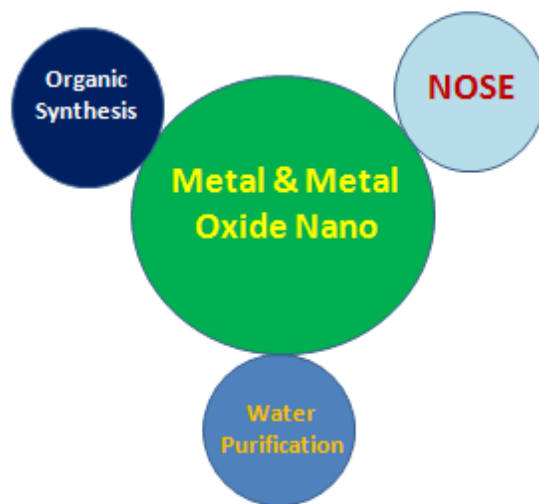


Chapter 1

Introduction



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1.1 General introduction

In the past few decades, a small word attracted enormous attention, interest and investigation throughout the world: “nano”. What it presents in terms of science and technology, which is also called nanoscience and nanotechnology, is much more than just a word describing a specific length scale. It has enormously changed every aspect of the way that we think in science and technology and it is hoped that it will definitely bring more and more surprises into our day to day life as well as the future world.¹⁻⁸ The increasing interest is due to their significantly improved properties compared to their bulk counterpart.⁹⁻¹¹ As particles are reduced from a micrometre to a nanometer size, the resultant properties can change dramatically. For example, electrical conductivity, hardness, active surface area, chemical reactivity and biological activity are all known to be altered. This could be attributed to the presence of a large fraction of atoms on the surface and hence a high surface energy, presence of decreased imperfections and quantum confinement effect.⁹ Manufactured NPs are at the forefront of nanotechnology and are being extensively used in a variety of applications, e.g. electronics and optoelectronics,¹² electrochemical,¹³ gas sensing,¹⁴ drug delivery,¹⁵ heavy metal removals from water¹⁶⁻¹⁸ etc.

1.2 Basic Concepts - Nanotechnology and Nanomaterial

1.2.1 What is nanotechnology?

“Nano” means one billionth (10^{-9}), so, 1 nanometer refers to 10^{-9} meter and is expressed as 1 nm. 1 nm is so small that things can only be molecules, clusters of atoms or particles in the quantum world. The nanometer is a notable point in the overall length scale because nanometer scale is the junction where the smallest manufacture objects “meet” the largest molecules in nature. The structures, instruments and systems having at least one dimension in nanometer scale are not only smaller than anything that we have ever made before, but also possibly the smallest solid materials that we are able to produce. Besides, in nanometer scale, the properties of materials that we are familiar with in our daily life, such as color, melting point, electronic, catalytic or magnetic properties, will change dramatically due to size effect of the nanomaterials. “At this size scale, everything, regardless of what it is, has new

properties. And that is, where a lot of the scientific interest is.” said Professor Alivisatos. This is just the beginning of what make “nano” so interesting.¹⁹⁻²²

The following is the definition of nanoscience and nanotechnology given by the U.S. National Nanotechnology Initiative (NNI): “Research and technology development at the atomic, molecular and macromolecular levels in the length scale of approximately the 1-100 nm range, to provide a fundamental understanding of phenomena and materials at the nanoscale and to create and use structures, devices and systems that have novel properties and functions because of their small and/or intermediate size”. Simply saying, nanoscience tells us how to understand the basic theories and principles of nanoscale structures, devices and systems (1-100 nm); and nanotechnology tells us what to do and how to use these nanoscale materials.^{23,24}

On December 29, 1959, Nobel Prize winner, physicist Richard P. Feynman said in his famous speech, “There is Plenty of Room at the Bottom”: “In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this (nanometer) direction.” Actually, in the years after, people wanted to move in this direction. However, not much progress was made in both nanoscience and nanotechnology until the 1980’s when Scanning Tunneling Microscope (STM) and other advanced analytical measurements were not invented. After STM, TEM (Transmission Electron Microscopy), SEM (Scanning Electron Microscopy) and AFM (Atomic Force Microscopy), highly advanced analytical tools were developed, which enables the characterization and manipulation of small objects down to a few nm, human being began to explore the nanoworld. Nowadays, many remarkable techniques, such as nanoimprint lithography, self-assembly technique, nanoscale crystal growth technique, are already available to make nanoscale products in relatively large amounts, showing the great potentials of nanotechnology in real applications.²⁵⁻³⁰

In general, nanotechnology can be understood as a technology of design, fabrication and applications of nanostructures and nanomaterials as well as understanding of physical properties and phenomena of nanomaterials and nanostructures.^{31,32} Nanomaterials, compared to bulk materials, have the scales

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ranging from individual atoms or molecules to submicron dimensions at least in one dimension.

1.2.2 Size Effects

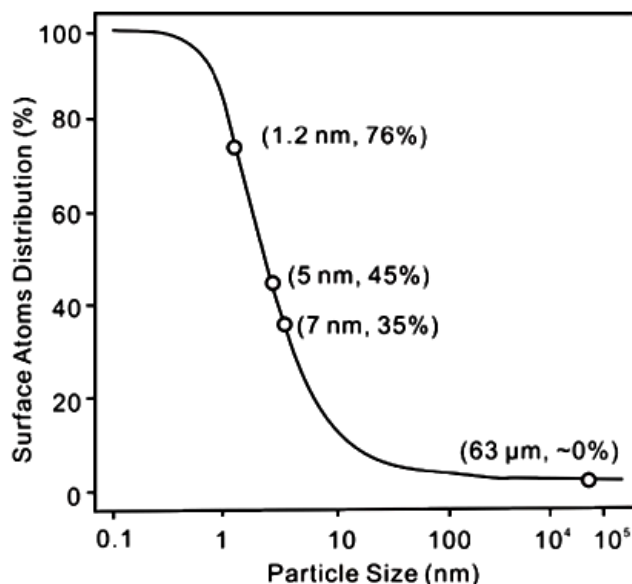


Figure 1.1: Surface atoms distribution vs palladium cluster diameter³³

The main difference between bulk material and nanomaterial lays on the size difference. With the decrease of the particle size, properties of nanomaterial differ from its bulk structure. The terminal, size effects, is used to describe the properties change accompanied with particle size change. With reducing particle size, the performance of surface atoms becomes dominant because at the lower end of the size limit. As can be seen from Figure 1.1, the surface atoms became dominant only when the palladium particle size reduced to below 10 nm.³³ Moreover, the properties changing with the particle size are also observed. For example, in catalysis by gold NPs of 1–2 nm in diameter exhibit unexpected catalytic activity, while gold is chemical inert as bulk metal.³⁴

1.2.3 Classification of nanomaterials

Depending on the dimensionality, these materials could be classified as zero, one, two and three dimensional.

Zero dimensional Nanomaterials

The materials having all three of its dimensions in the nanometer range are termed as zero dimensional, e.g. NPs, quantum dots (QDs) etc. The symmetric shape and easy synthesis with improved magnetic, optical, catalytic properties make them attractive functional materials.^{10,11}

One Dimensional Nanomaterials

A material is termed as one dimensional, when two of its dimensions are in the nano range and third dimension extends in the micro/millimetre range, e.g. nanorods, nanowires and nanotubes etc. These materials act as functional units as well as interconnect in thermoelectric, electronic and opto-electronic devices.³⁵

Two Dimensional Nanomaterials

When one of the dimensions is in nanorange in a material, it is referred to as two dimensional. Some of the examples under this category include nanoplatelets, nanosheets, nanodisks, thin films, etc.

