**Nanostructured metal oxides and their modes of synthesis**

**Dr.Veronica Deekala1\* and Dr. K. Chandra Mohan**

1\*Department of chemistry, Vikrama Simhapuri University, Nellore-524324

2. Department of Chemistry, Acharya Nagarjuna University, Guntur -522510

Email: veronicakaladhar3@gmail.com

**1. Introduction**

**1.1. Nanoparticles**

Nanotechnology is an interesting branch of material science. Nanotechnology deals the creation and handling of materials at the nanometer (nm) scale either by scaling up from single groups of atoms or by refining or reducing bulk materials. A nanometer is 1x10-9 m or one millionth of a millimeter. Particles in the size range of 1 to 100 nm are called nanoparticles. The physicochemical and biological properties showed by nanoparticles are significantly different from which we observe in bulk materials. Bulk materials possess relatively constant physical properties regardless of their size, but nanoparticles sized dependent physical and chemical properties. Nanoparticles are intermediates between the bulk materials and the atomic and molecular structures. Nanoparticles materials possess unique size dependent property known as specific surface area which is the ratio of surface area to volume. Smaller the size of particle greater will be the specific surface area. Larger surface area means more contact with the national switch enhance the reactivity and properties of the nanoparticles.

Nanotechnology has emerged as an interdisciplinary field combining biology, physics, and chemistry and material science. The production of nanoparticles can be achieved through two methodologies known as ‘top-down approach’ and ‘bottom-up method’. In the top-down method, the bulk material is broken down into particles at nanoscale through different processes like grinding, milling etc., In the bottom-up approach, the atoms self assemble to form new nuclei which grow into a particle of nanoscale.

Metal oxide NPs is involved high temperature response environments with the energy intensive technique such as laser ablation, ion implantation and chemical deposition. Metal oxides nanoparticles play a very important role in many areas of chemistry, physics and materials science[1].The metal elements are able to form a large diversity of oxide nanoparticles[2]. These can take on a vast number of structural geometries with an electronic structure that can show sharp insulator nature. In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the surfaces against corrosion. In the rising field of nanotechnology, a goal is to make nanoparticles with special properties of bulk or single particles[3]. Metal oxide nanoparticles can show unique physical and chemical properties due to their limited size and high density of corner or edge surface sites. Particle size is expected to influence three important basic properties. The first one compares the structural nature, to be correct the lattice stability and cell parameters[4-9]. Oxides are usually healthy and stable systems with well defined crystallographic structures. Conversely the growing importance of surface free energy and stress with declining particle size must be considered changes in thermodynamic stability associated with size can induce modification of cell parameters are structural transformations and in extreme cases, the nanoparticle can disappear due to interactions with its surrounding environment and at high surface free energy[10].

 In order to display mechanical or structural stability, nanoparticles must have a low surface free energy. As a result of this condition, phrases that have a low stability in nanoparticles can become very stable in nanostructures. Size induced structural distortions associated with changes in cell parameters have been observed, for example, in nanoparticles of zinc oxide, nickel oxide, cobalt oxide and copper oxide. As the particle size decrease, the increasing of surface and line atoms generate stress or strain and concomitant structural perturbations [11]. Beyond this “intrinsic” strain, there may be also “extrinsic” strain associated with a particular synthesis method which may be partially relieved by annealing or calcination. Also non stoichiometry is a common phenomenon [12]. On the other hand, interactions with the substrate on which the nanoparticles support can make difficult the situation and induce structural perturbations or phases not seen in the bulk state of the oxide [13-15]. The second important effect of size is related to the electronic properties of the oxide. In any material, the nanoparticles produce the quantum size or confinement effects which essentially arise from the presence of discrete atom like electronic states. From a solid-state point of view, these states can be considered as being a superposition of bulk like states with a concomitant increase in oscillator strength[16]. Additional general electronic effects of quantum incarceration experimentally probed on oxides are related to the energy shift of exaction levels and optical band gap.

An important factor to consider when dealing with the electronic properties of a bulk oxide surface are the long range effects of the made lung field, which are not present or limited in a nanostructure oxide. Metal oxides show a reorganization of charge when going from large periodic structures to small clusters or aggregate which must be roughly considered to be relatively small for ionic solids while significantly larger for covalent ones[17-20]. The degree of iconicity or covalence in a metal oxygen bond can however strongly depend on size in systems with partial ionic or covalent character, an increase in the ionic component to the metal-oxygen bond in parallel to the size decreasing has been proposed[21]. The incorporation of these techniques has provided a rapid prototyping technique, essential for the commercial development of current minimum feature sized semiconducting integrated circuits. However, the production of these devices has been achieved at a high price, with the primary challenges currently faced by high fabrication laboratories including the high cost of labourers and instruments, high-temperature reaction conditions. But more importantly, manufacturers are progressing in this manner at the expense of the environment, as they accumulate hazardous chemical [22]. For decades research teams in the semiconductor industry have been seeking alternative methods to passivity not only the rate of products but also the cost of spending. The most accessible resource for the synthesis of functional materials under ambient conditions is found in biology. From highly ordered nanostructures to genetically controlled reactive surfaces, systems in biology perpetually demonstrate their ability to find effective solutions to multifaceted, real-world problems using a rigorous process of natural selection[23].

The usefulness of biology incredible portfolio encourages researchers to develop modified synthesis derived from nature. Hence, their findings have been successfully organized into the field of bio mimetic or bio inspired research, which encompasses alternative approaches towards developing nanomaterials with technological applications[24-26]. Based primarily on the designs, mechanisms and processes found in nature, biomimetics encompasses the field of structural biology while interfacing engineering, materials science, physics and chemistry[27-30]. Biomimetics infers the manipulating and mimicking of natural architectures and processes of biologically produced minerals to direct the synthesis of non-natural materials. For instance, the architecture of one of the most abundant biological species on the planet the virus is recently been manipulated to serve as containers for the synthesis of a variety of functional molecular cargoes[31]. In particular, the positively charged interior of the cowpea chlorotic mottle virus (CCMV) has been used as a container for the nucleation of spatially confined metal oxide nanomaterials. On a larger and more complex scale, versatile strategies for substrate adaptation have been developed directly, through inspiration from the surface intervene mineralization of bioactive organisms[32].

The egg shell medium proteins from Chinese soft shelled turtle (composed primarily of aragonite, CaCO3) were isolated and revealed properties that are necessary for embryonic survival[33]. It is suggested that the matrix proteins contained pelovaterin peptides as their major unit that self-assembled into micelles, altering the interfacial energy of the eggshell. Applications of such controlled mineralization could be applied to the successful construction of functional two dimensional (2D) reactive surfaces, with reduced nonspecific adsorption[34–37]. In fact, most strategies incorporated by natural systems are not directly applicable to engineered materials, so the need for alternative synthetic routes are required for the incorporation of non-natural elements, such as barium, nickel, copper or aluminium, with functional nanoscale properties[38].

The details of a wide variety of mediated nanomaterial synthesis, their response to variable parameters and their ability to retain a functionalized, controlled stability over time. Structural and electronic properties obviously drive the physical and chemical properties of the solid. Many oxide nanoparticles have wide band gaps and a low reactivity[39]. A decrease in the average size of an oxide particles do in fact change the magnitude of the band gap, with strong influence in the conductivity and chemical reactivity[40-42]. Surface properties are somewhat particular group included in this subject due to their importance in chemistry. Solid, gas, liquid chemical reactions can be mainly confined to the surface and sub-surface regions of the solid. The two dimensional (2D) nature of surfaces has notable structural, typically a rearrangement or reconstruction of bulk geometries and electronic[43-46]. Furthermore, the presence of under coordinated atoms (like corners or edges) vacancies in an oxide nanoparticle should produce specific geometrical arrangements as well as occupied electronic states located above the valence band of the corresponding bulk material, enhancing in this way the chemical activity of the system[47-50].We will analyse how nanoparticles oxides are synthesized, their most significant physicochemical properties, and will focus the ending part on several, well-known oxides.

