>2</sub> composite nanofiber membrane with bioinspired spider web-like structure for efficient air pollution control, *Journal of Membrane Science*, 581, 2019, 252-61.
  116. NS Ramgir, Y Yang and M Zacharias, Nanowire-based sensors, *small*, 6(16), 2010, 1705-22.
  117. R Abdel-Karim, Y Reda and A Abdel-Fattah, Nanostructured Materials-Based Nanosensors, *Journal of The Electrochemical Society*, 167(3), 2020, 037554.
  118. VN Popov, Carbon nanotubes: properties and application, *Materials Science and Engineering: R: Reports*, 43(3), 2004, 61-102.
  119. MF De Volder, SH Tawfik, RH Baughman and AJ Hart, Carbon nanotubes: present and future commercial applications, *science*, 339(6119), 2013, 535-9.
  120. DR Kauffman and A Star, Graphene versus carbon nanotubes for chemical sensor and fuel cell applications, *Analyst*, 135(11), 2010, 2790-7.
  121. H Song, Q Li and Y Zhang, CNT-based sensor array for selective and steady detection of SO<sub>2</sub> and NO, *Materials Research Bulletin*, 124, 2020, 110772.
  122. CRT Tarley, VS Santos, BEL Baêta, AC Pereira and LT Kubota, Simultaneous determination of zinc, cadmium and lead in environmental water samples by potentiometric stripping analysis (PSA) using multiwalled carbon nanotube electrode, *Journal of hazardous materials*, 2009;169(1-3):256-62.
  123. N Chauhan and CS Pundir, An amperometric acetylcholinesterase sensor based on Fe<sub>3</sub>O<sub>4</sub> nanoparticle/multi-walled carbon nanotube-modified ITO-coated glass plate for the detection of pesticides, *Electrochimica Acta*, 67, 2012, 79-86.
  124. J Sarkar, GG Khan and A Basumallick, Nanowires: properties, applications and synthesis via porous anodic aluminium oxide template, *Bulletin of Materials Science*, 30(3), 2007, 271-90.
  125. K-Q Peng, X Wang and S-T Lee, Gas sensing properties of single crystalline porous silicon nanowires, *Applied Physics Letters*, 95(24), 2009, 243112.
  126. S Manivannan, S Park, J Jeong and K Kim, Aggregation-free optical and colorimetric detection of Hg (II) with M13 bacteriophage-templated Au nanowires, *Biosensors and Bioelectronics*, 2020, 112237.
  127. A Mirabi-Semnakolaii, P Daneshgar, AA Moosavi-Movahedi, M Rezayat, P Norouzi, A Nemati and M Farhadi, Sensitive determination of herbicide trifluralin on the surface of copper nanowire electrochemical sensor, *Journal of Solid State Electrochemistry*, 15(9), 2011, 1953-61.