Three Dimensional Nanomaterials

If the pore diameters are in the range of 2-30 nm in a nanomaterial, it is termed as three dimensional, e.g. hierarchical architecture, nanoflower, alumina, silica, zeolites, hybrid materials etc.

1.2.4 General characterization techniques

Characterisations of nanostructured materials have been largely based on the surface analysis techniques and conventional characterisation methods. In general, X-ray diffraction (XRD) has been widely used for the determination of crystallinity, crystal structures and lattice constants of NPs, nanofibres and thin films. The approximate particle size of NPs can be known from XRD data using Scherrer's formula. SEM^{36,37} and TEM^{38,39} together with electron diffraction are routine techniques used to take surface image as well as transmitted image of NPs. Optical spectroscopy is frequently used to determine the size of semiconductor QDs or the band gap and electronic structures of semiconductors.

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Besides the established techniques of electron microscopy, diffraction methods and spectroscopic tools, scanning probe microscopy (SPM) is a relatively new characterisation technique and has found wide spread applications in nanotechnology. The two major members of the SPM family are STM and AFM. Although both STM and AFM are true surface image techniques that can produce topographic images of a surface with atomic resolution in all three dimensions, combining with appropriately designed attachments, the STM and AFM have found a much broadened range of applications, such as nanoindentation, nanolithography, and patterned self-assembly. Almost all solid surfaces, whether hard or soft, electrically conductive or isolative, can all be studied with STM and AFM. Surfaces can be studied in gas (e.g. in air), in vacuum or in liquid. There are EDAX techniques generally attached to SEM machines by which elemental analysis can be done. FT-IR and UV-Visible spectroscopy are used wherever applicable to determine the nature of bond/conjugation.

1.3 Synthesis of metal and metal oxide nanoparticles

1.3.1 Background

Metal oxides play a very important role in many areas of chemistry, physics, and materials science.⁴⁰⁻⁴³ The metal elements can form a large diversity of oxide compounds through various synthesis techniques. They exhibit metallic, semiconductor or insulator character due to the electronic structure difference. The variety of attributes of oxides enable the wide applications in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings against corrosion, heavy metal adsorption from water and as catalysts. For example, almost all catalysts involve an oxide as active phase, promoter which allows the active components to disperse on. In the chemical and petrochemical industries, products worth billions of dollars are generated every year through processes that use oxide and metal/oxide catalysts.⁴⁴⁻⁴⁷

For the control of environmental pollution, catalysts or sorbents that contain oxides are employed to remove heavy metals as well as non-metals from polluted water.^{48,49} Till now, there are still many potential applications of these materials under continuous investigation and new synthesis methods being developed.⁵⁰ To exploit new applications metal oxide materials is one of the mean purposes of inorganic chemist.

To prepare nanomaterials, some novel synthesis procedures have been developed that may be described as physical and chemical methods. There are two approaches to the synthesis of nanomaterials and the fabrication of nanostructures: top-down and bottom-up.⁵¹ Top-down approach means to slicing or successive cutting of a bulk material to get nanosized particles. Bottom-up approach refers to the build-up of a material from the bottom: atom-by-atom, molecule-by-molecule, or cluster-by-cluster. For example, ball milling is a typical top-down method in making NPs, whereas the colloidal dispersion, emulsion is a good example of bottom-up approach in the synthesis of NPs. Both approaches play very important roles in nanotechnology. Other some techniques have also been developed which involves liquid–solid or gas–solid transformations.^{31-34,52-55} Moreover, these materials can be further functionalised by surface and structure modification. The good thermal and chemical stability of these inorganic materials enable them to be widely used. In order to explore novel physical and chemical properties and realise potential applications of nanostructures and nanomaterials, the ability to fabricate and process nanomaterials and nanostructures is the first priority in nanotechnology.

From both fundamental and industrial requirement, the development of systematic methods for the synthesis of metal oxide nanostructures is a necessity. Methods frequently used for the synthesis of bulk oxides may not be suitable for preparation of oxide nanostructures or nanomaterials. For example, a reduction in particle size by mechanically grinding a reaction mixture can give a limiting level of grain diameter, at best about 0.1 μm or bigger. However, chemical methods can be purposefully used to effectively reduce particle size into the nanometre range. One of the most widely used methods for the synthesis of bulk metal oxide ceramics involves heating the components together at a high temperature over an extended period of time. However, very high temperatures ($>800\text{ }^{\circ}\text{C}$) can be problematic when using this approach for the generation of oxide nanostructures. Direct co-precipitation (CP) of the oxide components from a liquid solution with subsequent calcination, or by using sol-gels or microemulsions in the synthesis process is better process to engineer the nanomaterials. With these approaches, one can vary the stoichiometry of the oxide nanostructures in a precise way. Such techniques are widely used for the

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synthesis of catalysts and ceramics. There are many modern ways to manufacture and engineer the nanomaterials. Some of the techniques are given below.⁵⁶⁻⁵⁷

1.3.2 Vapor route

1.3.2.1 Physical vapor deposition

Physical vapor deposition (PVD) is a versatile synthesis method and is capable of preparing thin film materials with structural control at the atomic or nanometer scale with careful monitoring of the processing conditions.⁵⁸ PVD involves the generation of vapor phase species either via evaporation, sputtering, laser ablation or ion beam deposition. Inert gas condensation combined with thermal evaporation is commonly used to fabricate metallic and metal-oxide powders with a well defined and narrow size distribution. This technique was originally introduced by Ganqvist and Buhrman in 1976 and developed by Gleiter in 1981.

1.3.2.2 Chemical vapor deposition

Chemical vapor deposition (CVD) is a process where one or more gaseous adsorption species react or decompose on a hot surface to form stable solid products. Otherwise, the fundamental theory of CVD is similar to PVD.⁵⁹

1.3.2.3 Spray conversion processing

This route involves the atomization of chemical precursors into aerosol droplets that are dispersed throughout a gas medium.⁵⁹ The aerosols are then transported into a heated reactor where the solution is evaporated or combusted to form ultrafine particles or thin films. This technique is versatile and inexpensive because of the availability of various low cost chemical solutions and has been used to produce a variety of high purity and non-agglomerated metal oxide NPs such as TiO₂, Al₂O₃, ZrO₂, V₂O₅ and Y₂O₃-ZrO₂.

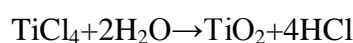
1.3.3 Liquid route

1.3.3.1 Sol-gel process

Sol–gel processing is particularly attractive because the chemical reactions can be tailored at the molecular level. Using molecular precursors to obtain an oxide or hydroxide network via hydrolysis and condensation reactions, sol–gel process provides new approaches and a better control in the preparation of nanomaterials. However, the alkoxides used are rather expensive, and the processing is tedious because it requires several sequential steps to form NPs or nanocrystalline solids. The sol–gel processing method⁶⁰ has been used for producing metal oxide and ceramic powders with high purity and high homogeneity for many years. The sol–gel route offers a degree of control of composition and structure at the molecular level. The process involves the generation of a colloidal suspension (‘sols’) which are subsequently converted to viscous gels and solid materials. Ebelman produced the first silica gels in 1846 and Cossa synthesized alumina gels in 1870. Since then, aerogels of zirconia, silazane, borate and other ceramics were synthesized using the sol–gel technique. In the process, reactive metal precursors were initially hydrolyzed, followed by condensation and polymerization reactions. Metal alkoxides are metal organic compounds having an organic ligand attached to a metal or metalloid atom. They are the result of direct or indirect reactions between a metal M and an alcohol ROH. Typical examples are methoxide (OMe; MOCH₃) and ethoxide (OEt; MOC₂H₅). During hydrolysis, the alkoxy groups (OR) are replaced by hydroxo ligands.