**2. Metal Oxides in Nature**

To date as many as biominerals have been identified as being necessary for the correct function of organisms, and more than 60% of these are reported to be coordinated to either hydroxyl moieties or water molecules, enabling the rapid release of ions in solution[51]. Metal oxides, in particular, provide a fundamental stepping stone for the development of functional nanomaterials. In an oxidative environment, such as the atmosphere of the earth, oxides are the lowest free energy states for most metals in the periodic table and demonstrate applications ranging from semiconductors to insulators[52]. As insulators, SiO2 and Al2O3 are the two most commonly used supports for catalysis, as they are irreducible oxides. Semiconductors, such as ZnO and SnO2, have high electrical resistivity that provides alternative templates for gas sensors. Surprisingly, the properties associated with metal oxides in technology are not so far removed from what is observed in natural systems. Through precisely tuned processes, nature is able to synthesize a variety of metal oxide nanomaterials under ambient conditions, the magnetic navigation device found in magnetotactic bacteria is one such example[53]. Here, magnetite nanocrystals are aligned with the Earth’s geomagnetic field and contained within specific organelles known as magnetosomes. Freshwater salmon for example utilizes these magnetic nanoparticles in the nasal cavities of their forehead as a biomagnetic compass during migration[54].

**3. Advantages of Nanoparticles**

The advantages of using nanoparticles include the following:

* Particle size and surface characteristics of nanoparticles can be easily changed to achieve both passive and active drug targeting after parenteral administration.
* They control and sustain release of the drug during the transportation and at the site of localization, altering organ distribution of the drug and subsequent clearance of the drug so as to achieve the increase in drug therapeutic efficacy and reduction in side effects.
* Controlled release and particle degradation characteristics can be readily modulated by the choice of matrix constituents. Drug loading is relatively high and drugs can be incorporated into the systems without any chemical reaction; this is an important factor for preserving the drug activity.
* Site-specific targeting can be achieved by attaching targeting ligands to the surface of particles or use of magnetic guidance.
* The system can be used for various routes of administration including oral, nasal, parenteral, intraocular etc. Limitations of nanoparticles In spite of these advantages, nanoparticles do have limitations.
* For example, their small size and the large surface area can lead to particle-particle aggregation, making physical handling of nanoparticles difficult in liquid and dry forms.
* In addition, small particle size and large surface area readily result in limited drug loading and burst release. These practical problems have to be overcome before nanoparticles can be made commercially available. The present review details the latest development of nano particulate drug delivery systems, surface modification issues, drug loading strategies, release control and potential applications of nanoparticles.

**4. Properties of Metal Oxide nanoparticles**

Physical and chemical properties of nanoparticles that may change at the nanoscale include.

* Color.
* Melting temperature.
* Crystal structure.
* Chemical reactivity.
* Electrical conductivity.
* Magnetism.
* Mechanical strength.

Oxides are becoming a very promising n-type oxide semiconductor. In the past decade, global research interest in wide band gap semiconductors is attracted towards oxide due to its excellent properties as a semiconductor material. The high electron mobility, high thermal conductivity, good transparency, wide direct band gap 3.37 ev, large exaction binding energy and easiness of growing it in the nanostructure form make metal oxide suitable for optoelectronics, transparent electronics, lasing, sensing and a wide range of applications.[55-59]

**4.1 Mechanical properties**

Main mechanical properties concern low yield (stress and hardness) and high (super plasticity) temperature observables. High heat capacity, high heat conductivity, low thermal expansion high melting point (1300oC) and Soft material with an approximate hardness of 4.5 mohs scales.[60-65]

**4.2 Chemical properties**

Metal oxides are used for both their redox and acid/base properties in the context of absorption and catalysis. They are used as additive to concrete, sunscreens, skin care lotions, antifungal properties, food additive, vulcanization of rubber, natural rubber related polymer converting more durable materials adding sulphur (accelerator) forming cross-links.

Doping refers to the intentional introduction of impurities into a material and is applied in many semiconductor industry fields[66-69]. Introducing impurities is fundamental to controlling the properties of bulk semiconductors and this has stimulated similar efforts to dope semiconductor nanocrystals[70-74]. Much work has been done to explore how dopants can influence semiconductor nanocrystals, crystallites a few nanometres in scale with unusual and size-specific optical and electronic behaviour[75]. The promise of nanocrystals as a technological material, for applications including solar cells, bio imaging and wavelength-tuneable lasers, may ultimately depend on tailoring their behaviour through doping.

Impurities can strongly modify electronic, optical and magnetic properties of bulk semiconductors[76]. For instance, it is reported that a substitution impurity with one more valence electron than the host atom it replaces can be ionized by thermal energy and donate its extra electron to the semiconductor (n-type doping). These electrons or holes are then available as carriers of electrical current. For nanocrystals, where applications often require thin conducting films, the ability to introduce these carriers is essential. Besides, dopants can also strongly influence the optical behaviour of materials. Take Co, Se nanocrystals are an example, the lasing threshold in these quantum dots can be reduced threefold by adding extra electrons[77]. As for the bio-imaging applications, fluorescent dopants may mitigate toxicity problems by producing visible or infrared emission in nanocrystals made from less harmful elements than those currently used. Moreover, carriers whose spins are aligned one way are conducted preferentially, while others are blocked, an effect that could be used in future spintronic devices[78].

In chemical vapour deposition (CVD), substrates are heated to high temperatures and exposed to precursor materials in the gaseous state. The precursors react or decompose on the substrate surface to form nanomaterial[79]. In chemical vapour synthesis (CVS) approach, within a flow reactor pure metal or metal–organic salts are by heating transformed into the vapour phase and introduced into a hot-wall reactor where they react with the oxidizing agent under conditions that favour the chemical[80-83]. Usually an inert gas, such as Ar , is used to carry the gaseous reactants to the reaction zone where nucleation and crystal growth occur. Finally, the product that is also in the gas phase is carried to a much cooler zone where it due to such temperature gradient transforms into a solid state and can get collected.

These methods are extensively employed to produce uniform and contamination-free metal oxide nanoparticles and films, such as ZnO nanowires, films and defect free ZnO nanoparticles nanocubes and nanospheres of magnetite, CuO, MgO and CaO, CoO[84]. When multi-metal oxides are considered, this technique allows for the production of B-doped ZnO, europium Li-doped MgO, Ca-doped. Moreover, via CVS technique Zn2+cations may selectively replace Mg2+ surface cations preferentially at the edges and corners of MgO nanocubes that resulted in unique optical and chemical surface properties of ternary ZnxMg1−xO nanoparticles. Reproducibility is another advantage associated with this method[85]. Careful choice of experimental parameters such as for instance the nature and concentration of the oxidizing agent used has a major effect on the nucleation process and consequently affects the average size of the particles. This has been reported for ZnO nanoparticles which could be produced via CVS technique in the average size ranging from 3, 5 or 11mm depending whether N2O or O2 or dry air were used as the oxidizing agent.

Control over particle size can be also realized by varying the reaction temperature since the nucleation and growth kinetics can be controlled by manipulation of temperature and reactant concentration[86]. Reactant delivery, reaction energy input and product separation may also affect the characteristics and quality of the product. These techniques can be modified to obtain desirable attributes in the nanoparticles and eliminate limitations associated with volatility of the reactants and degree of agglomeration. Some examples are laser assisted, electro spray assisted, thermally activated paralytic, metal organic, plasma-assisted and photo CVD methodologies. For instance, electro spray assisted chemical vapour deposition is employed to synthesize no agglomerated spherical titanium and zirconium oxide nanoparticles[87]. Winterers have used a laser assisted technique to synthesize Ni and Co doped with ZnO magnetic semiconducting nanoparticles.

Nanoparticle metal oxides represent a new class of important materials that are increasingly being developed for use in research and health-related applications. Highly ionic metal oxides are interesting not only for their wide variety of physical and chemical properties but also for their antibacterial activity. Although the in vitro antibacterial activity and efficacy of regular zinc oxides have been investigated, little is known about the antibacterial activity of nanoparticles of ZnO. Preliminary growth analysis data suggest that nanoparticles of ZnO have significantly higher antibacterial effects on staphylococcus aureus.

