Chapter 1

Introduction and theoretical background

This chapter gives a general introduction to the field of nanotechnology with a focus on two nanomaterials, viz. silver, zinc oxide and their composites and their general properties and anti-bacterial applications. The role of ionic liquid as surfactant for nanoparticles is also discussed. A brief introduction on the different types of bacteria and diseases has also been included.
1.1 Introduction to nanoscience and nanotechnology

The first use of the concept 'nano-technology' was in a talk given by physicist Richard Feynman at an American Physical Society meeting at Caltech on December 29, 1959 [1]. He noted, scaling issues would arise from the changing magnitude of various physical phenomena, gravity would become less important, surface tension and Van der waals attraction would become more important, etc. This basic idea appears plausible, and exponential assembly enhances it with parallelism to produce a useful quantity of end products. The term "nanotechnology" was defined by Tokyo Science University Professor Norio Taniguchi in a 1974 as, “Nanotechnology” mainly consists of the processing separation, consolidation and deformation of materials by one atom or by one molecule." Today, one can see the word nano everywhere even in commercial advertisements. The word "nano" is originated from the Greek word ‘dwarf’, used to mean something tiny. The prefix ‘nano’ indicates one billionth or $10^{-9}$ units. One nanometer (nm) is $10^{-9}$ meter. The nature of this unit being determined by the word that follows. The widely accepted definition of nanoparticles is, particles that have at least one of its dimensions in the nanometer size regime, typically 1-100 nm.

In general, apart from the spherical shape, the material can adopt other morphologies. The formation of non spherical morphology could be attributed to the restriction of certain crystal faces during material growth, such non-spherical materials are generally termed as anisotropic materials [2, 3]. They are categorized into three as, 1, 2 and 3-dimensional materials. Nanomaterials exhibit properties that are significantly different from their bulk counterparts.

The physico-chemical and opto-electronic properties of nanomaterials are influenced by their size, shape, surface and nature of material (metallic/semiconducting) [4]. For noble metal nanoparticles, the incident light causes collective oscillations of plasma electrons. The resonance frequency of this oscillation falls in the visible range of the electromagnetic spectrum and hence one can observe brilliant colors for noble metal nanoparticles (gold, silver, copper) [5-7]. On the other hand, for semiconductors, the confinement
of the excitons (electron-hole pair) within space smaller than the bulk band gap gives rise to size-dependent emissions from these particles. Effectively in both cases, the opto-electronic properties can be tailored by simple changes in nanoparticle dimensions [8]. Physical properties such as surface area also vary due to the availability of more interfaces in the small range. The surface to volume ratio is more in the nano state than in the bulk. The properties of nanomaterials that are different from bulk are: variation of the redox properties, color and anomalous melting points, enhanced toughness and strength, unusual crystal structures (in metals). The band gap in semiconductor particles increases as the particle size decreases due to the loss of in-between energy levels during the size reduction.

Nanotechnology is one of the frontier areas of science due to its versatile application in various fields. Nanomaterials find applications in the fields such as miniaturization in electronics, catalysis, optics, biological and in the energy sector. In addition, nanomaterials yield next-generation computer chips, better insulation materials, tougher and harder cutting tools, elimination of pollutants, high energy density batteries, efficient solar cells, high-power magnets, high-sensitivity sensors, automobiles with greater fuel efficiency, aerospace components with enhanced performance characteristics and electrochromic display devices [9-12].

1.2 Why nano materials?

A number of physical phenomena become pronounced as the size of the system decreases. These include statistical mechanical effects, as well as quantum mechanical effects, for example the “quantum size effect” where the electronic properties of solids are altered with great reduction in particle size. This effect does not come into play by going from macro to micro dimensions. However, it becomes dominant when the nanometer size range is reached. Additionally, a number of physical (mechanical, electrical, optical, etc.) properties change when compared to macroscopic systems. One example is the increase in surface area to volume ratio, altering mechanical, thermal and catalytic properties of materials. Materials reduced to the nano scale can show
different properties compared to what they exhibit on a macro scale, enabling unique applications. For instance, opaque substances become transparent (copper); inert materials become catalysts (platinum); stable materials turn combustible (aluminum); solids turn into liquids at room temperature (gold); insulators become conductors (silicon) [13]. A material such as gold, which is chemically inert at normal scale, can serve as a chemical catalyst at nanoscales. Much of the fascination with nanotechnology stems from these quantum and surface phenomena that matter exhibits at the nano scale. Noble metal nanoparticles have attracted interest since historical time due to their bright intense colors that are distinct from metallic luster at the bulk scale and unique to the small size of the particles [14, 15]. The decorative pigments in some historical artwork like the Roman Lycurgus cup from the 4th century and Renaissance pottery (e.g. plate from Gubbio, Italy) from the 16th century are now known to be composed of nanosize particles of gold, silver, copper and their alloys [16].

The past two decades have shown rapid advances in the ability to structure matter at the nanoscale with sufficient degree of control over the material size, shape, composition and morphology [17]. At the nanoscale, materials exhibit unique optical, electronic and magnetic properties not seen at the bulk scale, which makes nanostructures attractive for a wide range.

1.3 Silver nanoparticles (SNPs)

Over the past few decades, nanoparticles of noble metals such as silver exhibited significantly distinct physical, chemical and biological properties from their bulk counter parts [18]. Metallic nanoparticles exhibit size and shape-dependent properties that are of interest for applications ranging from catalysts and sensing to optics, antibacterial activity and data storage [19-24]. Bulk silver has well known antibacterial properties and has been used for this purpose as early as the Roman times. It was used during the 1st World War as an aid in wound dressing, but was superseded as an antibacterial with the advent of antibiotics. However, it is in the last few years that silver, in the form of silver nanoparticles, has made a remarkable comeback as an antibacterial,
antiviral and antimicrobial compound. For instance, the antibacterial activity of different metal nanoparticles such as silver colloids is closely related to their size; that is, the smaller the silver nuclei, and higher the antibacterial activity. Moreover, the catalytic activity of these nanoparticles is also dependent on their size as well as their structure, shape, size distribution, and chemical–physical environment. Thus, control over the size and size distribution is an important task in the synthesis of metal nanoparticles. Generally, specific control of shape, size, and size distribution is often achieved by varying the synthesis methods, reducing agents and stabilizers [25-29].