1.3.3.2 Wet chemical synthesis

Solution-based processing routes used for the synthesis of NPs include precipitation of solids from a supersaturated solution, homogeneous liquid phase chemical reduction, microemulsions, hydrothermal/solvothermal processing of NPs and nanocomposites, and ultrasonic decomposition of chemical precursors. These processes are attractive due to their simplicity, versatility and availability of low cost precursors. Inorganic salt compounds used in the wet chemical synthesis routes are more versatile and economical than alkoxides employed in the sol–gel process. A typical example is the formation of nanocrystalline titania powders via sonochemical hydrolysis⁶¹ of TiCl₄:



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1.3.3.3 Microemulsion techniques

It can be used for synthesis of metals or alloys by reduction, and synthesis of metal oxides or other inorganic nanomaterials. In a sealed vessel (bomb, autoclave, etc.), solvents can be brought to temperatures well above their boiling points by the increase in autogenous pressures resulting from heating. Performing a chemical reaction under such conditions is referred to as solvothermal processing or, in the case of water as solvent, hydrothermal processing. More recently, Cheng and co-workers⁶² developed a method for preparing nanoparticulate, phase-pure rutile and anatase from aqueous TiCl_4 by a hydrothermal process. This method has become one of the most important techniques for preparation of nanomaterials.

1.3.3.4 Ultrasonication techniques

Metal and metal oxide NPs can also be synthesized via ultrasonic and thermal decomposition of metal salts. Recently, ultrasonic waves have been employed to stimulate the chemical reaction of inorganic salts. Our works are mainly based on wet chemistry technique including high temperature solution phase synthesis for NPs production and microemulsion method for NPs modification.

1.3.3.5 Hydrothermal Method

Hydrothermal technique to manufacture nanomaterials has been widely explored and employed in inorganic synthesis for many years. The term hydrothermal usually refers to any heterogeneous reaction in the presence of aqueous solvents under high pressure and temperature conditions to dissolve and recrystallise materials that are relatively insoluble under ordinary conditions.⁶³

Hydrothermal technique was gradually developed by understanding of the mineral formation in nature under elevated pressure and temperature conditions in the presence of water. The importance of the hydrothermal technique for the synthesis of inorganic compounds was realised after the successful synthesis of some products such as the use of sodium hydroxide to leach bauxite [invented in 1892 by Karl Josef Bayer as a process for obtaining pure aluminium hydroxide which can be converted to pure Al_2O_3 suitable for processing to metal], and synthesis of large single crystal quartz by Nacken and zeolite by Barrer.⁶⁴⁻⁶⁶

Now-a-days, the hydrothermal technique has been widely accepted in several branches of science and technology because of reduced contamination and low synthesis temperature. The technique is being extensively used for crystallisation of materials, crystal growth, materials processing, thin film preparation and so on. The advantages of hydrothermal techniques compared to other techniques for powder preparation are listed below:

- ✓ Powders are formed directly from solution
- ✓ Powders are anhydrous, crystalline or amorphous. It depends on producing of hydrothermal powder temperature
- ✓ It is able to control particle size by hydrothermal temperature
- ✓ It is able to control particle shape by starting materials
- ✓ It is able to control chemical composition, stoichiometry, and is ideal for metastable structure synthesis
- ✓ Powders are highly reactive in sintering

Compared to pyrochemical method, hydrothermal method is of great advantage for the mild synthesis condition and easily adaptable parameters. One can adjust the synthesis temperature, time, pressure (by external control), caustic soda concentration, solid-liquid ratio and additives to control the properties of product titanate. Thus, hydrothermal synthesis is promising because this method has many operation parameters to control particle size and morphology.

1.3.4 Solid route

1.3.4.1 Mechanical ball-milling

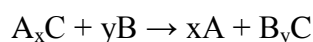
The mechanical alloying/milling process⁶⁷ is a solid state processing technique and was first developed by Benjamin of the International Nickel Company for the production of oxide dispersion strengthened (ODS) super alloys. In this process, high energy ball milling is used for synthesizing a variety of materials like forming equilibrium and non-equilibrium phases. The mechanical energy transfer to the powder particles in these mills takes place by shear action or impact of the high velocity balls with the powder. During the process, raw powder particles with a size of several microns experience severe plastic transformation undergo a repetitive cold welding and fracturing mechanism.⁵⁶ Vibratory mill, planetary mill, uniball mill and

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attritor mill are commonly used to perform mechanical transformation. Due to practical limitations, these methods can't produce very small particles. However, the advantage of this method is its relative simplicity, low cost and the possibility to scale it to tonnage quantities.

1.3.4.2 Mechano-chemical synthesis

This process involves mechanical activation of solid state displacement reactions with ball milling. Here mechanical energy is used to induce chemical reactions. The chemical precursors typically consist of mixtures of oxides, chlorides and/or metals that react either during milling or during subsequent heat treatment to form a composite powder consisting ultrafine particles within a soluble medium. The ultrafine particle is then recovered by selective removal of the matrix phase through washing with an appropriate solvent. Mechanochemical synthesis is generally based on the following displacement reaction:



In the equation, A_xC and B are precursors, A is the desired product and B_yC is a byproduct of the reaction. This process has been used successfully to prepare NPs⁶⁸ of a several materials like transition metals, oxide ceramics and oxide semiconductors.

1.3.4.3 Microwave techniques

Microwave chemistry is the science of applying microwave (MW) radiation to chemical reactions.⁶⁹⁻⁷¹ MWs act as high frequency electric fields and will generally heat any material containing mobile electric charges, such as polar molecules in solvent or conducting ions in a solid. Polar solvents are heated as their component molecules are forced to rotate with the field and lose energy in collisions. Semiconducting and conducting samples heat when ions or electrons within them form an electric current and energy is lost due to the electrical resistance of the material. MWs have been used to speed up chemical reactions in the laboratories which led scientists to investigate the mechanism of microwave dielectric heating and to identify the advantages of the technique for chemical synthesis.⁷²

MWs are electromagnetic waves. MW heating is well known in the food industry and of late has found a number of applications in chemistry, especially in organic chemistry. It is also being used for the development of different

nanomaterials. In comparison with conventional heating, this novel method shortens reaction time by a factor of approximately. Also, heating is not only quick but also uniformly spread through the entire bulk of the reaction mixture. This may result in narrow distribution of particle sizes. Some of the researchers have reported on the preparation of metallic Pt, Pd, Pt/Ag and Pd/Ag particles in ethylene glycol and glycerol in the presence of stabilizer poly(N-vinylpyrrolidone) (PVP).⁷³

1.4 Synthesis of some specific nanomaterials

1.4.1 Synthesis of Iron Oxide nanoparticles

So many systematic methods have been developed by researchers^{74-78,80-82} for the preparation of iron oxide and oxyhydroxide species with the some special features. Synthesis methods used include the use of various iron salts (chlorides, nitrates, sulfates etc.) as well as different precipitating agents such as ammonium carbonate, ammonia, NaOH, urea etc. Products with various surface areas ranging from 80 to 330 m²g⁻¹ have been developed. Even relatively rare techniques have been applied in order to production of nanosized iron oxide materials, pulsed infrared laser pyrolysis was found to give NPs of 30 nm.⁸³ Some researchers have prepared nanocrystalline akaganeite particles by an advantageous innovative technique, through the precipitation from aqueous solutions of Fe(III) chloride salt and ammonium carbonate as precipitating agent.⁸⁴