 Metal oxide nanomaterials like ZnO and CuO have been used for several purposes, a common feature that these nanoparticles exhibit is their antimicrobial behaviour against pathogenic bacteria. The antimicrobial activity of ZnO, CuO, and Fe2O3 nanoparticles against Gram-positive and Gram-negative bacteria. The nanosized particles of pure ZnO, CuO, and Fe2O3 were synthesized by the sol-gel combustion method. Furthermore, the antibacterial activity of all the three synthesized nanomaterials is compared and varied considerably. Antimicrobial activity increased with increase in surface to volume ratio due to a decrease in particle size of nanoparticles. Here, ZnO nanoparticles showed excellent bactericidal potential, while iron oxide nanoparticles had the least bactericidal activity. Our results indicate that nanomaterials were most effective against Gram-positive bacterial strains compared to Gram-negative bacterial strains [88].

ZnO is currently being investigated as an antibacterial agent in both microscale and nanoscale formulations. ZnO exhibits significant antimicrobial activities when particle size is reduced to the nanometer range, then nanosized ZnO can interact with bacterial surface and with the bacterial core where it enters inside the cell, and subsequently exhibits distinct bactericidal mechanisms [89-96].

ZnO nanoparticles have a wide range of antibacterial effects on a number of other microorganisms. The antibacterial activity of ZnO may be dependent on the size and the presence of normal visible light. The data suggest that ZnO nanoparticles have a potential application as a bacteriostatic agent in visible light and may have future applications in the development of derivative agents to control the spread and infection of a variety of bacterial strains [97].

The antibacterial activity of ZnO nanoparticles with various particle sizes. ZnO is prepared by the base hydrolysis of zinc acetate in a precipitation method using Zn(NO3)2 and NaOH. Bacteriological study showed the enhanced biocide activity of ZnO nanoparticles compared with bulk ZnO in repeated experiments. This demonstrated that the bactericidal efficacy of ZnO nanoparticles increases with decreasing particle size. It is proposed that both the abrasiveness and the surface oxygen species of ZnO nanoparticles promote the biocide properties of ZnO nanoparticles [98]. New materials with good antibacterial activity and less toxicity to other species attract numerous research interests. Taking advantage of zinc oxide (ZnO) and graphene oxide (GO), the ZnO and GO composites were prepared by a facile one-pot reaction to achieve superior antibacterial properties without damaging other species. In the composites, ZnO nanoparticles, with a size of about 4 mm, homogeneously anchored onto GO sheets. The typical bacterium Escherichia coli and HeLa cell were used to evaluate the antibacterial activity and cytotoxicity of the ZnO and GO composites, respectively. The synergistic effects of GO and ZnO nanoparticles led to the superior antibacterial activity of the composites. GO helped the dispersion of ZnO nanoparticles, slowed the dissolution of ZnO, acted as the storage site for the dissolved zinc ions, and enabled the intimate contact of E. coli with ZnO nanoparticles and zinc ions as well. The close contact enhanced the local zinc concentration pitting on the bacterial membrane and the permeability of the bacterial membrane and thus induced bacterial death. In addition, the GO doped ZnO composites were found to be much less toxic to HeLa cells, compared to the equivalent concentration of ZnO nanoparticles in the composites. The ZnO and GO composites are promising disinfection materials to be used in surface coatings on various substrates to effectively inhibit bacterial growth, propagation, and survival in medical
devices [99].

The antibacterial properties of zinc oxide nanoparticles were investigated using both Gram-positive and Gram-negative microorganisms. These studies demonstrate that ZnO nanoparticles have a wide range of antibacterial activities toward various microorganisms that are commonly found in environmental settings. The antibacterial activity of the ZnO nanoparticles is inversely proportional to the size of the nanoparticles in S.aureus. Surprisingly, the antibacterial activity did not require specific UV activation using artificial lamps; rather activation is achieved under ambient lighting conditions. Northern analyses of various reactive oxygen species (ROS) specific genes and confocal microscopy suggest that the antibacterial activity of ZnO nanoparticles might involve both the production of reactive oxygen species and the accumulation of nanoparticles in the cytoplasm or on the outer membranes. Overall, the experimental results suggest that ZnO nanoparticles could be developed as antibacterial agents against a wide range of microorganisms to control and prevent the spreading and persistence of bacterial infections [100].

The effect of zinc oxide (ZnO) nanoparticles prepared by mechano chemical method on the antibacterial activity of different antibiotics is evaluated using disk diffusion method against Staphylococcus aureus and Escherichia coli. Although ZnO nanoparticles (500μg) decreased the antibacterial activity of amoxicillin, penicillin G, and nitro furcation in S. aureus, the antibacterial activity of ciprofloxacin increased in the presence of ZnO nanoparticles in both test strains. A total of 27% and 22% increase in inhibition zone areas is observed for ciprofloxacin in the presence of ZnO nanoparticles in S. aureusand E. coli, respectively. The enhancing effect of this nanomaterial on the antibacterial activity of ciprofloxacin is further investigated at three different contents (500, 1000 and 2000 μg/disk) against various clinical isolates of S. aureus and E. coli.

The enhancing effect of ZnO nanoparticles on the antibacterial activity of ciprofloxacin is concentration-dependent against all test strains. The source of toxicity of copper oxide nanoparticles with respect to its leaching characteristic and speciation. Complexion mediated leaching of CuO nanoparticles by amino acids is identified as the source of toxicity toward Escherichia coli, the model microorganism used in the current studies. The leached copper–peptide complex induces a multiple-fold increase in intracellular reactive oxygen species generation and reduces the fractions of viable cells, resulting in the overall inhibition of biomass growth. The cytotoxicity of the complex leachate is however different from that of equivalent soluble copper salts (nitrates and sulphates). A pH-dependent copper speciation during the addition of copper salts gives rise to uncoordinated copper ions, which in turn result in greater toxicity and cell lysis, the latter of which is not observed for CuO nanoparticles even at comparable pH. Since leaching did not occur with micrometer-sized CuO, no cytotoxicity effect is observed, thus highlighting the prominence of materials toxicity at the nanoscale[101]. ZnO nanoparticles have been synthesized with and without the use of surfactants under different reaction conditions [102].

Nano knowledge is the creation and use of materials at the smallest possible scale. Nanotechnology can be useful in investigative techniques, drug delivery, sunscreens, antimicrobial bandages, disinfectant, a friendly manufacturing process that reduce waste products (ultimately leading to atomically precise molecular manufacturing with zero waste), a catalyst for greater efficiency in current manufacturing process by minimizing or eliminating the use of toxic materials, to reduce pollution (e.g. Water and air filters) and an alternative energy production (e.g. Solar and fuel cells)[103]. Bio nanotechnology is the integration between biotechnology and nanotechnology for developing biosynthetic and environmental friendly technology for the synthesis of nanomaterials[104]. Nanoscale particles have emerged as novel antimicrobial agents owing to the high surface area to volume ratio, which is coming up as the current interest in the researchers due to the growing microbial resistances against metal ions, antibiotics and the development of resistant strains. The recent growth in the field of porous and nommetric materials prepared by non-conventional processes has stimulated the search of new applications of ZnO nanoparticulate[105]. Zinc oxide is an interesting semiconductor material due to its application on solar cells, gas sensors, ceramics, catalysts, cosmetics and visitor[106].

Chemical method is used to the preparation of ZnO nanoparticles[107]. Nano materials obtained were thermally treated at various temperatures. The influence of temperature on structural, textural, and morphological properties of the materials is studied by powder X-ray diffraction, infrared spectroscopy, scanning electron microscopy, nitrogen adsorption and thermal analysis[108]. Certain chemicals can interfere directly with the proliferation of microorganisms at concentrations that can be tolerated by the host. The antimicrobial activity of zinc oxide nanoparticles is well known[109]. Hence we make use of this property to inhibit growth of Bacillus subtitles, Escherichia coli using disc diffusion method[110]. These two bacterial strains were selected as they are highly contagious; thence we can evaluate the potential antimicrobial activity of zinc oxide nanoparticles.

The transition metal oxide is greatly attracted towards a wide range of application in durable solar absorber lithium-ion battery as an electrode material, super capacitor sensor[111]. Among the transition metal groups, cobalt oxide is one of the most important materials because of its fascinating properties and thermal stability[112]. The Co structure of p-type semiconducting materials stability at high temperature, high mechanical strength and direct band gap1.48-2.19eV. The cobalt oxide nanoparticles show good conductivity due to the existence of Co3+[113]. Reported the synthesis of CoO nanoparticles at 450oC using a solgel method.