Silver nanoparticles shows face centered cubic structure and exhibits various 1D nanostructures such as nanowires, nanotubes, nanoflakes, nanorods etc. by varying its preparative parameters. And thus, it has been attracting vast interest in the field of nanotechnology. Silver nanoparticles have been prepared by several physical and chemical methods. In physical processes, SNPs are generally synthesized by evaporation–condensation, which could be carried out using a tube furnace at atmospheric pressure. The source material within a boat centered at the furnace is vaporized into carrier gas [30-33], laser ablation [34]. However, synthesis of SNPs by physical methods has some drawbacks. Chemical reduction is the most frequently applied method for the preparation of SNPs as stable and colloidal dispersions in water or organic solvents. Commonly used reductants are borohydride, citrate, ascorbate, hydrazine hydrate and elemental hydrogen. The reduction of silver ions (Ag\(^+\)) in aqueous solution generally yields colloidal silver with particle diameters of several nanometers. Initially, the reduction of various complexes with Ag\(^+\) ions leads to the formation of silver atoms (Ag\(^0\)), which is followed by agglomeration into oligomeric clusters. These clusters eventually lead to the formation of colloidal SNPs [35-37]. If left to its own, it leads to formation of dark brown to black precipitate. To prevent this, usually a number of surfactants are used. The most commonly used polymers as surfactants are poly vinylpyrolidone (PVP), poly ethylene glycol (PEG), poly methacrylic acid (PMAA), poly methyl methacrylate (PMMA) [38-40]. Bai et al used poly acrylamide as stabilizer and
reducing agent to synthesize gold nanoparticles [41]. Bozanic et al used chitosan polymer for the synthesis of SNPs [42]. Recently, biosynthetic methods employ naturally occurring reducing agents such as polysaccharides, biological microorganism such as bacteria and fungus or plants extract, i.e. green chemistry, and these are emerged as a simple and viable alternative to more complex chemical synthetic procedures to obtain SNPs. The leaf extract of Rosa rugosa was used for synthesis of silver and gold nanoparticles by Dubey et al [43], fungus Hormoconis resinae was used for synthesis of SNPs by Varshney et al [44] and bacterial culture supernatant of Pseudomonas aeruginosa by Ganesh Kumar et al [45].

Silver has been known for its antimicrobial properties since ancient times [46]. However, the first medical preparations with this metal were made only in the 19th century. Silver nitrate is quite effective against different microorganisms but in the 40s of the 20th century interest to silver preparations had decreased greatly, when antibiotics were discovered [47]. Later, with the rise of nanotechnology this interest increased again, when it became possible to manufacture different materials with defined shape and size at the nano scale level. Now a days, nano structured silver is studied very extensively especially for medical purposes. Nanosilver has significant anti-inflammatory, immune modulative [48] and antiviral [49-54] effects, but the most prominent and well-studied is the antimicrobial effect of nanosilver. It is known that SNPs and nanocoatings could be an effective agent against not only gram-negative and gram positive bacteria but also fungi in concentration of about tens of milligrams per liter [55,56]. Furthermore, some researchers report about synergistic effect of SNPs and antibiotics [57]. Nevertheless, the mechanism of antimicrobial effect has not been completely clarified yet. The possible mechanism of SNPs action on the microbial cell was described in works of Li et al. [58] and Aruguete et al. [59], as nanoparticles accumulate at the surface of the cell wall, degrade lipo polysaccharides and form pits, release silver cations in cytoplasm, cause the forming of reactive oxygen species, and bind to cytochromes, thus blocking respiratory chain. Some authors suggested that antimicrobial properties of SNPs
are dependent on their geometrical parameters. Choi et al [60] showed that inhibition of nitrifying bacteria is related with fraction of 5 nm-sized SNPs and performed a study which elucidates dependence of antimicrobial activity of SNPs from their geometry. They determined that triangle-shaped nanoparticles were more effective than spherical and rod-shaped types against *E. coli*. Despite the fact that SNPs has broad spectrum of antimicrobial activity, resistance to this metal is formed very rarely, some mechanisms of resistance formation in *Salmonella typhimurium*, *E. coli* strains [61] and *Bacillus cereus* [62] are reported. Researchers have also note that resistance may be as a result of using nanosilver in concentrations below minimal inhibition concentration (MIC). Anti-inflammatory and immune modulative effects of nanosilver are are associated with suppression of cytokines synthesis, and inhibition of matrix metallo proteins [47]. A number of medical preparations and products were made with addition of nanostructured silver. These are predominantly topical medicines such as crèmes, gels and dressings [47, 48], some of them passed clinical trials and available for treatment [47]. Preparations with nanosilver are effective in treatment of wound burns, allergic contact dermatitis and skin microbial infections. Silver nanoparticles could be combined with natural or synthetic polymers to improve their efficiency as medicine. For example, chitosan-silver composites have not only antibacterial activity but also decrease blood clotting time [63]. Another study has been dedicated to the so-called poly rhodamine-silver nanofibers, which has significant antimicrobial effect which was greater than conventional silver-sulfadiazine preparation [64]. The ability of SNPs to increase greatly fluorescence emission formed the basis of so-called silver enhancement technique which is useful for diagnostic purposes [64]. Silver nanoparticles as well as gold nanoparticles have specific optical properties, and can be used in surface enhanced raman spectroscopy, sensing and imaging [65].

1.4 Zinc oxide

Zinc oxide is an inorganic compound with the formula ZnO and it has hexagonal wurtzite crystal structure (Fig.1.1). It usually appears as a white
powder and is nearly insoluble in water (water solubility of zinc oxide ranges from 1.6 mg/L to 5 mg/L). The powder is used in a variety of applications typically as an additive into products including plastics, ceramics, glass, cement, rubber (e.g. car tyres), lubricants, paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, fire retardants, etc. There are three most representing one-dimensional (1D) nanostructures that are being actively studied in nanotechnology: carbon nanotubes, silicon nanowires, and ZnO nanorods or nanowires.

**Fig.1.1 Hexagonal Wurtzite Crystal structure of ZnO**

Zinc oxide is one of the few dominant nanomaterials for nanotechnology. The absence of a centre of symmetry in its wurtzite structure, along with large electromechanical coupling results in strong piezoelectric and pyroelectric properties. Zinc oxide is therefore widely used in mechanical actuators and piezoelectric sensors. In addition, ZnO has been found highly attractive because of its remarkable application potential in solar cells, sensors, displays, gas sensors, varistors, electro-acoustic transducers, photo-diodes and UV light emitting devices, sun-screens, gas sensors, UV absorbers, anti-reflection coatings, and catalyst photo-catalysis [66–76]. Potentiality of ZnO for removing dye from textile effluent under UVC light has been proved by
Behnajady et al [69]. ZnO is an n-type semiconductor; the high exciton binding energy (60 meV) in ZnO crystal allows efficient excitonic emission at room temperature. Only ZnO and TiO$_2$ among the 3d transition metal oxide semiconductor series, have sufficient stability on photo-excitation state. The band gap energy of ZnO is 3.37 eV. Their stability can be justified with decreasing the possibility of electron–hole recombination. This phenomenon is related to dissimilar parity of produced photo excited electron–hole pair under UV irradiation [75]. Zinc oxide nano-particles have some advantages, compared to silver nano-particle, as lower cost, white appearance [75] and UV-blocking property [76]. Zinc oxide powder can absorb infra-red light and infra-red electromagnetic wave with 5–16.68 dB in the range of 2.45 18 GHz. ZnO is also used to reinforce polymeric nano composites [75]. It is also useful for enhancement wear resistant phase and anti-sliding phase in composites as a consequence of its high elastic modulus and strength [77]. Li et al have investigated the durability of anti-bacterial activity of nano-ZnO functionalized cotton fabric to sweat. The cotton fabrics were treated with of 11g/L ZnO and padded them to 100 % wet pick-up. The durability of anti-bacterial activity of the finished fabric in alkaline, acidic and inorganic salt artificial sweat solution was been evaluated. The results have showed better salt and alkaline resistance than acid resistances for the treated fabrics. A negative surface charge has been deduced for ZnO nanoparticles and illumination increased the anti-bacterial performance compared to normal conditions [78]. Tetrapod-like nano-particle ZnO was also used for producing acrylic composite resin [77]. Zinc oxide nano-belts, nanowires, nanotubes and nanocages have been also produced by Pan et al. [66, 74]. Xu and Cai et al were grown ZnO nano-rod on cotton fabric samples through the dip-pad-cure process [79]. They were tried to cover the prepared nano-rod with a super hydrophobic agent to produce a cotton fabric with super hydrophobic properties based on the Cassie and Baxter theory (Equation 1)