Other researchers have reported⁸⁵ that nanostructures were prepared by precipitation from aqueous solutions of iron(III) chloride, nitrate and sulfate (0.506 M with respect to Fe³⁺ each). For the hydrolysis process, aqueous solutions of ammonium carbonate and carbamate (0.23 g/dm³ each) as well as ammonia solution were used. The preparation of the gels was carried out in a three-necked round-bottom flask, placed in a thermostat at 298 K. The precipitating agent was added dropwise, using a dosimetric pump at a constant flow rate (0.15 x 10⁻⁴ dm³s⁻¹). Vigorous mechanical stirring (620 rpm) was applied in order to achieve good mixing of the reactants and to prevent agglomeration of the gel. The starting pH of the hydrolysis process was 1.7, while the final one, measured with a Crison MicropH 2002 instrument, was adjusted to 8. After the addition of the precipitating agent, the stirring

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was continued for at least 15 min. The precipitate thus obtained was decanted in a dialysis tubing cellulose membrane and the latter was placed in a bath of distilled water. Upon standing, the anions of the suspension were removed by osmosis through the membrane. The water of the bath was replaced many times until no more anions were detectable in it. The resulting cake, on the membrane surface, was isolated from the mother liquor and freeze-dried by a bench-scale instrument, until the temperature of the frozen gel reached the ambient temperature. The material obtained after the freeze-drying process appeared in the form of ultrafine powder. The prepared samples were stored in a desiccator under nitrogen atmosphere.

Schwertmannite is an iron oxide hydroxide with formula of $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$ and it is an effective fluoride and phosphate adsorbent. It can be easily applied in an industrial scale.⁸⁶ Its very fine particle size, however, makes it difficult to be applied to the classical usual filtration techniques for solid–liquid separation. Thus, magnetic filtration can be considered as a suitable candidate for separation of fine schwertmannite particles from its suspended liquid. Schwertmannite,^{86,87} was generated by homogenous hydrolysis of $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ using urea as a neutral agent. After dissolving about 25 g of $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ in distilled water, the solution was preheated at about 60 °C and slowly stirred for 10 min and then a 10 mL of the slurry containing the fresh nanomagnetite particles was added to the solution. Then, 500 mL of 5 M urea solution was added drop-wise for about 2–4 h into the solution. When precipitating of crystals begun, the color of the solution was changed from red to brownish yellow and the reaction was continued until half of the initial solution was vaporized. After solid–liquid separation, solid part was rinsed for removal of impurities.

The surface modified goethite was synthesized⁸⁸ by taking 100 mL of 1 M ferric nitrate solution in a conical flask followed by addition of 7.5 g of $\text{N}_2\text{H}_6\text{SO}_4$ with continuous stirring. The clear solution was heated at 363 K for 1 h in a closed reactor and cooled followed by pH adjustment to 3.0 by dropwise addition of 1 M NaOH solution. The precipitate was filtered and washed with distilled water till free of sulphate and nitrate. The precipitate was dried for 24 h at 373 K. Formation of pure goethite was confirmed from chemical analysis and XRD pattern while TEM studies confirmed it to be nano-sized. The synthesized nano goethite was tested for its response to fluoride adsorption under different experimental conditions including

time, pH, anions and initial fluoride concentrations. Time data fitted well to pseudo second-order kinetic model. The isothermic data showed good fit to Freundlich isotherm model. High loading capacity of 59 mgg^{-1} adsorbent was observed. The optimum pH was found to be in the range of 6–8 for fluoride adsorption, which is suitable for purification of contaminated ground water. Contaminated ground water sample containing 10.25 mgL^{-1} fluoride could be purified in three stages using 8 gL^{-1} adsorbent dose.

Some researchers have reported that magnetite iron oxide NPs, Fe_3O_4 (MIONs) can be synthesized⁸⁹ by coprecipitation of a stoichiometric mixture of ferrous and ferric chlorides (molar ratio 1:2) in an ammonium hydroxide solution with constant stirring.⁹⁰ The NPs were collected with the help of the magnet and thoroughly washed with distilled water to remove excess amounts of ammonium hydroxide. Experimental conditions such as temperature, addition rate of ammonia and stirring rate are of critical parameters that can affect the size of NPs. The average size of the NPs synthesized was about 80 nm. The above methodology was simple, sensitive and cheap, especially in absence of sophisticated techniques like spectrofluorometry or ion chromatography is not available. The material is subjected to adsorption of fluoride and it was found that both the adsorption and desorption of fluoride are fast and could be completed within 5 min. Limit of detection (LOD) and linear dynamic range of the method are comparable with some of the previously reported methods.⁹¹⁻¹⁰⁹ The above method was successfully applied for determination of fluoride in water samples and the results are in agreement with those of standard SPADNS method.

A novel magnetic nanosized adsorbent using hydrous aluminum oxide embedded with Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4@\text{Al}(\text{OH})_3$ NPs) have been synthesized¹¹⁰ and applied to remove excessive fluoride from aqueous solution. This adsorbent provides the advantages of magnetic nanoparticle and hydrous aluminum oxide floc with magnetic separability and high affinity toward fluoride, which provides distinctive features like easy preparation, high adsorption capacity, easy isolation from sample solutions by the application of an external magnetic field. The Fe_3O_4 NPs were prepared by chemical coprecipitation methods as reported in previous works¹¹¹⁻¹¹³ and the $\text{Fe}_3\text{O}_4@\text{Al}(\text{OH})_3$ NPs were synthesized according to previous reported methods with some modification.¹¹⁴ 5.2 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 2.0 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 0.85 mL of

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HCl (12 molL^{-1}) were dissolved in 25 mL of deionized water. Then, the solution was added dropwise into 250 mL of 1.5 M NaOH solution under continuous stirring using nonmagnetic stirrer at $80 \text{ }^{\circ}\text{C}$. The obtained Fe_3O_4 NPs were separated from the reaction medium by magnetic field and washed with 200 mL deionized water at least four times, then resuspended in 100 mL deionized water. 1 M aluminum nitrate was added dropwise into the Fe_3O_4 NPs suspension and the pH value of the mixture was adjusted to 8.0 by addition of 2 M NaOH within 1 h. The mixture was stirred for 2 h after the addition. During the whole process, temperature was maintained at $80 \text{ }^{\circ}\text{C}$ and nitrogen gas was used to prevent the intrusion of oxygen. The mass ratio of Fe_3O_4 to $\text{Al}(\text{OH})_3$ was 2:3, 2:5, 2:6 by varying the proportion of $\text{Al}(\text{OH})_3$ to Fe_3O_4 NPs suspension and the resulting particles was termed as $\text{Fe}_3\text{O}_4@ \text{Al}(\text{OH})_3$ (2:3), $\text{Fe}_3\text{O}_4@ \text{Al}(\text{OH})_3$ (2:5) and $\text{Fe}_3\text{O}_4@ \text{Al}(\text{OH})_3$ (2:6), respectively. Finally, the formed NPs were then thoroughly washed with deionized water and resuspended in deionized water. The adsorption capacity was 88.48 mgg^{-1} at pH 6.5. Furthermore, the residual concentration of fluoride using $\text{Fe}_3\text{O}_4@ \text{Al}(\text{OH})_3$ NPs as adsorbent could reach 0.3 mgL^{-1} with an initial concentration of 20 mgL^{-1} , which met the standard of World Health Organization (WHO) norms for drinking water quality.