Nanostructure materials have been widely investigated for the fundamental scientific and technological interests in accessing new classes of functional materials with unprecedented properties and applications[114]. CoO is a very important material extensively used in catalysis, gas sensors, electrochromic films, battery cathodes, heterogeneous catalytic materials and magnetic materials[115].

Cobalt oxide nanoparticles exhibit interesting properties and applications when compared with their bulk, such as lithium storage[116]. The most stable phase of cobalt oxides with a direct band gap of 1.48- 2.19 eV, is used as a p-type semiconductor and received considerable attention[117]. Various methods have been developed to synthesize CoO nanoparticles, including the hydrothermal, microwave assisted and reverse micelles[118]. However, the hydrothermal method is green and less expensive. Synthesis of CoO nanoparticles via hydrothermal method generally requires reducing and precipitating agents. Until now, various nanoparticles of CoO have been prepared by different methods[119]. Therefore, development of a facile and rapid method to prepare high purity CoO nanoparticles having various morphologies is highly desirable [120]. Here in the report synthesis, characterization and possible growth mechanism of CoO nanoparticles by hydrothermal method.

A nanoparticle is prepared in aqueous KOH solution with stabilizing agents by hydrothermal method[121]. Have been studied electrical conductivity of cobalt oxide at the different temperature. The Co method is a simple process for the formation of nanoparticle and size of nanoparticles controlled by using this method[122]. The composites of different metal oxide can be prepared using this method and modified particle surface by doping other nanoparticles.

Magnetic cobalt nanoparticles, exhibit unique phenomena such as super par magnetism, high coercively, high saturation field and exchanged anisotropy due to a thin layer of antiferromagnetic oxide formed around the ferromagnetic core of the nanoparticles because of their subsequent exposure to air. These phenomena are attributed to size and surface effects that dominate the behaviour of magnetic particles in nanosized range[123-125]. Co is a well-known ferromagnetic material which is commonly used as an alloying element in permanent magnets. In recent years, many efforts have been devoted to the synthesis of CoO nanostructures with different morphologies such as nanoparticles, hollow spheres, nanorods, nanoplates, nanowires, nanotubes and nanocubes and nanoporous structures have been prepared[126].

CoO nanoparticles have been prepared by various physical and chemical techniques such as combustion method, microwave irradiation, hydrothermal and solvothermal method, solgel process, chemical spray pyrolysis, sonochemical method, polyol method. Most of these methods need some special instruments, harsh conditions and relatively high processing temperature higher than 350°C. In addition, these methods are either time-consuming or require expensive instruments[127].

Among various soft chemical methods for preparing nanoscale materials, the thermal decomposition method is widely used due to the process simplicity[128-130]. This technique offers several unique advantages over other methods including easy work-up, low-temperature processing, short reaction time and production of inorganic nanomaterials with narrow size distribution. In recent years, several precursors have been used to synthesize CoO nanoparticles via the thermal decomposition technique[131]. However, the most important issue in this technique is to design a precursor which would allow the synthesis of nanomaterials at a low temperature.

Applications such as catalysts, gas-sensors, electrochromic film, fuel cell, magnetic materials, an anode of the organic light emitting diodes and thermoelectric materials, considerable attention has been focused on the production of nanostructured metal oxide materials such as NiO nanoparticles. Nickel oxide (NiO) is an important transition metal oxide with the cubic lattice structure. It has attracted increasing attention owing to potential use in a variety of applications such as catalysis, battery cathodes, gas sensors, electrochromic films and magnetic materials. It can also be extensively used in dye sensitized photocathodes. It exhibits anodic electrochromism, excellent durability and electrochemical stability, large spin optical density and various manufacturing possibilities[132]. Also for low material cost as an ion storage material, NiO semiconductor becomes a motivating topic in the new area of research. Because of the volume effect, the quantum size effect, the surface effect and the macroscopic quantum tunnel effect, nanocrystalline NiO is expected to possess many improved properties than those of micrometre-sized NiO particles.

Presently, microbial resistance to antibiotics has been reaching a critical level. In exploring various options to address this problem, inorganic nanomaterials, like metal oxide nanoparticles, have emerged as promising candidates since they possess greater durability, lower toxicity and higher stability and selectivity when compared to organic ones. Nanostructured metal oxides have already been extensively studied for their promising use in technology. This has resulted in the development of numerous reproducible procedures for the synthesis of nanoparticles with desired characteristics like size, shape, morphology, defects in the crystal structure, mono disparity providing a rich background for research relevant to antibacterial applications. Characterization of these nanoparticles can be helpful in modifying and tuning their antibacterial and cytotoxic effects. For instance, it has been established that the antibacterial activity increases with decreasing the particles size[133]. Recent achievements in nanotechnology of metal oxides include an elaboration of nanostructured oxides consisting of two or more metallic components.

Their potential applications are immense due to their unique electronic, optical, magnetic and other physicochemical properties[134]. Multi metal oxide nanoparticles are being studied extensively as potential antimicrobial agents owing to the beneficial synergistic effects of their components. These nanoparticles have shown promising solutions to problems seen in pure metal oxide nanoparticles, like high cytotoxicity or agglomeration. We have discussed the existing synthesis routes and the antibacterial activity of metal oxide nanoparticles with a particular focus on polymetallic oxides. Additionally, a strong emphasis has been given to their cytotoxic nature.

**5. Different methodologies for the synthesis of metal oxide nanoparticles**

Mainly two methodologies have been used for the synthesis of nanomaterials. Top–down and Bottom–up are the two approaches. Top–down method involves mainly physical methods where abulk material is cut into pieces till the desired size is achieved. Lithographic techniques, laser induced chemical etching and ball milling fall in to this category. However, these methods are effective only down to the micrometer level. Reaching nanometer scale makes these methods more expensive and technically difficult. The Bottom–up method mainly involves chemical and biological approaches to make nanoparticles. These involve controlled condensation of solute molecules that is formed during a chemical reaction. The restriction of the condensation or the growth leads to the formation of particles of desired size and shape. However unlike the chemical synthesis of molecules of a desired structure, the synthesis of nanomaterials with uniform size and shape is difficult. Thus, large scale synthesis of nanomaterials remains a challenge [135].



**Fig.1.Top-Down and Bottom-Up Approaches for Synthesis**

**6. Nanoparticles**

The development of systematic studies for the synthesis of oxide nanoparticles is a current Challenge and essentially the corresponding preparation methods may be grouped in two main streams based upon the liquid-solid and gas-solid nature of the conversions. Liquid-solid conversions are possibly the most broadly used in order to control morphological characteristics with certain “chemical” versatility and usually follow a “Bottom-up” method.

**7.**  **Liquid phase synthesis**

Precipitating nanoparticles from a solution of chemical compounds can be classified into five major categories:

* Co-Precipitation method.
* Sol-Gel method.
* Micro emulsion method.
* Solvothermal method.
* Chemical Vapor Deposition method.
* Ball milling.
* Green Chemical Synthesis.

7.**1 Solution precipitation**

The precipitation of nanometersized particles with in a continuous fluid solvent. An inorganic metal salt, such as nitrate and so on is dissolved in water. These hydrates are added with basic solutions, such as KOH. The hydrolyzed species condense and then washed, filtered, dried and calcined in order to obtain the final product.

7.2 **Co-Precipitation method**

The Co-precipitation Method involves dissolving a salt precursor in water (or other solvent) to precipitate the hydroxide form with the help of a base. However, the use of surfactants, Sol-gel method and high-gravity reactive precipitation appear as novel and viable alternatives to optimize the resulting solid morphological characteristics.

**7.3 Sol-gel method**

The Sol-gel method provides a highly useful means of preparing inorganic oxides. It is a wet chemical method and a multistep process involving both chemical and physical processes such as hydrolysis, polymerization, drying and densification. The name sol-gel is given to the process because of the distinctive viscosity increase that occurs at a particular point in the sequence of steps.