$$\cos \theta^* = f_1 \cos \theta_s - f_2 \cos \theta_v$$  \hspace{1cm} (1)
where, $f_1$ is the fraction of fluid area in contact with the substance, and $f_2$ is the fraction of the fluid area in contact with air. $\theta'$ indicates the contact angle at a surface composed of solid and air, $\theta_s$ and $\theta_v$ are the corresponding water contact angles on smooth solid surface and vapour surface. The equation can be used for hydrophobic surfaces that trap air in the hollows of the rough surface and the liquid–air contact angle ($\theta_v$) is $180^0$ [79, 80].

1.5 Silver–zinc oxide nanocomposite

A nanocomposite is a multiphase solid material where one of the phases has dimensions of less than 100 or structures having nano-scale repeat distances between the different phases that make up the material. In the broadest sense this definition can include porous media, colloids, gels and Co-polymers, but is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phase(s) differing in properties due to dissimilarities in structure and chemistry. In mechanical terms, nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase and / or its exceptionally high aspect ratio.

Beside of high potential of silver [81,82] and ZnO [83] nanoparticles in biomaterial, the synergistic effect of silver-ZnO nanocomposite particles resulted by synthesizing silver nanoparticles on the surface of ZnO nanoparticles has been proven.

1.6 Surface modification of nanoparticles

Naturally, surface modification starts with an existing surface and yields a new surface with possibly new properties. Surface modification can improve the inherent characteristics of the nanoparticles and serve to prepare nanocomposite inexistent in nature and improve surface wettability, adhesion, and thus such modified surfaces are one of the main subjects of the surface analysis of polymers [84].

According to the principles of surface modification, the surface modification of nanoparticles can be divided into partial chemical modification, mechanical and chemical modification, external membrane modification, high-
energy surface modification, surface modification using precipitation, esterification, coupling and grafting reactions. Since nanoparticles have different surface structures and surface interactions compared to the sub-micron sized particles, nanoparticles have an extremely high tendency of adhesion and aggregation. In order to improve the dispersion stability of nanoparticles in liquid media, it is necessary to modify the particle surface by polymeric surfactants or other modifiers to generate an effective repulsive force between nanoparticles. The adsorption of polymeric dispersant is one of the simplest surface modification techniques to improve the dispersion stability of nanoparticles in liquid media [85]. We have used poly vinyl alcohol, ionic liquid and biomolecules as surfactants for the synthesis and surface modification of silver nanoparticles and zinc oxide nanoparticles.

1.7 Ionic liquids (ILs)

Most of the familiar liquids are formed from neutral molecules and are non-ionic. There is a different class of room-temperature liquids that, unlike the molecular liquids, is constituted of ions. These liquids are called ionic liquids (ILs). For a substance to be considered a room temperature ionic liquid (RTIL), its melting point should be below 100°C. ILs are nothing but room temperature molten salts.

Molten salts are in general defined as liquid electrolytes which consist of simple anions and cations that pack efficiently and, therefore, have high lattice energy [86].

Recently due to implications of the ILs as solvents where the accessible physical property sets with many ILs are often unique. There is now, growing interest in the materials applications of ILs which utilize novel tunable physical and chemical property sets for such applications as energetic materials, lubricants, metal ion complexation, etc. Ionic liquids make a unique architectural platform on which, at least potentially, the properties of both cation and anion can be independently modified, enabling tunability in the design of new functional materials, while retaining the core desired features of an IL.
Chapter 1

As a solvent, IL posses several advantages over conventional organic solvents, which make them environmentally compatible. Ionic liquid exhibit many properties which make them potentially attractive media for many organic transformations due to easy handling, recyclability and thus leading to cheap and environmentally benign reaction conditions.

1. They have essentially no vapor pressure, i.e. they do not evaporate and are easy to contain.
2. They generally have reasonable thermal stability.
3. They have high solvating capacity for both polar and non-polar compounds.
4. They have good solubility of gases, e.g. H₂, CO and O₂, which makes them attractive solvents for catalytic hydrogenations, carbonylations, hydroformylations and aerobic oxidations.
5. They are immiscible with majority of organic solvents, e.g alkanes, hence can be used in two-phase systems. Similarly, lipophilic ionic liquids can be used in aqueous biphasic systems.
6. Polarity and hydrophilicity or lipophilicity can be readily adjusted by a suitable choice of cation / anion and thus, ILs has been referred to as “designer solvents”.

1.7.1 Types of ionic liquids

The ionic liquid used here is room temperature ionic liquid (RTIL). The RTIL includes acidic, basic and neutral type of ionic liquid. The IL used in our study, is 1-(dodecyl) 2-amino-pyridinium bromide, is neutral type of IL.

1.7.2 Typical Ionic liquid used in study

![Fig.1.2 Structure of 1-(dodecyl) 2-amino-pyridinium bromide IL](image-url)
This thesis describes use of 1-(dodecyl)-2-amino-pyridinium bromide IL for the synthesis of silver nanoparticles. The structure of this IL is given in Fig. 1.2. This IL plays an important role of surfactant or surface modification due to amine functionality.

1.8 Ionic liquid in nanomaterial

Room temperature ionic liquid generally features a good stability to air, water, various organic and inorganic substances and a wide liquid range. Ionic liquids have been used in the synthesis of nanostructured materials, identification of appropriate surface capping agent in these new solvents remains an important issue. Several currently used capping agents tend to cause irreversible aggregation of nanoparticles. The use of ILs as a capping agent or surfactant for the synthesis of various metallic nanoparticles has been reported in recent years [120,128].

1.9 IL as surfactants

Surfactants (usually referred to as surface active agents) are amphipathic molecules that consist of a non-polar hydrophobic portion, usually a straight or branched hydrocarbon or fluorocarbon chain containing 8-18 carbon atoms, which is attached to a polar or ionic portion (hydrophilic) (Fig. 1.3). The hydrophilic portion can, therefore, be nonionic, ionic or zwitter ionic, and accompanied by counter ions in the last two cases. Surfactants organize in or on the surface of water in such a way that the Gibbs free energy of the system is minimized.

![Typical structure of surfactant](image)

**Fig. 1.3** Typical structure of surfactant
Certain surfactants with appropriate hydrophobic/hydrophilic balance can form micelles in water (typical examples are detergents). A typical schematic for a surfactant is illustrated in Fig. 1.3.