1.4.2 Synthesis of copper oxide nanoparticles

Metal oxides play an important role in many areas of chemistry, physics, and materials science.¹¹⁵⁻¹²⁰ The metal elements can form a large diversity of oxide compounds.¹²¹ CuO is an important oxide especially used for water purification, although copper is an essential trace element for the normal function of many organs, including the nervous system, immune system, heart, skin, and for the formation of capillaries¹²²⁻¹²³ and copper is well metabolized by humans.¹²⁴ There are some synthesis methods of CuO nanomaterials reported elsewhere and are given below.

CuO NPs were synthesized by the thermal method.¹²⁵ Copper (II) acetate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot x\text{H}_2\text{O}$, Aldrich, 98%) and sodium hydroxide (NaOH, Merck, 99%) were used as the precursors and ethanediol ($\text{C}_2\text{H}_6\text{O}_2$, Ajex Finechem, 99.5%) was used as solvent. In a typical procedure to synthesize the CuO NPs, 25 mM of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot x\text{H}_2\text{O}$ and 100 mM of NaOH were dissolved in ethanediol at $80 \text{ }^{\circ}\text{C}$ by stirring for 2 h. The pH of the solution was maintained at 9 under continuous stirring. Then, the final products were washed with DI water and ethanol several times by

centrifugation. The obtained brown powder was subsequently dried at 80 °C in air. The resultant powder was then characterized using TG/DTA for calcinations temperatures.

Some researchers have reported¹²⁶ the synthesis of CuO NPs in liquid ammonia in the presence of sodium metal. Firstly, Cu NPs were obtained by reducing copper nitrate with the alkali metal in liquid ammonia, then, CuO NPs were formed in the ambient conditions. A 250 ml three-necked flask was kept in the thermostat bath. The flask was equipped with a sleeve, which was connected with outer-cycle of the thermostat so that the ammonia gases can be condensed to liquid ammonia. The temperature of the thermostat was set to -40 °C. After the temperature was lower than -34 °C, ammonia gas was produced by dropping ammonia liquor onto solid sodium hydroxide and it was dried through two solid NaOH columns before being led into drain sleeve. Ammonia gas was condensed to liquid ammonia in the flask, after about 80 ml liquid ammonia were collected, 1.44 g Cu(NO₃)₂ (6.0 mmol) were added to the flask, under violent stirring. After the dissolution of Cu(NO₃)₂ in liquid ammonia, the colour of solution was blue. Later, 0.69 g (30 mmol) of sodium metal was carefully added to the flask and the colour of solution became dark. After 30 min at -40 °C, 60 ml of absolute ethanol was carefully added to the flask to quench the reaction. The reaction mixture was kept at ambient temperature over night. The ammonia gas from the flask was absorbed by distilled water. The black precipitate was filtered and washed six times with 80 ml absolute ethanol, then dried in vacuum at room temperature for 2 days. The black powder was the expected product, CuO NPs.

Hollow CuO microspheres with diameters of 1–1.5 µm were synthesized on a large scale via a complexing-reagent assisted approach at low temperature, in which Cu(CH₃COO)₂·H₂O served as copper source and (CH₂)₆N₄ (HMTA) served as not only complexing reagent but also indirect soft template. In a typical procedure,¹²⁷ 40 mL aqueous solution consisting of 1.25 mmol Cu(CH₃COO)₂·H₂O and 2.5 mmol (CH₂)₆N₄ was stirred continuously for about 2 h. Then the reaction was stopped, and the solution was left to stand at room temperature for 1 day. A celeste precipitation was obtained, the precipitation was filtered off, washed with distilled water and absolute ethanol several times, respectively, and the dried in an oven at 50 °C for several hours to obtain the [Cu(C₆H₁₂N₄)₂](OOCCH₃)₂ nanosheets. An appropriate

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amount of the nanosheets was loaded into a 60 mL Teflon-lined stainless-steel autoclave, which was then filled with distilled water to 85% of the total volume. The autoclave was sealed, maintained at 180 °C for 18 h and was cooled to room temperature slowly in open air. The precipitate was filtered off, washed with distilled water and absolute ethanol for several times, and then dried in a vacuum at 40 °C for 6 h. hollow CuO microspheres were confirmed from XRD, SEM, TEM etc.

1.4.3 Synthesis of Palladium nanoparticles

Palladium NPs are of great importance as catalytic materials in organic synthesis like C-C coupling, C-N coupling, heterobond coupling, oxidation-reduction reaction as well as for a number of other applications such as hydrogen storage and sensing etc. There is few reported publication describing synthesis of Pd NPs for enhancing the organic reaction in any means. Some of the reported synthesis procedures have been given below.

The synthesis of Pd NPs in solution¹²⁸ and on surfaces through a seed-mediated growth route is reported. For the Pd NPs synthesized in solution, the diameters of the Pd NPs can be readily tuned from 33 to 110 nm, maintaining good monodispersities by using different amounts of ~3 nm gold NPs as seeds. The Pd NPs synthesized are polyhedral in shape and show a much higher intensity ratio of the (111) to (200) diffraction peaks in comparison to that of the JCPDS card 05-0681. When used as Surface-Enhanced Raman Scattering (SERS) substrates, these Pd NPs show different SERS enhancement as a function of their size, Pd NPs of about 62 nm showing the highest SERS enhancement among the three different sizes of Pd NPs employed in this study. The procedure depicted here to grow Pd NPs in solution can also be used to grow small Pd NPs on gold-sputtered substrates, which display facile electrocatalytic ability for O₂ reduction.

In another article, Pd NPs are prepared via chemical and electrochemical routes.¹²⁹ The preparation of Pd NPs with well-controlled particle sizes and shapes¹³⁰ of a high monodispersity is challenging and it finds application in producing materials that are more effective and efficient than the current state of the art. For example, particle size can play a critical role in a catalytic process and a monodispersed particle with an optimal size enables the most efficient use of the valuable metal and the highest selectivity in the subsequent reaction. Many routes have been employed for

the synthesis of surfactant-stabilised Pd NPs. Gittins and Caruso prepared Tetra-n-Octylammonium Bromide (TOAB) stabilised Pd NPs in a two-phase (toluene/water) reaction.¹³¹ This is a modification of the Brust route, which used thiol ligands. In the modified method, ammonium salt acts as both a phase transfer agent and a stabiliser. The work has illustrated that the two key factors to obtain small NPs with a narrow size distribution were the concentration of the capping agent and the stirring rate used upon addition of the reductant.¹³² Second one can be explained by considering that the reduction of Pd(II) to Pd(0) occurs at the phase boundary (organic to aqueous). Therefore, controlling the size of the water droplets formed in the toluene/water mixture has a dramatic effect on the subsequent particle size.

A similar approach was adopted by Bönnehan and coworkers,¹³³ who combined the stabilising agent (NR^{4+}) with the reducing agent to allow a high concentration of the stabiliser to build up at the reduction centre (entropic stabilisation factor), which reduces the need to add an excess of the capping agent or reductant. However, this has the disadvantage that a stoichiometric ratio of the two is always maintained and an additional cost of preparing the reducing agent is present.