Most of the so-gel literature deals with synthesis from all oxides. The sol-gel techniques have better advantages such as homogeneity compared to the traditional methods, high purity, lower processing temperature and more uniform phase distribution in multicomponent systems, better size and morphological control, the possibility of preparing new crystalline and nanocrystalline materials. The various steps in the sol-gel technique may or may not be strictly followed in practice. Thus, many complex metal oxides are prepared by a modified sol-gel route without actually preparing metal all oxides e.g. a transition metal salt solution is converted into a gel by the addition of an appropriate organic reagent.

**7.4 Micro emulsion method**

Micro Emulsions represent an approach based on the formation of ternary mixture containing water, surfactant and oil. Metal precursors on water will precede precipitation as oxo-hydroxides within the aqueous droplets, typically leading to monodispersed materials with size limited by the surfactant-hydroxide contact.

**7.5 Solvothermal method**

In solvothermal method, metal complexes are decomposed thermally either by boiling in an inert atmosphere or using an autoclave with the help of pressure. A suitable surfactant is usually added to the reaction media to control particle size growth and limit agglomeration. The solvothermal method uses a solvent under pressure and temperature above its critical point to increase the solubility of solids and to speed up reactions of solids. Most materials can be made soluble in the proper solvent by heating and pressurize the system near to its critical point. Lower supersaturation state can be achieved by this method.

**7.6** **Chemical Vapor Deposition (CVD) method**

There are a number of CVD processes used for the formation of nanoparticles, some of them are classical, metal-organic, plasma-assisted and photo Chemical Vapor Deposition (CVD) methodologies. The advantages of this methodology consist of producing uniform, pure and reproducible nanoparticles and films although requires a careful initial setting up of the experimental parameters.

7.7 **Pechiney method**

This method is named after its American inventor, MaggioPechiney.Wet chemical powder preparation techniques (the Pechiney method and the glycine-nitrate method) are investigated in order to obtain powders with characteristics appropriate for cathode fabrication. In the field of electroceramics, synthesis of ceramic powder is a crucial factor since the powder characteristics can affect the subsequent processing steps and influence the properties of the final sintered body. Pechiney method is easy to perform and yield pure fine powders with a good chemical homogeneity. The Pechiney method is based on the ability of certain alphahydroxyl carboxylic acids to form the polybasic acid chelate with metallic ions. This process is completed by calcing ash products at higher temperature.

**8. Green Synthesis of nanoparticles**

Nanoparticles can be synthesized by physical, chemical and biological paths. The conventional physical and chemical methods for nanoparticle production have some adverse aspects like critical conditions of temperature and pressure, use of expensive and toxic chemicals, long reflux time of reaction, toxic by-products etc.

Biosynthesis of nanoparticles employs a biological system or its components for the formation of nanoparticles. The biological entities may vary from simple microorganisms like bacteria or fungi and plants. The plant-mediated synthesis, usually called as the ‘green synthesis’ is safe and a one-step protocol towards the synthesis of nanoparticles. The unique property of metal tolerance of plants has been exploited in the green synthesis of nanoparticles. Green synthesis is a kind of bottom-up approach wherein the bioactive phytochemicals derived from plants are utilized for the production of nanoparticles.

The use of plants in the synthesis of nanoparticles has become one of the popular alternatives over the conventional methods. They are several advantages of green synthesis over other procedures.

Abstract research on nanomaterials has been revolutionized in the last few years because of the attractive properties they have in comparison to the bulk phase of similar materials. These are physical, chemical, catalytic and optical properties. Among these nanomaterials, the metal oxide nanostructures have become of particular interest to scientists for the development of different optical, biochemical and biomedical nanodevices. In the present research work using the advantageous features of nanotechnology, high performance nanodevices for optoelectronics with a wide band gap compound nanostructure and highly sensitive sensor devices have been demonstrated. The nanotechnology is used to fabricate sensitive and precise nanodevices based on nanomaterials for the application of sensing. Among the metal oxide nanostructures, ZnO, CuO and NiO are attractive materials because of their unique properties, their high surface area to volume ratio, their energy band gap of 3.37 eV, 1.2 eV and 3.7 eV, respectively, biocompatibility, high electron mobility, fast electron transfer rate and they are envirommental friendly in many applications. When used in sensor devices, nanomaterials have indicated high selectivity for possible use to detect the various analytics even in small volumes. Metal oxide nanostructures have shown to be good for optoelectronic nanodevices because of their electrical characteristics, high optical absorption and low processing temperature. The synthesis of different morphologies of metal oxide semiconductor nanostructures and their composite using the hydrothermal method are demonstrated for various applications. ZnOnanorods using different concentrations of composite seed layer of inorganic and organic materials when using the hydrothermal growth method is presented. The effect of the composite seed layer on the abstract aligmment, density and optical properties of the grown ZnO nanorods. Utilizing the advantage of ZnO nanostructure, a comparative study of ZnO nanorods and thin films for chemical and biosensing application is carried out. The ZnOnanorods and thin films were functionalized with strontium ionophore membrane, immobilized the galactose oxidase and lactate oxidase for determining the strontium ions, D-galactose and L-lactic acid. The effects of different urea concentrations on the morphology of CuO nanostructures is studied as described, CuOnanoflowers were functionalized with cadmium ion ionophore for the detection of Cd ions, while CuO nanosheets were grown by the low temperature growth method and were used for the development of a nonenzymatic glucose sensor, composite nanostructures of CuO doped with ZnO and NiO doped with ZnO were applied to develop dopamine sensor and fast sensitive UV photodetector respectively. A nanohybrid of CuO doped with ZnO nanostructure is used as a non-enzymatic electrode to detect dopamine by cyclic voltametry and amperometric techniques UV absorption from ZnO nanosheets achieved by the supra molecules assisted growth solution using the hydrothermal method. The synthesized nanomaterial is used in the fabrication of UV photodetector based on p-NiO doped n-ZnO hetero structures.

**8.1 Merits of green synthesis**

* Simple and fast.
* Inexpensive and cost effective.
* Good stability of nanoparticles.
* Non-involvement of toxic chemicals.
* Non-toxic byproducts.
* Eco-friendly.
* Safe to handle.
* Easy availability of variety of sources (renewable reducing agents).
* Suitable for large scale production at lower cost.
* Compatible for pharmaceutical and biomedical applications.

 The green synthesis process involves two basic mechanisms namely, “reduction”and “stabilization”capping). The bio-molecules present in the plants such as proteins, amino acids, vitamins, polyphenols, polysaccharides, terpenoids, organic acids are responsible for the synthesis of nanoparticles. These bio-molecules mediate the synthesis by reducing metal ions into neutral atoms as well as stabilize the growth of nanoparticles formed with desired size and shape.

* Raw materials used (extracts of leaves, flowers, seeds, fruits, stems, roots whole plants, etc.)
* Phytochemicals present in the extract
* Choice of solvent medium (water, methanol, ethanol, hexane, etc.)
* Extraction procedure (drying, boiling, filtering, centrifugation)
* Temperature of reaction process and incubation
* pH of the reaction medium.

One of the plant materials is given as an example that is militia pinnate belongs to the family pea family, Fabaceae, native in tropical and temperate and is one of the important pulse crops of India. It is a source rich in proteins containing up to 25%. Alkaloids, amino acids, polyphenols, glycosides, terpenoids and steroids have been identified as major phytochemicals present in Indian Beach. The sprout of germinated seeds of Indian Beach is well known for its high content of proteins which play the vital role in the stabilizing mechanism of the green synthesis of nanoparticles. Similarly, green tea is a rich source of polyphenols, amino acids, proteins, terpenoids, etc. Which are critically important for the efficient green synthesis of nanoparticles.

**9. Conclusion**

The metal oxide is non-toxic material and is listed as ‘generally recognized as safe’ (GRAS) by the United States food and drug administration. Due to the antimicrobial properties metal oxide has been used as linings and coating in food containers. Metal oxide nanoparticles, owing to their small size and larger specific surface area exhibit enhanced antimicrobial activities. Several mechanisms of antimicrobial activity have been proposed by several authors.