The physicochemical and solvation properties of ILs can be effectively “tuned” by simple tailoring of the substituent groups comprising the cation and or anion. ILs possessing long aliphatic substituents has been reported to undergo micellization in aqueous solutions. However, current knowledge of IL micelle structure and behavior in aqueous solution is limited. Even less understood is the structure of ILs in solutions of organic solvent–water mixtures. Due to their structural tenability, ILs represents a unique class of “designer surfactants” in which the substituents on the head group can be widely varied [87]. Ionic liquid that carry long-chain alkyl groups are expected to be surface active (SAILs); this expectation has been verified, e.g., for 1, 3-dilalkylimidazolium chlorides, bromides, and tetra fluoro-borates [88]. The SAILs can act as morphology templates for the synthesis of inorganic materials with novel or improved properties.

1.10 Photocatalytic activity of zinc oxide nanoparticles and silver loaded zinc oxide nanoparticles

During the past decades, environmental problems such as air and water pollution have provided the impetus for sustained fundamental and applied research in the area of environmental remediation [89]. With the steady and fast growing field of nanoscience and nanotechnology, nanostructured zinc oxide has become a promising photocatalyst for its high catalytic activity, low cost, and environmental friendliness [90-93]. Major limitation to achieving high photocatalytic efficiency in the ZnO nanostructure systems is the quick recombination of charge carriers. The design and modification of ZnO photocatalysts with high sensitivity and reactivity has attracted much attention. It was found that the photocatalytic performance can be greatly improved by developing ZnO-based heterostructures or composite [94-97]. The prospect of developing novel photocatalysts of metal silver hybridized with ZnO boosts
relevant research because of the increase in the rate of electron-transfer process by silver [98-104].

Thesis describes the photocatalytic activity of zinc oxide and silver loaded zinc oxide nanoparticles.

1.11 Introduction and principle of antibacterial activity study

It is well known fact that some diseases are caused by bacteria. Most of these bacteria causes infection immediately and may or may not result in death. Some bacterial infections are not visible immediately, for example tooth decay is caused by four species of bacteria, *S. sanguis, S. sobrinus, S. mits* and *S. mutans*. The organic acids released by the bacteria results in tooth decay.

As the WHO immunization programmes continue, some of these infectious diseases are being brought under control and toll on human life is decreasing. Environmental disasters such as flood, draught and earthquake etc. increase the death toll from disease by making people more vulnerable through shock weakness, and reduced sanitation. During the year 2000 bacterial disease led to the death of more than 5 million peoples which account for 10% of 52 million human deaths occurring on average every year. Bacterial and other infectious diseases are far more significant in underdeveloped countries as direct result of poverty, reducing sanitary practices, medical care and awareness.

1.12 Note on Bacteria: structure, type and infection:

The majority of bacteria fall within the general dimensions of 0.75-4 mm. They have unicellular structures which may occur as cylindrical (rod-shaped) or spherical (coccoid) forms. Bacteria are harmful and cause several diseases. Bacteria such as *Diplococcus pneumoniae* cause pneumonia (now called Streptococcus); *Staphylococcus aureus*, cause boils and food poisoning; and *Streptococcus pyogenes*, cause sore throat. There are two types of bacterial cells gram positive and gram negative.

1.12.1 Microscopic structures of bacteria used in bactericidal testing
Chapter 1

1.12.1.1 *Escherichia coli*

![Microscopic structure of *E. coli*](image)

**Fig.1.4** Microscopic structure of *E. coli*

*Escherichia coli* is a cause of enteritis in young infants and the young farm animals, where it can cause diarrhoea and fatal dehydration. It is a common infectant of the urinary tract and bladder in humans, and is a cause of pyelitis, pyelonephritis and cystitis. Microscopic structure of *E. coli* is shown in Fig.1.4.

1.12.1.2 *Staphylococcus aureus*

![Microscopic structure of *S. aureus*](image)

**Fig.1.5** Microscopic structure of *S. aureus*
Chapter 1

*Staphylococcus aureus* produces a golden yellow pigment. It is a cause of skin lesions such as boils and can affect bone tissue in the case of *Staphylococcus osteomyelitis*. It produces a toxin, which, if ingested with food in which the organism has been growing, can give rise to food poisoning. A common manifestation of its infection is the production of pus, i.e. the organism is pyogenic. Other common conditions associated with staphylococcal infections are styes, impetigo and conjunctivitis. Microscopic structure of *S. aureus* is shown in Fig.1.5.

1.12.1.3 *Pseudomonas aeruginosa*

![Microscopic structure of P. aeruginosa](image)

*Fig.1.6* Microscopic structure of *P. aeruginosa*

*Pseudomonas aeruginosa* is a common bacterium that can cause disease in animals, including humans. It is found in soil, water, skin flora, and most man-made environments throughout the world. It thrives not only in normal atmospheres but also in hypoxic atmospheres, and thus, colonized many natural and artificial environments. The symptoms of such infections are generalized inflammation and sepsis. *P. aeruginosa* is resistant to many antibacterial agents and is biochemically very versatile, being able to use many disinfectants as food sources. Microscopic structure of *P.aeruginosa* is shown in Fig.1.6.

1.12.2 How bacteria cause disease?

We come into contact with millions of bacteria every day. They are present in air we breathe, in and on food we eat and on the surface of most of
the things we touch. Apart from our normal flora, bacteria that come into contact with us have to pass our various defense mechanisms, our dry skin and acid stomach. Physical actions such as movements of matter through our elementary canal, brushing our teeth and washing all help to make life difficult for bacteria. Those bacteria which do not colonize our system generally do so by breaking through mucus barrier that lines most of our elementary canal or entering through damaged tissue that is wound and bits etc. Once a bacterium has entered the system it is free to grow and spread. Nearly all infectious disease start out as a small localized infection and will only spread through the system if the bacteria gains access to the blood stream.

The pathogenicity of invasive bacteria or their ability to cause disease is generally the result of toxin, a substance produced by bacterial cell, sometimes simply by product of its normal metabolism, which interact negatively with our body by interfering the normal functioning. This is done by damaging specific cell, blocking transmission of some internal signal or by over stimulating sort of cells. By taking into consideration all these facts the biochemists developed antibacterial materials. Both silver nanoparticles and zinc oxide nanoparticles are very good antimicrobial agents and their composite shows high antibacterial activity.

1.13 Nanoparticles for antibacterial study

1.13.1 Silver as a biocide

Bulk silver (Ag) is a transition metal element having atomic number-47 and atomic mass107.87. The medicinal uses of bulk silver have been documented since 1000 B.C. Bulk silver is a health additive in traditional Chinese and Indian ayurvedic medicine [105]. Its action as an antibiotic comes from the fact that it is a non-selective toxic "biocide." Silver based antimicrobial biocides are used as wood preservatives. In water usage, silver and copper based disinfectants are used in hotel distribution systems to control infectious agents (for example, Legionella). Silver together with copper, is commonly used to inhibit bacterial and fungal growth in chicken farms and in post harvested cleaning of oysters. Silver has been used to sterilize recycled
water aboard at the MIR space station and on the NASA space shuttle [106]. Microdyn (colloidal silver in gelatin) is sold in supermarkets to disinfect salad vegetables and drinking water. Johnson Mathey Chemicals (Nottingham, UK) developed an inorganic composite (immobilized slow-release silver product) for use as a preservative in cosmetics, toiletries, and similar retail hygiene-sensitive products [107]. In Japan, a new compound amenitop (silica gel microspheres containing a silver-thiosulfate complex) is mixed into plastics for lasting antibacterial protection [108]. Silver resistance is important to monitor because modern technology has developed a wide range of products that depend on silver as a key microbial component. In the late 1970s, Robert O. Becker discovered that silver ions promote bone growth and kill surrounding bacteria. Silver kills some 650 different pathogens. Silver based topical dressing has been widely used as a treatment for infections in burns, open wounds and chronic ulcers. The SNPs and Ag⁺ carriers can be beneficial in delayed diabetic wound healing as diabetic wounds are affected by many secondary infections. These nanoparticles can help the diabetic patients in early wound healing with minimal scars [109]. Silver nitrate is still a common antimicrobial agent used in the treatment of chronic wounds [110].