One of the major advantages of using surfactants as protecting agents for NPs is that their relatively weak and poorly defined interactions with the metal surface gave reagents a high degree of accessibility to the surface of the NPs. This feature has been utilised in ligand exchange reactions (where the surfactant can be displaced by a stronger binding ligand¹³⁷ as well as in catalysis. For example, tetra-n-alkylammonium halide-stabilised Pd NPs have demonstrated good catalytic activity in liquid phase hydrogenation reactions. However, once immobilised onto a solid support, the NPs remain active and the heterogeneous catalyst can undergo huge turnovers.¹³⁴

Palladium-reduced graphene-carbon nanotube (Pd-rGO-CNT) nanocomposite was synthesized by putting one milliliter of a K_2PdCl_4 (10 mM) aqueous solution and 5 mg of rGO-CNT composite were added to a 10 ml aqueous solution and maintained in a vial under vigorous stirring for 30 min in an ice bath. Afterwards, the reaction mixture was washed three times with pure water and centrifuged to remove the remaining reagents. The Pd-rGO nanocomposite was synthesized using a similar procedure.¹³⁵

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The rGO-CNT hydrogel was prepared by the addition of 30 mg of CNTs to a 2 mgmL⁻¹ homogeneous GO aqueous dispersion (the mass ratio of GO to CNT was 25:1) under sonication for approximately 30 mins. The mixture was subsequently sealed in a 50 ml Teflon-lined autoclave and maintained at 180 °C for 12 h. After the mixture was cooled in room-temperature air with natural convection, a black gel-like 3D cylinder was obtained. The size of the hydrogel could be freely adjusted by changing the volume of the GO aqueous dispersion. The as-obtained samples were freeze-dried overnight for use in subsequent experiments. The 3D rGO hydrogel was fabricated by the same method but without the addition of CNTs.

Some people have developed¹³⁶ an efficient method to generate highly active Pd NPs supported on graphene (Pd/G) by microwave-assisted chemical reduction of the aqueous mixture of a palladium salt and dispersed GO sheets. The Pd/G demonstrated excellent catalytic activity for the carbon-carbon cross-coupling reactions (Suzuki and Heck) with a broad range of utility under ligand-free ambient conditions in an environmentally friendly solvent system. It also offers a remarkable turnover frequency (108,000 h⁻¹) observed in the microwave-assisted Suzuki cross-coupling reactions with easy removal from the reaction mixture, recyclability and significantly better performance than the well-known commercial Pd/C catalyst. The remarkable reactivity of the Pd/G catalyst toward Suzuki cross-coupling reactions is attributed to the high degree of the dispersion and concentration of Pd(0) NPs supported on graphene sheets with small particle size of 7–9 nm due to an efficient microwave-assisted reduction method.

1.5 Application of metal oxide nanoparticles

1.5.1 Basic Concepts of catalyst

Metal oxides have wide industrial applications in catalysis field by acting as active compositions or as supports. There are a lot of opportunities in modifying nanostructures to improve the catalytic activity and selectivity of existing catalysts. Such endeavours are particularly fruitful when a fundamental approach is adopted, whereby the design of the catalyst composition and microstructure is targeted towards solving the bottleneck of specific reactions.

Catalysts are species that are capable of accelerating thermodynamically feasible reactions and remained unaltered at the end of the reaction. They cannot

change the thermodynamic equilibrium of reactions.^{137,138} The performance of a catalyst is largely measured in terms of its effects on the reaction kinetics. The catalytic activity is a process of indicating the effect the catalyst has on the reaction rate and can be termed as the rate of the catalytic reaction, the relative rate of a chemical reaction (i.e. in comparison to the rate of the uncatalysed reaction) or via other parameter like the temperature required to achieve a specific chemical conversion after a particular time period under specified conditions. For example, the term ‘turnover frequency’ (TOF) in catalysis is used to describe molecules reacting per active site in unit time. Catalysts may also be evaluated in terms of their effect on the selectivity of reaction, specifically on their ability to give one specific reaction product. In some cases, catalysts may be used primarily to give specific reaction selectivity rather than high conversion rate.

Stability is another important catalyst parameter since catalysts are supposed to lose activity and selectivity with prolonged use. In chemicals manufacture, catalysis is generally applied to make an enormous range of products: heavy chemicals, commodity chemicals and fine chemicals. Catalysis is described as homogeneous when the catalyst is soluble in the reaction medium and heterogeneous when the catalyst exists in a phase distinctly different from the reaction phase of the reaction medium.¹³⁹ Almost all homogeneous catalytic processes are liquid phase and operate at moderate temperatures (<150 °C) and pressures (<20 atm). Corrosion of reaction vessels by catalyst solutions and expensive, time consuming separation processes are common problems. Traditionally, the most commonly used homogeneous catalysts are inexpensive mineral acids, notably H₂SO₄ and bases such as KOH in aqueous solution. The chemistry and the associated technology are well understood to a great extent. Many other acidic catalysts such as AlCl₃ and BF₃ are widely used in commodity and fine chemicals manufacture via some classical organic reactions such as esterifications, alkylations, acylations, hydrations, rearrangements, dehydrations and condensations. More recently, there have been significant scientific and technological innovations through the use of heterogeneous catalysis, involving a solid phase catalyst that is brought into contact with a gaseous phase or liquid phase reactant medium in which the catalyst is insoluble. This has been termed as “contact

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catalysis” sometimes used as an alternative designation for heterogeneous catalysis. Some examples of catalyzed organic reaction are given below.

In developing green, cheaper and less time consuming techniques for some synthesis reaction like formation of biphenyl/hetero-biphenyl, Pd NPs has been used.¹⁴⁰⁻¹⁴² It has been reported that in presence of copper/copper oxide NPs homocoupling of arylboronic acid produces biphenyl in high yield.¹⁴³⁻¹⁴⁶ An interesting result found on supported gold catalysts is that moisture plays an essential role in low-temperature CO oxidation, by donating to the formation and regeneration of the surface active sites.^{147,148} Haruta *et al.* reported that this effect of the moisture is dependent on the catalyst support.¹⁴⁹ The extensive studies on the photocatalytic water splitting reaction on TiO₂ surface,¹⁵⁰ have shown that water molecules can either dissociate at oxygen vacancies on the TiO₂ surface, producing surface OH groups or physically adsorb on these sites. Theoretical studies have revealed that surface OH-groups on TiO₂ can facilitate adsorption and activation of molecular oxygen.^{151,152} Based on the above knowledge, a logical hypothesis could be proposed, in which the defect sites on TiO₂ surface may acts as a key role in the catalytic oxidations using molecular O₂ as oxidant. The enhanced O₂ and H₂O adsorption due to these defects results in increased activity. Therefore, a systematic study of the surface structure and the activity are necessary to explain this phenomenon.

1.5.2 Photocatalyst

The energy that the Earth receives from the Sun is gigantic: 3×10^{24} joules a year, which is about 10,000 times more than the global population currently consumes.¹⁵³ In other words, if we could only exploit 0.01% of this incoming solar energy for the profit of humankind, it is possible to solve the problem of energy shortage. In 1972, Fujishima and Honda discovered the photocatalytic splitting of water on TiO₂ electrodes, which is the first photocatalyst suitable for water splitting and the beginning of a new era of modern heterogeneous photocatalysis.¹⁵⁴

Thereafter, so many researchers have worked on photo-electrochemical process such as splitting of water,^{155,156} reduction of carbon dioxide for the conversion of solar energy into chemical energy^{157,158} and wet-type solar cells.¹⁵³ In addition to applying photocatalysts for energy renewal and energy storage, applications of photocatalysts to environmental cleanup have been one of the most active areas in heterogeneous

photocatalysis.^{159,160} There are example of application of TiO₂ based catalysts for the complete destruction of organic contaminants in polluted air and waste water.^{161,162}

To improve the photocatalytic efficiency, various modification methods like transition metal doping (V, Cr, Nb, Fe), nonmetal doping (N, S, C), noble metal loading and building mixed phase interface have been applied to improve the overall photocatalytic activity of TiO₂. There are already good reviews exist in *Chem. Rev.* by Yates *et al.* in the modifications of TiO₂ photocatalysts.^{162,163}

1.5.3 Nanomaterials as adsorbents in water purification

Heavy metal contamination of drinking water is an emerging problem in our society. There are so many classical materials available for removal of contaminants from water, but the materials are not working upto our satisfaction in presence of more than 3-4 mixed contaminants in water as well as in low pH of drinking water. The core issue of such technology is to devise materials that are able to absorb these ions irreversibly, selectively, efficiently and in large quantities from contaminated water. Before going into the adsorbents exploration, heavy metal and non-metal contamination need to be discussed.