**10. References**

1. [Greiner, D., Papathanasiou, N., Pflug, A., Ruske, F., Klenk, R. International Journal on the Science and Technology of Condensed Matter Films.](http://refhub.elsevier.com/S0927-0248%2814%2900323-7/sbref12),[**2009,** 517.](http://refhub.elsevier.com/S0927-0248%2814%2900323-7/sbref12)

1. [Murdoch, G.,Hinds, S.,Sargent, E.,Tsang, S., Lu, Z.,Journal of Applied physics,Lett.](http://refhub.elsevier.com/S0927-0248%2814%2900323-7/sbref13),[**2009**, 94**.**](http://refhub.elsevier.com/S0927-0248%2814%2900323-7/sbref13)
2. [Ruske,F., Roczen,M., Lee,K., Journal of Applied physics., **2010**,107 (1).](http://refhub.elsevier.com/S0927-0248%2814%2900323-7/sbref14)
3. [Acharya, A., Moghe,S., Panda,R., Phase,D., Ganesan,V., T International Journal on the Science and Technology of Condensed Matter Film solidFilms., **2012,** 516**.**](http://refhub.elsevier.com/S0927-0248%2814%2900323-7/sbref16)
4. [Bai,L., Zheng,B., Lian,J., Jiang,Q., Solid State Sciences journal of Elsevier.,**2012**, 14 (6) 698.](http://refhub.elsevier.com/S0927-0248%2814%2900323-7/sbref17)
5. [Fan,X., Sun,H., Shen,Z., Lu,Y., [Journal of Physics: Condensed Matter](http://iopscience.iop.org/journal/0953-8984).,**2008**, 20 (23) 235221.](http://refhub.elsevier.com/S0927-0248%2814%2900323-7/sbref18)
6. [Mahmoud, W.E., Ghamdi, A.L., El-Tantawy, F., Al-Heniti, S., Journal of AlloysCompd., **2009**, 485**.**](http://refhub.elsevier.com/S0927-0248%2814%2900323-7/sbref20)
7. [Tang,H., Lü,H., Zhang,Q., Zhao,J., Lin,Y., Solid State Sciences journal of Elsevier.,**2011**, 13 (2)384.](http://refhub.elsevier.com/S0927-0248%2814%2900323-7/sbref22)
8. [Vijayalakshmi, S., Venkataraj, S., Jayavel, R.,Journal of Applied physics.,**2008**, 41-45403.](http://refhub.elsevier.com/S0927-0248%2814%2900323-7/sbref25)
9. Chen, X., Y, Yip., C.T, Fung., Chan, MK., Journal of Applied physics., **2010,** 100.
10. Hoertz, P., Chen,G., Kent,C., Meyer,T., Journal of Inorganic Chemistry., **2010**, 8179.
11. Nofz, M., Sojref, R.,Feigl, M., Dressler,M., Doerfel,I., Keram,K.,[Journal of Physics: Condensed Matter](http://iopscience.iop.org/journal/0953-8984).,**2009**, 27.
12. Yang, X., Peng, X., Xu,C., Wang, F., Journal of the Electrochemical Society., **2009,** 167.
13. Hoertz, P., Chen,Z., Kent. C., Meyer, T., Journal of Inorganic Chemistry.,**2010,** 8179.
14. Lopez-Garcia, J. Maffiotte,C., Guillen. C., Solar Energy Materials & Solar Cells journal of Elsevier., **2010.**
15. Nofz,M., Sojref, R., Feigl, M., Dressler, M., Doerfel, I., Keram,K.,[Journal of Physics: Condensed Matter](http://iopscience.iop.org/journal/0953-8984)., 2009.
16. Yang,X., Peng, X. Xu, C., Wang,F., Journal of the Electrochemical Society. **2009,**167**.**
17. Shigeta,P., Goto, K., Journal of applied physics.,. **2009,**10**.**
18. Zmara,D., Grinblat J., Margel S. The Journal of Materials Chemistry.,**2012,** 22:2188–95.
19. Kasmi,A., Tian Z-Y., Vieker, H., Beyer A., Chafik, T. Applied Catalysis B: Environmental journal of Elsevier., **2016,**186:10–8.
20. Naeem, R., Ahmed, S., Lo, KM., Basirun, WJ.,Sagu JS., Wijayantha, K., Depos.journalof Sensor Letters is a multidisciplinary.,**2015,** 21:360–8.
21. Haniam,P., Kunsombat, C., Chiangga, S., Songsasen, A. The Scientific World Journal.,**2014.**
22. Yadav, SC., Uplane, MD. International Journal of Engineering Science and Technology**., 2012.**
23. Pflitsch, C., Siddiqui, R., Atakan,B., Journal of Applied physics., **2008,**90, 527.
24. Azam,A., Ahmed,AS., Oves,M., Memic,A. International Journal of Nanomedicine., **2012** 7:3527 –3535.
25. Raghupati, KR., Koodali, RT., Manna, AC., Langmuir is a peer-reviewed scientific journal.,**2011,** 27:4020– 4028.
26. Mahapatra,O., Gopalakrishnan,C., Arunachalam, KD. **2008,**Journal of Experimental Nanoscience., 3:185–193.
27. Tran,N., Mir A., Mallik, D., SinhaA., Webster, TJ. International Journal of Nanomedicine**., 2010,** 5:277–283.
28. Ma, Y., Ricciuti, C., Miller T., Kadlowec, J., Pearlman, H[. Journal of American Chemical Society.,[**2008**, 22.](http://pubs.acs.org/doi/abs/10.1021/ef800327m)](http://pubs.acs.org/doi/abs/10.1021/ef800327m)
29. Segets,D., Gradl, J., Taylor, RK., Vassilev, V., Peukert ,W. Journal of American Chemical Society., [20093:1703.](http://pubs.acs.org/doi/abs/10.1021/nn900223b)
30. Chaari, M., Matoussi, A., [Physica B: Condensed Matter journal of Elsevier**.,2012,** 407: 3441- 3447.](https://dx.doi.org/10.1016/j.physb.2012.04.056)
31. Ahmad,M., Pan,M., Yan,C., Zhu,W., Journal of Materials Science and Engineering.,**2010,**174.
32. Barick,K.,Singh,C., Aslam,S.,, Bahadur,M.,Materials Science Journal of Springer.,**2010,**134 (1-3**).**
33. Gupta, J., Barick, K., Bahadur, C., Journal of Alloys and Compounds.,**2011,** 509.
34. Gaya, U., Abdullah, A. H., Journal of Photochemistry and Photobiology C: Photochemistry Reviews., 9 (1), 1-12**.2008.**
35. Samaele,N.,Amornpitoksuk,P., Suwanboon, S.,Materials Letters journal of Elsevier., 2010, 64 (4).
36. Rezende, C.P., Silva, J.B., Mohallem, N.D.S., Brazilian Journal of Physics. **2009,** 1, 248**.**
37. Robert,F.Mulligan., Agis,A.Iliadis and Peter Kofinas.,Journal of Applied Polymer Science., **2003.**
38. NagarajanPadmavathy., Journal of Technology of Advanced Material., 8., 1.**2008.**
39. Moon,J., Kim,T.K., Saders,B.V., Choi,C., Liu,Z., Jin. S and Chen. Journal of Solar Energy Materials & Solar Cells.,**2015.**
40. Zheng, Y., Li, P., Li. H and Chen. S. International Journal of Electrochemical Science.,**2014** 7369 – 7381.
41. Sun, H., Ahmad, M., and Zhu,  journal of the International Society of Electrochemistry.,89, **2013,**199 – 205.
42. Madhu,R., Veeramani, V., Chen, S.M., ACS Journal Applied Materials & Interfaces., **2015,** 7(29)**.**
43. Xu, J.M., Zhang, J., Wang, B., and Liu,F. Journal of Alloys Compounds., **2015,** 619, 361–367.
44. Sahoo, P., Djieutedjeu, H., and Poudeu, T., Pierre,F., Journal of Materials Chemistry.,1,**2013,** 15022**.**
45. Niasari, M.S., Mir, N and Davar, F., Journal of Physics and Chemistry of Solids.,**2009,** 70, 847–852.