1.13.2 Colloidal silver

The smaller is a particle, the greater is its surface area to volume ratio and the higher its chemical reactivity and biological activity. Colloidal silver appears to be a powerful, natural antibiotic and preventative against infections. Acting as a catalyst, it reportedly disables the enzyme that one-celled bacteria, viruses and fungi need for their oxygen metabolism. They suffocate without corresponding harm occurring to human enzymes or parts of the human body chemistry. The result is the destruction of disease-causing organisms in the body and in the food [111].

1.14 Introduction to antibacterial activity of ZnO

Antibacterial agents are broadly of two types, organic and inorganic. zinc oxide has proved to be a powerful antibacterial agent in the formulation of the microscale and nanoscale systems for therapeutics applications. ZnO
nanoparticles showed greater antibacterial activity compared to micro-particles. The exact mechanism of the antibacterial action has not yet been clearly identified. The ZnO particles have bactericidal effects on both gram-positive and gram-negative bacteria. They even have antibacterial activity against spores which are resistant to high temperature and high pressure. From the literature it is evident that the antibacterial activity of ZnO nanoparticles depends on the surface area and concentration, while the crystalline structure and particle shape have little effect. Further, it is also mentioned in the literature that smaller the size of ZnO particles better is its antibacterial activity. Some researchers have proposed in their study that the generation of hydrogen peroxide is the main factor of the antibacterial activity, while it also indicated that the binding of the particles on the bacteria surface due to the electrostatic forces could be another factor.

1.15 Antimicrobial potential of ZnO nanoparticles

It has already been shown that the nano-ZnO impregnated onto cotton textiles showed excellent antibacterial activity against two representative bacteria, *S. aureus* and *K. pneumoniae* and promising protection against UV radiation. A novel and simple method is to prepare ZnO–soluble starch nanocomposite and its application onto cotton fabrics to impart antibacterial and UV protection functions [112]. Zinc oxide is currently being investigated as an antibacterial agent in both microscale and nanoscale formulations, results have indicated that ZnO nanoparticles show antibacterial activity apparently greater than micro particles. While the exact mechanisms of the antibacterial action have not yet been clearly understood. It has been suggested that reactive oxygen species (ROS) generated on the surface of the particles, release of zinc ion, membrane dysfunction, and nanoparticles internalization are the main cause of cell swelling [113]. High temperature treatment of ZnO particles has a significant effect on their antibacterial activity. The mechanisms of the antibacterial activity of ZnO particles are not well understood although proposed that the generation of hydrogen peroxide be a main factor of the antibacterial activity [114], and may be the binding of the particles on the
bacterial surface due to the electrostatic forces. A mechanism of the antibacterial behaviour of ZnO particles could be studied by using a chemiluminescence and oxygen electrode analysis [115]. The H₂O₂ was produced in ZnO slurry and the concentration of H₂O₂ produced was linearly proportional to the ZnO particle concentration of the slurry. The results obtained in this work clearly show that the presence of ZnO nanoparticles leads to damages the membrane wall of bacteria. Such damages may be partly due to direct interactions between ZnO nanoparticles and bacterial membrane surface.

1.16 Literature survey
The extensive literature survey on SNPs, ZnO, and Ag – ZnO nanocomposites is tabulated in Table 1

<table>
<thead>
<tr>
<th>Ref No</th>
<th>Description</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>116</td>
<td>Biogenic synthesis of silver and gold nanoparticles by <em>G. stearothermophilus</em> has been attempted. The exposure of <em>G. stearothermophilus</em> cell free extract to the metal salts leads to the formation of stable silver and gold nanoparticles in the solution. These nanoparticles were characterized by UV–visible spectra, FT-IR, TEM, and XRD. The silver and gold nanoparticles have absorption maxima at 423 nm and 522 nm respectively. The TEM micrograph revealed the formation of polydispersed particles in the case of silver nanoparticles and monodispersed particles with respect to the gold nanoparticles. The involvement of these proteins was confirmed by FT-IR and SDS PAGE.</td>
<td>2011</td>
</tr>
<tr>
<td>117</td>
<td>Biosynthesis of SNPs was achieved by a novel, simple green chemistry procedure using citrus sinensis peel extract as a reducing and a capping agent. The effect of temperature on the synthesis of SNPs was carried out at room temperature (25°C) and 60°C. The successful Formation of silver nanoparticles has been confirmed by UV–visible, FT-IR, XRD, EDAX, FE-SEM and</td>
<td>2011</td>
</tr>
</tbody>
</table>
TEM analysis and their antibacterial activity against gram-negative and gram-positive bacteria has been studied.

The synthesis of SNPs prepared by chemical reduction from aqueous solutions of silver nitrate, containing a mixture of hydrazine hydrate and sodium citrate as reductants and sodium dodecyl sulfate as a stabilizer. The results of the characterization of the SNPs show agglomerates of grains with a narrow size distribution (from 40 to 60 nm), whereas the radii of the individual particles are between 10 and 20 nm. Antibacterial activity was measured and results showed reasonable bactericidal activity against *E. coli*, *P. aeruginosa* and *S. aureus*.

Two silver salts, silver tetrafluoroborate and silver trifluoro methane sulfonate were dissolved in two different (RTILs), 1-Butyl-3 methyl imidazolium tetrafluoroborate ([Bmim] [BF4]) and 1-Butyl-1 methyl pyrrolidinium trifluoro methane sulfonate ([Bmpy] [Tfms]). Tritonx-100 (TX-100) surfactant and cyclohexane as nonpolar medium were used to dissolve these RTILs to create reverse micellar system. Pure reverse micellar system is characterized by DLS measurement. These pure RTIL reverse micellar systems were used to prepare stable SNPs solution without using any other auxiliary solvent in the whole process.