1.5.3.1 Arsenic contamination in water and remedies

In recent years, the presence of arsenic in contaminated groundwater has an alarming concern on a global scale.¹⁶⁴ According to the guidelines of the United States Environmental Protection Agency (USEPA), 10 mgL⁻¹ arsenic is permitted in drinking water. Arsenic is a toxic compound present in nature. As(III) is reported to be 25–60 times more toxic than As(V) and thousand times more toxic than methylated arsenicals.¹⁶⁵ The degree of toxicity of arsenic compounds is as follows: Arsine>As(III)>As(V)>methylated arsenicals.¹⁷¹ Though the arsenic concentration of uncontaminated soil¹⁶⁶ is normally less than 6 mgkg⁻¹, anthropogenic sources of As such as arsenical pesticides,¹⁶⁷ fertilizers,¹⁶⁸ mine drainage,¹⁶⁹ smelter wastes,¹⁷⁰ and agricultural drainage water from certain arid regions¹⁷¹ can elevate the levels of As in soil and water.

Arsenic may occur naturally (dissolution of arsenic-bearing minerals or it may be produced by anthropogenic activities~industrial discharge: electroplating, gold mining, fossil fuels, and others). Arsenic enters into the human body through arsenic-

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bearing food, drink, or air. The major passage of entrance is through drinking water. Arsenic contamination of groundwater and associated health risks have been reported in many parts of the world such as Bangladesh,¹⁷²⁻¹⁷⁵ India,^{176,177} China,^{178,179} Taiwan,¹⁸⁰ Thailand,¹⁸¹ United States,¹⁸² Latin America,¹⁸³ Japan,¹⁸⁴ and Nepal.¹⁸⁵

Ingestion of arsenic-contaminated water can cause serious effects on the human body, and these effects are well documented.^{186,187} Human health effects of chronic arsenic toxicity (CAT) are designated by the term arsenicosis which was first coined by some group¹⁸⁸ and later used by WHO to imply a chronic disease caused by continuous exposure in humans to arsenic. Most of the reports of chronic arsenic exposure in man focus attention on skin manifestations because of their diagnostic specificity. However, data derived from population based studies, clinical case series and reports relating to intake of inorganic arsenic in drinking water, medications or occupational and environmental exposure, show that chronic arsenic exposure adversely affects multi organ systems of human body. The symptoms of chronic arsenic toxicity (arsenicosis) are insidious in onset and are dependent on the magnitude of the dose and duration of its exposure. The arsenical pigmentation (spotty rain drop like) is found on skin of human body¹⁸⁹ due to arsenicosis.

Various treatment processes such as coagulation-precipitation, adsorption onto activated alumina, reverse osmosis and ion exchange have been reported in the literature to remove arsenic from drinking water.¹⁹⁰ Some researchers¹⁹¹ evaluated the effectiveness of nanocrystalline titaniumdioxide (TiO₂) in removing arsenate [As(V)] and arsenite [As(III)] and in photocatalytic oxidation of As(III). Batch adsorption and oxidation experiments were conducted with TiO₂ suspensions prepared in a 0.04 M NaCl solution and batch adsorption was carried out in presence of several competing ions like phosphate, silicate and carbonate. The TiO₂ was effective for As(V) removal at pH<8 and showed a maximum removal for As(III) at pH of about 7.5 in the challenge water. The adsorption capacity of the TiO₂ for As(V) and As(III) was much higher than fumed TiO₂ and granular ferric oxide. More than 0.5 mmol/g of As(V) and As(III) was adsorbed by the TiO₂ at an equilibrium arsenic concentration of 0.6 mM. The presence of the competing anions had a moderate effect on the adsorption capacities of the TiO₂ for As(III) and As(V) in a neutral pH range. The nanocrystalline TiO₂ is an effective adsorbent for As(V) and As(III) as well as acts as an efficient photocatalyst.

1.5.3.2 Lead contamination in water and remedies

Presence of heavy metals in water continues to be an alarming concern because of their toxicity, accumulation in the food chain and persistence in nature. Lead is one of the irritating such a heavy metal, which causes a multitude of physiological, biochemical, and behavioral abnormality; particularly in children.¹⁹² Among the top 20 hazardous substances elaborated by the Agency for Toxic Substances and Disease Registry (ATSDR) and the U.S. Environmental Protection Agency (USEPA), lead occupies the second place, just below arsenic.¹⁹³ Manufacture of storage batteries, paints, pigments, oil, ammunition, solder, plumbing fixtures, ceramics, glass, cable coverings, radioactivity shields, lead smelting and mining are the important industrial activities which contribute lead to leach into the aqueous medium.¹⁹⁴⁻¹⁹⁶ Concentration of lead ions in many industrial waters was reported to be as high as 200-500 mgL⁻¹, which is very high compared to drinking water quality standard of 0.05 mgL⁻¹.¹⁹⁷ Hence, it is essential to reduce the lead levels in drinking water, wastewater and water used for agriculture to the maximum permissible concentration.

With the emergence of nanoscience and technology in the last decade, research has been initiated to exploit the unusual and unique properties of nanomaterials for environmental remediation.¹⁹⁸⁻²⁰³ Various methods of synthesis of manganese oxides nanomaterials are available in the literature and the products have capability to show different physical and chemical properties. Among the various methods available for controlled synthesis, the “soft chemistry” routes, which are based on solution phase processes, are effective for the synthesis of nanostructured materials with controlled shapes and structures.^{204,205} T. Pradeep *et al.*²⁰⁶ reported an *in-situ* soft chemical synthesis of a novel hybrid material, cellulose–nanoscale-manganese oxide composite (C–NMOC), and its application for Pb(II) removal from aqueous solutions. The adsorption studies reveal that Pb(II) uptake onto C–NMOC is a fast process and >90% of the uptake occurred within the first 10 min contact time. The maximum Pb(II) uptake capacity of C–NMOC (4.64% Mn loading) was estimated to be 80.1 mgg⁻¹.

Some of the researchers²⁰⁷ have investigated the biosorption of Pb(II) and Cd(II) ions from aqueous solution using the green algae (*Ulva lactuca*) biomass as a function of pH, biomass dosage, contact time, and temperature. Langmuir, Freundlich

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and Dubinin–Radushkevich (D–R) models were applied to describe the biosorption isotherm of the metal ions by *U. lactuca* biomass. The monolayer biosorption capacity of *U. lactuca* biomass for Pb(II) and Cd(II) ions was found to be 34.7 mgg^{-1} and 29.2 mgg^{-1} respectively. From the D–R isotherm model, the mean free energy was calculated as 10.4 kJ/mol for Pb(II) biosorption and 9.6 kJ/mol for Cd(II) biosorption, indicating that the biosorption of both metal ions was taken place by chemisorptions.