46. Arciga-Duran, E., Ballesteros, J.C., Torres- Martinez, L.M., Juarez – Ramirez. I and Gomez Solis C. Journal of Catalysis.,**2005,** 1-27.
47. Moon, J., Kim, T.K., Saders, B.V., Chen R. Journal of Solar Energy Materials & Solar Cells.,**2015,** C 134, 417–424.
48. Yarestani,M., Khalaji ,A.D., Journal of Sciences, Islamic Republic of Iran., 25(4), **2004,**339- 343.
49. Manigandan, R., Suresh, R.,Giribabu, K.,Journal of Advanced Materials.,**2012,** 584., 263-266.
50. Amekura, H., Umeda, N., Takeda, Y., Lu J and Kishimoto, N.,Journal of applied physics., **2004,** 85,6.
51. Yuan, W., Xie, D., Dong, Z., Su, Q., Zhang, J., Du. G and Xu, B. Materials Letters journal of Elsevier., **2013,** 97: 129-132.
52. Sun,C., Su, X., Xiao, F., Niu, C., and Wang, Journal of  Sensors and Actuators B: Chemical.**2011,** B157: 681-685.
53. Manigandan, R., Giribabu, K., Suresh, A., International Journal of Chemical Science Transactions.,**2013,** 2: S47-S50.
54. Teng, Y., Yamamoto, S., Kusano,Y., Materials Letters journal of Elsevier., **2010,** 64: 239- 242.
55. Lester,E., Aksomaityte, G., Li., J., Gomez,S., Gonzalez- Gonzalez J and Poliakoff, M., Prog., Crystal Growth and Characterization of Materials.,**2012,** 58: 3- 13.
56. Vijayakumar, S., KiruthikaPonnalagi, A., Nagamuthu, S and Muralidharan, G., International Journal of ElectrochimicaActa., **2013,** 106: 500-505.
57. Vidal-Abarca, C., Lavela,P., and Tirado.L., Journal of Electrochemical and Solid-State Letters., **2008** 11: A198-A201.
58. Xu, J., Gao L., Cao, J., Wang, W and Chen, Z., International Journal of ElectrochimicaActa., **2010,** 56: 732-736.
59. Pan, L., Xu, M and Zhang, ZD.,Journal of Cluster Science.,**2010,** 21, 655-667.
60. Hui, KS.,Hui, KN., Yin, CL and Hong, X., Materials Letters journal of Elsevier.,**2013,** 97: 154-157.
61. Ren, M., Yuan, S., Su, L and Zhou, Z., Journal of Solid State Sciences., **2012,** 14: 451-45
62. Makhlouf , SA., Bakr , ZH., Aly, KI and Moustafa, MS., Journal of Chemical Physics.,**2013,** 64: 107-117.
63. Farhadi, S., Pourzare, K., and Sadeghinejad, S., Journal of Nanostructure in Chemistry.,**2013,**3: 16-22.
64. Farhadi, S., Pourzare, K., and Bazgir, S,. Journal of Alloys Compounds.,**2014,** 587: 632-637**.**
65. Khalaji, AD., Nikookar, M., Charles, C., Triki S., Thetiot, Y., Journal of Cluster Science.,.**2014,** 25, 605-615.
66. Khalaji, AD., and Malekan, F.n., Journal of Cluster Science.,.**2014,** 25, 517-521.
67. Rathod, P.B., Nemade, K.R and Waghuley. S.A. International Journal of Physical Chemistry B., **2015,** 491-95.
68. Sambandam, A., Lee, G-J., J. Wu., Journal of applied physics.,**2012,** 682-686.
69. Darezereshki, C., Bakhtiari,F., Min. Journal of Chemistry Section B., **2011,** 47 -73.
70. Yuan, G., Jiang, H., Lin,C., Liao,S., Journal of Crystal Growth., **2007,** 303 -400.
71. Lim,Y., Choi,J., Hanrath, T. Journal of Nanomaterials., **2012.**
72. Wang,H., Xu,J., Zhu,J., Chen,H., Journal of Crystal Growth.,.**2002,** 244.
73. Sambandam, A., Lee, G-J., Wu,J., Journal of Ultrason. Sonochem.,**2012,** 682.
74. Zhou, K., Wang, R., Xu.,Li.B. Journal of Nanotechnology.,**2006,** 3939.
75. Yao, W., Yu,S., Zhou,Y., Jiang,J., Wu,Q., Zhang, L., ACS Journal of Physical Chemistry B., **2005,** 1401.
76. Zhu, J., Li,D., Chen, H., Yang, X., Lu, L., Wang, X., Materials Letters journal of Elsevier., **2004,** 58 -3324.
77. Darezereshki, E., Bakhtiari, F., Min, Journal of Mining and Metallurgy, Section B: Metallurgy., **2011,** 47 -73.
78. Manimaran, R., Palaniradja, K., Alagumurthi, N., Sendhilnathan, S., Hussain, Journal of Applied Nanoscience.,**2013.**
79. Rai, V., Jamuna, B., Mendez-Vilas., A.(Ed.). University of Mysore, International journal of Nanoscale. India.,**2011.**
80. Das, D., Nath, B., Phukon, P., Dolui, S., International Journal of Colloids and Surfaces B: Biointerfaces.,**2012,**101**.**
81. Zhao, J., Wang, Z., Dai, Y., Xing, B., International Journal of Water Research.,**2013.**
82. Jammi, S., Sakthivel, S., Rout,L., Mukherjee, T., Mandal.S., Mitra.R., Punniyamurthy.T., Journal of organic chemistry., **2009,** 74.
83. Chandrasekaran, S., Journal of Solar Energy Materials & Solar Cells.,**2013,**109.
84. Ko,J., Kim, S., Hong,. J., Ryu, J., Kang, K., Park, K., Journal of Green Chemistry., **2012,**14.
85. El-Trass,A., ElShamy,H., Mehasseb,I., Kemary,M. Journal of Applied Surface Science.,**2012**, 258**.**
86. Lim, Y., Choi, J., Hanrath, T., Journal of Nanomaterials.,**2012.**
87. [Ameer, Azam.,](https://www.ncbi.nlm.nih.gov/pubmed/?term=Azam%20A%5BAuthor%5D&cauthor=true&cauthor_uid=23233805) [Arham, SAhmed.,](https://www.ncbi.nlm.nih.gov/pubmed/?term=Ahmed%20AS%5BAuthor%5D&cauthor=true&cauthor_uid=23233805) [Mohammad, Oves.,](https://www.ncbi.nlm.nih.gov/pubmed/?term=Oves%20M%5BAuthor%5D&cauthor=true&cauthor_uid=23233805) [Mohammad Khan.S.,](https://www.ncbi.nlm.nih.gov/pubmed/?term=Khan%20MS%5BAuthor%5D&cauthor=true&cauthor_uid=23233805)[Sami Habib,](https://www.ncbi.nlm.nih.gov/pubmed/?term=Habib%20SS%5BAuthor%5D&cauthor=true&cauthor_uid=23233805) S and [Adnan. MemicInt Journal Nanomedicine.,](https://www.ncbi.nlm.nih.gov/pubmed/?term=Memic%20A%5BAuthor%5D&cauthor=true&cauthor_uid=23233805)**2012,** 7.
88. Buzea, C., Pacheco, I., Robbie, K. Biointerphases. Journal of Alloys Compounds. **2007,** 2(4).
89. Brayner, R., Ferrari-Iliou, R., Brivois, N., Djediat, S., Benedetti, MF.,Fiévet, F., ACS Journal of NanoLetters., **2006**, **6**(4).
90. Jones, N., Ray, B., Ranjit, K.T., ACS Journal of NanoLetters.,**2008,** 279(1).
91. Jalal, R., Goharshadi, E.K., Abareshi, M., Moosavi.M.,Yousefi.A., Mater, P. Journal of Chemical Physics.,**2010**,121(1).
92. Seil, J.T., Webster, T.J. Int. Journal of Nanomedicine.,**2012**, 7.
93. Emami-Karvani, Z., ChehraziAfr, P. African journal of microbiology research .**2011,** 5(12).
94. Padmavathy,N., Vijayaraghavan,R., Journal of Advanced Materials.,**2008**, 9(3), 035004.
95. Raghupathi, K.R., Koodali, R.T, Manna, A.C. Langmuir Journal of American Chemical Society.,**2011,** 27(7).
96. Jones, Nicole, Ray, Binat, Koodali, T, RanjitAdhar, C. Manna. ACS Journal of NanoLetters.,**2008,** 279(1).