A fabrication process for non-volatile memory (NVM) transistors using ZnO nanoparticles, polymethyl silsesquioxane (PMSSQ) and soluble pentacene is reported. ZnO nanoparticles mixed into the PMSSQ solution were used to create a nanocomposite layer for charge trapping in the NVM. It has been demonstrated that the nanocomposite layer in a metal–insulator–semiconductor structure can cause a hysteresis of ~ 6 V in a capacitance–voltage (C–V) plot, indicating a significant charge trapping capability. A threshold voltage shift of ~ 2.3 V between a programmed and
erased NVM transistor and a carrier mobility of \( \sim 0.002 \text{ cm}^2/\text{V-s} \) were achieved. The fabricated NVMs have a limited life cycle of 4 program/erase cycles.

| 121 | Nanocomposite LDPE films containing Ag and ZnO nanoparticles were prepared by melt mixing in a twin-screw extruder. Orange juice was sterilized and was inoculated with 8.5 log cfu/mL of lactobacillus plantarum. Packages prepared from nanocomposite films were then filled with this orange juice and then stored at 4\(^0\)C. Reduced numbers of L. plantarum were observed (p < 0.05) in nanocomposite packages of orange juice containing nanosilver and nano-ZnO. The packaging made from nanocomposite film containing nanosilver showed a more pronounced antimicrobial effects, as compared with nano-ZnO during 112 days storage of inoculated orange juice. |
| 2011 |

| 122 | Highly luminescent silica-coated ZnO nanoparticles dispersed in an aqueous medium were synthesized using the sol–gel process. The samples prepared at various temperatures exhibited an emission peak at around 480 nm (blue color) and a quantum efficiency of 60% at maximum by the quantum confinement effect of ZnO nanoparticles, with diameters ranging from 3.1 to 3.5 nm, under ultraviolet excitation. No degradation of the quantum efficiencies and no peak shifting in the emission spectra were observed for 7 days following the preparation, which indicated no growth of ZnO nanoparticles in the aqueous medium. |
| 2011 |

| 123 | The antibacterial activity of nanosilver against E. coli bacteria is investigated by immobilizing nanosilver on nanostructured silica particles and closely controlling Ag content and size. These Ag/SiO\(_2\) nanoparticles were characterized by SEM/TEM, EDAX spectroscopy, X-ray diffraction, The exposed Ag surface area was measured qualitatively by O\(_2\) chemisorption. Furthermore, the fraction of dissolved nanosilver was determined by measuring the | 2010 |
released Ag\(^+\) ion concentration in aqueous suspensions of such Ag/SiO\(_2\) particles. The antibacterial effect of Ag\(^+\) ions was distinguished from that of nanosilver particles by monitoring the growth of E. coli populations in the presence and absence of Ag/SiO\(_2\) particles. The antibacterial activity of nanosilver was dominated by Ag\(^+\) ions when fine SNPs (less than about 10 nm in average diameter) were employed, those release high concentrations of Ag\(^+\) ions.

| 124 | The synthesis of SNPs using banana peel extracts (BPE) was reported. SNPs were formed when the reaction conditions were altered with respect to pH, BPE content, concentration of silver nitrate and incubation temperature. The colorless reaction mixtures turned brown and displayed UV–visible spectra characteristic of SNPs. The SEM observations revealed the predominance of nanosized silver crystallites after short incubation periods. When there mixtures were incubated for 15 days, some micro-aggregates were also observed. EDAX studies and X-ray diffraction analysis confirmed the presence of SNPs. FT-IR indicated the role of different functional groups (carboxyl, amine and hydroxyl) in the synthetic process. These SNPs shows antibacterial as well as antifungal activities. |
| 125 | The aqueous leaf extract of Chenopodium album was used as mild reducing agent for SNPs and GNPs in single-pot process. Quasi-spherical shapes were observed for biosynthesized SNPs and GNPs within range of 10–30 nm, respectively. The UV–visible spectra gave SPR for SNPs and GNPs at 460 and 540 nm, respectively. Influence of leaf extract quantities, metal concentrations, contact time, reaction temperature and pH were evaluated to find their effects on nanoparticle synthesis. The produced nanocrystals of silver and gold were analyzed with TEM, XRD, EDAX and FT-IR. |

2010
A non-toxic route was used for the preparation of SNPs using tryptophan as reducing/stabilizing agent in the presence of CTAB. Role of water soluble neutral polymer PVP has been studied on the growth of yellow colour SNPs formation. The synthesized nanostructures were characterized by UV–visible spectroscopy, and TEM. The formed nanoparticles showed the highest absorption plasmon band at 425 nm. Rate of silver sol formation increases with the [Trp], [CTAB] and [PVP], reaching a limiting value and then decreases with the increase in concentrations of these reagents. On the basis of kinetic data, a suitable mechanism is proposed and discussed for the silver sol formation.

The behavior of ILs in the phase transfer was reported. The proposed mechanism of phase transfer was the formation of a hydrophobic ion-pair between the cation of the stabilizer on the particle surface and the anion of the ILs, which cause the change in the surface hydrophilic properties and facilitate the phase transfer of aqueous nanoparticles into an organic phase. This mechanism was supported by NMR, FT-IR, XPS and ESI-MS. Further more, we investigated the effects of parameters on the phase transfer were investigated and found that phase-transferring efficiency increases with the extraction time and the concentration and hydrophobicity of the ILs.

The synthesis of porous chitosan–silver nanocomposite films, in view of their increasing areas of application in wound dressing, antibacterial application, and water purification was reported. The entire process consists of three-steps including silver ion-PEG matrix preparation, addition of chitosan matrix, and removal of PEG from the film matrix. Uniform porous and brown colour chitosan films impregnated with SNPs were successfully fabricated by this facile approach. Both, PEG and CS played vital roles in the reduction of metal ions nanoparticles as well as
provided good stability to the formed nanoparticles. The developed nanocomposite films were characterized by UV–visible, FT-IR and TGA for the confirmation of nanoparticles formation and morphology was tested by optical microscopy, SEM, and TEM. Further, the examined antibacterial activity results of these films revealed that synthesized nanocomposite films exhibited superior inhibition.

| 129 | SNPs were synthesized by the photoreduction of silver perchlorate (AgClO₄) in Water-IL microemulsions consisting of nonionic surfactant Tween 20, water, and ionic liquids, [1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF₄]) or 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIm][BF₄])], mixed with a high-pressure (25 MPa) CO₂. The time evolution of the SNPs formation by photoreduction was investigated by UV–visible, cryo-TEM, extended X-ray absorption fine structure (EXAFS), and small-angle X-ray scattering (SAXS) measurements. The average diameters of SNPs were estimated from TEM to be 3.2 and 3.7 nm. |