1.5.3.3 Other heavy metal/non-metal contamination in water and remedies

1.5.3.3.1 Chromium in water

Chromium, is a common contaminant, is the twenty-first most abundant element in the earth's crust and it is used in diverse metal products and processes.²⁰⁸ Cr(VI) is comparatively mobile in the environment. Chromium compounds are widely used by modern industries, resulting in large quantities of this element being discharged into the environment. Some of the main uses of chromium compounds is (a) plastic coatings, (b) electroplating of metal for corrosion resistance, (c) leather tanning and finishing, and (d) in pigments and for wood preservative. Thus, chromium occurs in wastewater resulting from these operations in both trivalent and hexavalent forms. Tanning is one of the oldest and fastest growing industries in India. There are about 2161 tanneries in India excluding cottage industries, which processed 500,000 tonnes of hides and skins annually.²⁰⁹⁻²¹¹ In 2161 tanneries in India, a total of 314 kg skin is processed per year. A total annual discharge of wastewater from these tanneries is $9,420,000 \text{ m}^3$.

Removal of toxic hexavalent form of Cr(VI) from water is a challenging job and scientists are trying to solve these problems. Some selected photocatalysts like TiO_2 , ZnO and CdS have been used²¹² for the removal of heavy metals from industrial effluents. The removal of chromium is maximum at pH 2 for different amounts of photocatalysts. The removal of Cr(VI) at lower pH values may be attributed to the fact that negatively charged chromate is neutralized in the presence of a large number of H^+ ions. The chromium removal percentage increases as the dosage of photocatalysts increases and the mass removal rate increases with an increase in photocatalyst loading. The highest photodegradation rate was found on TiO_2 ; a nanocrystalline powder was the most effective for the degradation of Cr(VI). More than 96% removal of Cr(VI) is possible at the 50 ppm concentration. With an increase in the dose of photocatalysts,

initial concentration of Cr(VI) and increase in contact time up to 180 min are favorable. TiO₂ was found to be the best photocatalyst. ZnO was a less effective photocatalyst than TiO₂ as it removes 80% Cr(VI), and CdS is a very poor photocatalyst as it removes only 45% Cr(VI). The TiO₂ thin film prepared by sol-gel method removed only 46.5% Cr(VI) within same time. The removal of metals using thin film technique is less effective than that using the nanosized powder.

Others researchers²¹³ have reported that adsorption of arsenic and chromium by mixed magnetite and maghemite NPs from water is a promising technology. A commercially grade nanosize 'magnetite', later named as mixed magnetite-maghemite NPs, was used in the uptake of arsenic and chromium from different water samples. The commercially available 20-40 nm magnetite-maghemite mixture particles were obtained from Reade Advanced Materials (Rhode Island, U.S.A.). The surface area of the 20-40 nm magnetiteemaghemite mixture particles were measured using the Brunauer-Emmett-Teller (BET) method and found to have average value of 49 m²/g. The intent was to identify or develop a practical method for future groundwater remediation. The results of the study showed 96-99% arsenic and chromium adsorption under controlled pH conditions. The maximum arsenic adsorption occurred at pH 2 with values of 3.69 mgg⁻¹ for arsenic(III) and 3.71 mgg⁻¹ for arsenic(V) when the initial concentration was kept at 1.5 mgL⁻¹ for both the arsenic species, while chromium(VI) concentration was 2.4 mgg⁻¹ at pH 2 with an initial chromium(VI) concentration of 1 mgL⁻¹. Thus magnetite-maghemite NPs can readily adsorb arsenic and chromium in an acidic pH range.

1.5.3.3.2 Fluoride in water

Fluoride in drinking water in the range of 1–1.5 mgL⁻¹ has a beneficial effect on teeth and bones, but prolonged exposure at higher fluoride concentrations (4–10 mgL⁻¹) results in dental, skeletal²¹⁴ and non-skeletal forms of fluorosis in children as well as adults.^{215,216} Fluoride is a persistent and non-degradable poison that accumulates in soil, plants, wild life and in humans. Various methods have been suggested to reduce the fluoride concentration in drinking water, viz., adsorption,^{217,218} precipitation,²¹⁹ ion-exchange,²²⁰ reverse osmosis,²²¹ nano-filtration,²²² electrodialysis,²²³ and Donnan dialysis.²²⁴ Among the potential separation technologies

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mentioned above, adsorption can be accepted as one of the most suitable technique for decontamination of drinking water, especially after precipitation/coagulation process. By polishing drinking water using adsorption technique, it is possible to meet the permissible levels of fluoride defined by WHO and EPA. Furthermore, the technique is relatively low in cost, robust, environmentally benign and simple.²²⁵

The efficiency of adsorption technique depends upon the nature of adsorbents used. Many adsorbents were tried for fluoride removal namely activated alumina,²²³ hydrated cement,²²⁶ hydroxyapatite,²²⁷ activated carbon,^{228,229} quick lime,²³⁰ hydrotalcite,²³¹ clay,²³² ion exchanger,²³³ cotton cellulose,²³⁴ waste residue,²³⁵ geomaterials,²²⁶ plaster of Paris,²³⁷ brick powder,²³⁸ composite,²³⁹ etc.

Due to small size and high surface area to volume ratio, metal NPs often exhibit interesting optical, electronic, magnetic, and chemical properties that differ considerably from their bulk counterparts.²⁴⁰⁻²⁴³ Nanomaterials showed good performances near neutral pH values. It is probable that most of those materials would not be stable at extreme pH values and therefore may not have application value to polishing industrial wastewaters containing fluoride unless the pH is adjusted.

Iron oxide is a well known adsorbent used for decontamination of water.²⁴⁴ Due to small size and high surface area to volume ratio, nanoscale materials often exhibit interesting optical, electronic, magnetic, and chemical properties that differ considerably from their bulk counterparts²⁴²⁻²⁴⁵ as well as act as efficient adsorbent. In this case, if iron oxide can be synthesized in nanoscale, it may act as efficient adsorbent towards decontamination of water. However, until now, to the best of our knowledge, there have been no reports regarding the synthesis of spherical type iron oxide-hydroxide NPs through the wet chemical process. Few reports are available regarding synthesis and use of metal oxide NPs for decontamination of drinking water.²⁴⁶ Keeping this in mind, in the present study, we synthesized iron oxide-hydroxide NPs through a novel wet chemical process and experiments were carried out to remove fluoride from drinking water by adsorption technique.

1.6 Aims and objective of the thesis

As described in the plan of research, our principal objective was to synthesise NPs utilizing cheaper and less time consuming greener synthetic processes and their subsequent application to enhance some organic reactions through Nanoparticles-

catalyzed **Organic Synthesis Enhancement (NOSE)** approach as developed by our group and decontamination of water.

Purification of drinking water is a globally challenged and necessary field in order to provide pure water to our armed forces (specially in the glacier and desert regions and places where no electricity is there) and civil populace.

Keeping in mind these issues we proposed to undertake our study with the following objectives:

1. To promote economical, efficient and environmentally friendly experimental procedures (preferably in water) for both the synthesis of NPs and development of 'NOSE' approach.
2. To accomplish a comprehensive study of synthesis of various type of inorganic NPs.
3. Study and characterization of the prepared NPs by using high resolution TEM, SEM, XRD, BET, FTIR and other techniques.
4. To study the application of the NPs synthesized in catalysis and decontamination of water.

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