97. Nagarajan, Padmavathy and Rajagopalan, Vijayaraghavan. National Institute for Materials Science [and Technology of Advanced Materials.,](http://iopscience.iop.org/journal/1468-6996)**2008,**[9](http://iopscience.iop.org/volume/1468-6996/9) [(3)](http://iopscience.iop.org/issue/1468-6996/9/3).
98. [Yan-Wen,Wang,](https://pubs.acs.org/author/Wang%2C%2BYan-Wen) [Aoneng, Cao,](https://pubs.acs.org/author/Cao%2C%2BAoneng) [Jiang,](https://pubs.acs.org/author/Jiang%2C%2BYu) [Xin Zhang,](https://pubs.acs.org/author/Zhang%2C%2BXin) [Jia-Hui Liu.,](https://pubs.acs.org/author/Liu%2C%2BJia-Hui) [YuanfangLiu](https://pubs.acs.org/author/Liu%2C%2BYuanfang) and [Haifang Wang,](https://pubs.acs.org/author/Wang%2C%2BHaifang)  ACS Applied Materials & Interfaces scientific journal., **2014,** 6 (4).
99. [Krishna. R., Raghupathi.,](https://pubs.acs.org/author/Raghupathi%2C%2BKrishna%2BR)[Ranjit, T, Koodali.,](https://pubs.acs.org/author/Koodali%2C%2BRanjit%2BT) and [Adhar, C., Manna](https://pubs.acs.org/author/Manna%2C%2BAdhar%2BC)Journal of American Chemical Society,*.***2011,** 27 (7).
100. [Cindy, Gunawan.,](https://pubs.acs.org/author/Gunawan%2C%2BCindy)[Wey Yang, Teoh.,](https://pubs.acs.org/author/Teoh%2C%2BWey%2BYang) [Christopher P.Marquis](https://pubs.acs.org/author/Marquis%2C%2BChristopher%2BP)and [RoseAmal.,](https://pubs.acs.org/author/Amal%2C%2BRose)  Journal of American Chemical Society*.,***2011,** 5 (9).
101. [Sharma,](https://www.sciencedirect.com/science/article/pii/S0040609010011880#!) Deepali.,[Rajput,](https://www.sciencedirect.com/science/article/pii/S0040609010011880#!) Jaspreet., [S.Kaith.B., MohinderKaur., SapnaSharma. International Journal on the Science and Technology of Condensed Matter Films.,](https://www.sciencedirect.com/science/article/pii/S0040609010011880#!)[**2010,** 519(3)](https://www.sciencedirect.com/science/journal/00406090/519/3).
102. Son, D., You. C and Ki, T., **Journal of** Applied Surface Science at ScienceDirect.,**2009,** 255.
103. Chang.M.H.,Liu.H.S., C.T. Tai., Materials Science Journal of Springer.,**2011,** 378-386 **.**
104. Castro-Hurtado.I., Herran.J.,Perez.N., Olaizola.S.M., Mandayo.G., Castano. E., journalof Sensor Letters is a multidisciplinary.,**2011**, 64-68.
105. Du, Y., Wang.W., Li, X., Zhao.J., Ma, J., Liu, Y., Lu.G., Materials Letters journal of Elsevier.,**2012**, 168–170**.**
106. Hu, Y., Qian, H., Mei, T., Guo, J., White, T., journal of Materials Letters., **2010,** 1095– 1098.
107. Wang, G., Lu, X., Zhai, T., Ling, Y., Wang, H., Tong, Y., Li, Y., International journal of Nanoscale.,**2012**,3123 3127.
108. Bang, JH.,Suslick, KS. Journal of Advanced Materials.,**2010,** 1039–59.
109. Balavijayalakshmi, J., Journal of Environmental Nanotechnology.,**2013,** 53–5.
110. Tazikeh, S., Akbari A., Talebi, A., Talebi, E., Journal of Applied Chemistry.,**2016,**1–4.
111. Mukhtar, M., Munisa, L., Saleh, R. International journal of Materials Sciences and Applications.,**2012,** 543–51.
112. Lee., C.-T.; Yan., J.-T. International journal of Sensors &Actuators.,**2010**,147., 723.
113. Kidwai.M.;Bhardwaj., S. Journal of Applied Catalysis A: General at ScienceDirect.,**2010,** 387, 1.
114. Ma, H.-L.Fan., Niu, D.W., Chin. X.-S., Journal of Physics B., 19, **2010**, 76102/1.
115. [Douayar, A., Abd-Lefdil, M., Nouneh, K., Prieto, P., Diaz, R.,Fedorchuk,O., Kityk, I. Journal of applied physics,. **2013**,110.](http://refhub.elsevier.com/S0925-8388%2815%2931323-2/sref32)
116. Chen, X.,Yip, Y.,Fung, M.,Djurisic, K., Chan.A.B, W. K. Journal of applied physics., **2010,**100,15.
117. Jood, P., Mehta R.J., Zhang, Y et al., ACS Journal of Nano Letters., 11, 10. **2011,** 4337**.**
118. Favier.A.,Muñoz.D., Martín de.S., Journal of Physics: Conference Series.,**2016,**707.
119. Venkatesh, P.S., Ramakrishnan, V., Jeganathan, K., Journal of CrystEngComm.,**2012,** 2593.
120. LinJ, M., Zhang, Y., Ye,Z., Journal of Applied Surface Science., 2009, 255, 14.
121. Verma, A., Khan, F., Kar, D., Chakravarty, B.C., International Journal on the Science and Technology of Condensed Matter Films.,**2010,** 518.
122. [khtar, M.N., Yahya, N., Hussain, P., Journal of Basic and Applied Sciences., **2009**, 9.](http://refhub.elsevier.com/S0304-8853%2813%2900663-X/sbref10)
123. [Deraz, M., Journal of Analytical and Applied Pyrolysis.,**2010**, 88.](http://refhub.elsevier.com/S0304-8853%2813%2900663-X/sbref18)
124. [Kambale, R.C., Adhate, N.R., Kolekar, B., Journal of Alloys andCompounds.,**2010**,491.](http://refhub.elsevier.com/S0304-8853%2813%2900663-X/sbref20)
125. [Phadatare, M.R., Salunkhe, A.B., Khot, V.B., Pawar, H., Journal of Alloys andCompounds.,**2013**,56.](http://refhub.elsevier.com/S0304-8853%2813%2900663-X/sbref23)
126. [Kulal,S.R, Khetre,S., Waghmode, D.P, Kolekar,G.B, Sabale,S, Bamane,R, Materials Letters journal of Elsevier., **2012,**](http://refhub.elsevier.com/S0304-8853%2813%2900663-X/sbref24)2638.
127. [Dom,R,Subasri.R., Radha,K., Borse,P.H., Journal of Solid State Communications.](http://refhub.elsevier.com/S0304-8853%2813%2900663-X/sbref25),[**2011**, 151**.**](http://refhub.elsevier.com/S0304-8853%2813%2900663-X/sbref25)
128. [Sertkol,M., Koseoglu,Y., Baykal,A., Toprak,M., Journal of Magnetism Materials](http://refhub.elsevier.com/S0304-8853%2813%2900663-X/sbref28).,[2010, 322.](http://refhub.elsevier.com/S0304-8853%2813%2900663-X/sbref28)
129. [Manikandan,A., JudithVijaya,J., Bououdina,B., Journal of MolecularStructure., 2013,1035.](http://refhub.elsevier.com/S0304-8853%2813%2900663-X/sbref30)
130. Rekha,K., Nirmala,M., Nair,M., Anukaliani,A., Physics B:Condensed Matter.,**2010**, 405.
131. Fu,M., Li,Y., Siweiwu, T., Lu,P., Liu,J., Dong, F., Journal of Applied Surface Science., 258, **2011**, 1587-1591.
132. Xu,C., Cao,L., Su,G., Liu,W., Liu.H., Yu,Y.,Hazard. Materials Letters journal of Elsevier., 176, **2010,** 807–813**.**
133. Nandapure,I., Kondawar, S.B., Nandapure, A.I. International Journal of Scientific Research., 4(1), **2015,** 440-441**.**
134. Sangeetha Gunalan., Rajeshwari Sivaraj., Venckatesh Rajendran, International Journal of Natural Science: Materials, 2012, pp. 693-700