<p>| 130 | Novel hybrid material thin films based on PVA/TEOS with embedded SNPs were synthesized using sol–gel method. Two different strategies for the synthesis of SNPs in PVA/TEOS matrix were applied based on reduction of the silver ions by thermal annealing of the films or by preliminary preparation of silver nanoparticles using PVA as a reducing agent. The successful incorporation of SNPs ranging from 5 to 7 nm in PVA/TEOS matrix was confirmed by TEM and EDX analysis, UV–visible spectroscopy and XRD analysis. The antibacterial activity of the synthesized hybrid materials against etalon strains of three different groups of bacteria like <em>S. aureus</em>, <em>E. coli</em>, <em>P. aeruginosa</em> has been studied as they are commonly found in hospital environment. |</p>
<table>
<thead>
<tr>
<th>Page</th>
<th>Text</th>
</tr>
</thead>
<tbody>
<tr>
<td>131</td>
<td>The treatment of textiles with Ag/TiO$_2$ nanoparticles causes a brownish color that limits the application of this otherwise good composite. A novel method was introduced to overcome this problem. To this end, the effect of various concentrations of cross-linkable polysiloxane (XPs) and Ag mixed with XPs on TiO$_2$ treated fabrics has been investigated. The results reveal the performance of the method in the application of Ag and TiO$_2$ nanoparticles separately. In addition to the major effect of XPs on durability, the synergistic effect of applying XPs, especially Ag mixed with XPs, on TiO$_2$ has been confirmed. Other characteristics of treated fabrics such as antibacterial, self-cleaning, stain photo-degradability, UV protection, air permeability and washing durability were also investigated.</td>
</tr>
<tr>
<td>132</td>
<td>Antifungal activities of ZnO nanoparticles and their mode of action against two postharvest pathogenic fungi were investigated. ZnO NPs with sizes of 70 ±15 nm and concentrations of 0, 3, 6 and 12 mmol$L^{-1}$ were used. Traditional microbiological plating, SEM, and Raman spectroscopy were used to study antifungal activities of ZnO nanoparticle and to characterize the changes in morphology and cellular compositions of fungal hyphae treated with ZnO nanoparticles. Results show that ZnO nanoparticles at concentrations greater than 3 mmol$L^{-1}$ significantly inhibit the growth of fungi, which suggest that ZnO nanoparticles could be used as an effective fungicide in agricultural and food safety applications.</td>
</tr>
<tr>
<td>133</td>
<td>A conducting FTO electrode, first modified with ZnO nanorods and subsequently attached with photosynthesized SNPs designated as SNPs/ZnOnanorods/FTO electrode, was used as an amperometric sensor for the determination of hydrogen peroxide. The first layer ZnOnanorods was obtained by CBD, and was utilized simultaneously as the catalyst for the photoreduction of</td>
</tr>
</tbody>
</table>
Ag ions under UV irradiation and as the matrix for the immobilization of SNPs. The immobilized SNPs showed excellent electrocatalytic response to the reduction of hydrogen peroxide. The resultant amperometric sensor showed 10-fold enhanced sensitivity for the detection of H$_2$O$_2$, compared to that without SNPs. The selectivity of the sensor was investigated against ascorbic acid (AA) and uric acid (UA). The XRD, SEM, EDAX, TEM and CV were utilized to characterize the modified electrode. Sensing properties of the modified electrode were studied both by CV and amperometric analysis.

Briers-like ZnO nano architectures, which consisted of sword-like ZnO nanosheets, have been prepared by a facile organic CTAB, CH$_3$ (CH$_2$)$_{15}$N$^+$ (CH$_3$)$_3$ Br$^-$ inducing deposition process on the titanium substrate. The nanostructured composite has been characterized by XRD, FE-SEM, FT-IR, and XPS. The XRD pattern indicated that the sword like ZnO nanosheets are the high ordered nano layered inorganic–organic composites. The ordered layered nanocomposite exhibits room temperature PL characteristics.

The antifungal activity of SNPs prepared by the modified Tollens process was evaluated for pathogenic Candida spp. by means of the determination of the minimum inhibitory concentration (MIC), minimum fungicidal concentration (MFC), and the time-dependency of yeasts growth inhibition. Simultaneously the cytotoxicity of the SNPs to human fibro blasts was determined. The SNPs exhibited inhibitory effect against the tested yeasts at the concentration as low as 0.21 mg/L of Ag. The SNPs effectively inhibited the growth of the tested yeasts at the concentrations below their cytotoxic limit against the tested human fibroblasts determine data concentration equal to 30 mg/L Of Ag. In contrast, ionic silver inhibited the growth of the tested yeasts at the
concentrations comparable to the cytotoxic level (approx. 1mg/L) of ionic silver against the tested human fibroblasts.

<table>
<thead>
<tr>
<th>Page</th>
<th>Text</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>136</td>
<td>SNPs produced on the surface of soda-lime glass by nanosecond high-power ion beam irradiation were studied by optical methods. Influence of the ion irradiation characteristics on the optical properties of SNPs was discussed.</td>
<td>2009</td>
</tr>
<tr>
<td>137</td>
<td>A novel strategy for the biological synthesis of anisotropic gold and quasi-spherical SNPs by using apiin as the reducing and stabilizing agent. The size and shape of the nanoparticles can be controlled by varying the ratio of metal salts to apiin compound in their action medium. The resultant nanoparticles were characterized by UV–visible NIR, TEM, FT-IR spectroscopy, XRD and TGA. The interaction between nanoparticles with carbonyl group of apiin compound was confirmed by using FT-IR analysis. TEM photograph confirming the average size of the gold and silver nanoparticles were found to be at 21 and 39 nm. The NIR absorption of the gold nanotriangles is expected to be of application in hyperthermia of cancer cells and in IR-absorbing optical coatings.</td>
<td>2009</td>
</tr>
<tr>
<td>138</td>
<td>The synthesis of nanomaterials using a fungus, <em>Penicillium brevicompactum</em> WA 2315 has been attempted. The aqueous silver ions were reduced to SNPs when treated with the fungal supernatant. After 72 h of treatment, SNPs obtained were in the range of 23–105 nm as obtained from TEM. The nanoparticles were characterized by UV-visible, FT-IR, SEM, TEM and XRD.</td>
<td>2009</td>
</tr>
<tr>
<td>139</td>
<td>Three categories of plants growing under three different extreme conditions were taken for assaying their promises to undertake nano-transformation. It was found that all of them successfully synthesize SNPs. XRD and TEM analyses were performed to ascertain the formation of SNPs. XRD indicated that SNPs have</td>
<td>2009</td>
</tr>
</tbody>
</table>
FCC unit cell structure. Individual nanoparticles having the particle sizes of 2–5 nm were found. Possible involved mechanisms for the synthesis of SNPs from above plant systems have also been proposed.

| 140 | A surface was developed for surface-enhanced resonance Raman spectroscopy (SERR) in the near-ultraviolet range. For this purpose, SNPs were synthesized; exhibiting localized SPR at an excitation wavelength of 410 nm. SERR spectra of cytochrome c were used as a reference system to quantify the enhancement factor of the newly developed surface. Clusters therefore did not contribute to the enhancement factor at the wavelength of 413 nm. The overall surface enhancement factor finally achieved at this particular wavelength was in the range of 104-105. |

| 141 | The synthesis of SNPs by reducing silver nitrate with ethanol in the presence of PVP was reported. Reaction conditions, such as silver nitrate concentration, PVP concentration, reaction time, and reaction temperature, had been studied. The synthesized SNPs were added to electronically conducting fillers by re-dispersing them in ethanol. The proposed process offers the possibility to effectively use SNPs for improving the conductivity of ECAs. |

| 142 | The preparation of stable, uniform SNPs by reduction of silver ions by ethanol was reported. It is a simple process of recent interest for obtaining SNPs. The samples were characterized by XRD and TEM, which reveal of the nano nature of the particles. These studies infer that the particles are mostly spherical in shape and have an average size of 16 nm. The UV-visible spectra showed that an absorption peak, occurring due to SPR, exists at 410 nm. |

| 143 | It has been found that composites of CS and SNPs can exhibit excellent antibacterial activities. However, the weak mechanical |

**2009**
performances of these composite materials limit their wide application. A nanocomposite of CS graft MMA containing SNPs was prepared by in-situ chemical reduction of Ag ions in an aqueous acetic acid solution of CS and graft co-polymerization of MMA onto CS. TEM, XRD and UV-visible spectra of the nanocomposite confirmed the formation of SNPs. XPS proved that Ag–O bonds were existing in the composite. TGA, DTA showed that the decomposition temperature of CS was 319.8°C. While that of the composite shifted to a higher temperature of 422.1°C. Antimicrobial experiments showed that the antimicrobial rates of the CS-g-MMA/Ag composite to *E. coli*, *B. subtilis*, *S. aureus* and *P. aeruginosa* were 93–98%. The antimicrobial activity of the as-prepared nanocomposites was higher than that of CS alone.

The PET fabric samples were treated with crosslinkable polysiloxane via different methods, simultaneous or after treatment with various concentrations of SNPs. Finally, the antibacterial efficiency of modified fabrics was quantitatively evaluated and compared against *K. pneumonia* and *S. aureus* according to AAT CC100. A good biostatic efficacy against *S. aureus* appeared even by applying a low nanosilver content. However, a higher nanosilver content was necessary to attain such antibacterial effects against *K. pneumoniae*. Crosslinked polysiloxane resulted in a remarkable control in the release of silver from the coating and can improve the long-term microbiological activity. Simultaneous application of SNPs and polysiloxane emulsion on the fabric surfaces showed improved antibacterial efficiency as compared to separate application. The polysiloxane treatment has compensated for this difference to some extent. The experiment results revealed that polysiloxane also compensated for some adverse effects of nanosilver treatment such as decreasing conductivity and softness.
### Chapter 1

<table>
<thead>
<tr>
<th>Page</th>
<th>Text</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>145</td>
<td>The structural and biological properties of silicon wafers coated with ZnO thin films were evaluated using AFM, XPS and MTT viability assay. The antimicrobial properties of ZnO thin films were established using disk diffusion and CDC Biofilm Reactor studies. The results suggested that ZnO and other semiconductor materials may play a leading role in providing antimicrobial functionality to the next-generation medical devices.</td>
<td>2009</td>
</tr>
<tr>
<td>146</td>
<td>A very simple but well controlled chemistry in an aqueous medium allows one to efficiently control the main characteristics of oxide nanoparticles. Examples concerning titania, alumina, iron and manganese oxides were discussed to illustrate various effects on the control of size, shape and structure of nanoparticles. Some examples of functionalization of these particles were also illustrated.</td>
<td>2009</td>
</tr>
<tr>
<td>147</td>
<td>The effect of surface capping with PVA on the photo carrier relaxation of the aqueous chemically grown ZnO nanowires has been investigated. The decay in the photocurrent during steady UV illumination due to the photocarrier relaxation has been reduced in the capped nanowires, as evidenced from a decrease in the photocurrent only by 12 % of its maximum value under steady illumination for 15 min and a decrease in the photocurrent by 49 % of its maximum value during the same interval of time in the as-grown nanowires. The surface modification is confirmed from the FE-SEM, HR-TEM, and FT-IR results. The PL spectrum shows an enhanced ultraviolet mission and a reduced defect-related emission in the capped ZnO nanowires compared to bare ZnO.</td>
<td>2009</td>
</tr>
<tr>
<td>148</td>
<td>Novel waterborne polyurethane/flower-like ZnO nanowhiskers (WPU/f-ZnO) composite with different f-ZnO content (0–4.0 wt %) was synthesized by an in-situ copolymerization process. In order to disperse and incorporate f-ZnO into WPU matrix, f-ZnO was modified with g-amino propyl triethoxysilane. Morphology of</td>
<td>2009</td>
</tr>
</tbody>
</table>
f-ZnO in WPU matrix was characterized by SEM. The properties of WPU/f-ZnO composites such as mechanical strength, thermal stability as well as water swelling were strongly influenced by the f-ZnO contents. Antibacterial activity of WPU/f-ZnO composite films against *E. coli* and *S. aureus* was also tested. The results revealed that the antibacterial activity enhanced with the increasing f-ZnO content, and the best antibacterial activity was obtained at the loading level of 4.0 wt % f-ZnO.

An efficient, mechanochemical reaction for synthesizing ZnO NPs has been investigated. The starting materials were zinc sulfate hepta hydrate and KOH, and KCl served as the matrix salt. The reaction was carried out in a paste state at room temperature with a short grinding time and no post reaction calcination. The nanoparticles thus obtained had a mean diameter of 22.1 nm and exhibited excellent UV-blocking properties.

A simple controllable method is reported for the coating of ZnO nanowires with SNPs and ZnO/ CNTs composite. It has been achieved through DC electrophoresis of AgNO$_3$ electrolyte and CNTs in the presence of isopropanol dispersion of ZnO nanowires. The influence of SNPs and CNTs on the field emission properties of the composite materials was studied. The results demonstrate a remarkable enhancement of field emission current of ZnO nanowires in case of CNTs mixture and SNPs coating.

The size-tunable and water-soluble SNPs have been successfully synthesized with the assistance of glutathione. The as synthesized SNPs are ready to bind covalently with a model protein (bovine serum albumin) in mild conditions. The optical property of surface-modifiable SNPs was extremely sensitive to their size and the surface modification, suggesting a potential in the biomedical analysis and detection. Furthermore, SNPs with an average diameter of 6 nm effectively suppress the proliferation of human
leukemic K 562 cells in the dose- and time-dependent manners, suggesting the promising potential of SNPs in cancer therapy.

<table>
<thead>
<tr>
<th>Page</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>152</td>
<td>SNPs synthesized by a reagent less method involving only UV radiation have been used in colorimetric assay for the detection of ammonia in solution. The SNPs were synthesized by the exposure of a silver nitrate solution to a low-power UV source in the presence of polymethyl acrylate, which acted both as reducing and capping agent. The synthesis of the SNPs was studied by monitoring the changes in position and amplitude of LSPR band using UV–visible spectroscopy. The morphology of the particles was studied using TEM which confirmed the formation of spherical particles with an average particle size around 8 nm. Interestingly, the SNPs solution was found to display a strong color shift from purple to yellow upon mixing with increasing concentration of ammonia ranging from 5 to 100 ppm. Hence, the nanoparticles prepared with this method could be used as colorimetric assay for sensing applications of ammonia in water.</td>
</tr>
<tr>
<td>153</td>
<td>The water-IL microemulsion and IL-water microemulsion were prepared, in which hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexa fluorophosphate was used. The CV behavior and electroplating in the water IL and IL-water microemulsion systems containing silver nitrate were investigated for the first time. Both the CV curves exhibit the presence of reduction and oxidation peaks corresponding to the deposition and dissolution of silver from the two microemulsion systems. However, the CV obtained from IL/W microemulsion system exhibits a crossover, which is different from that obtained from W/IL microemulsion system.</td>
</tr>
<tr>
<td>154</td>
<td>A new one phase method for the synthesis of SNPs in aqueous systems that has been developed by using newly synthesized mono and dihydroxylated ILs and cationic surfactants based on 1,3-</td>
</tr>
</tbody>
</table>
disubstituted imidazolium cations and halogens anions was reported. The hydroxyl functionalized ILs and hydroxyl functionalized cationic surfactants also simultaneously acts both as the reluctant and protective agent. TEM, UV-visible and NMR, were used for characterization of HFILs, HFCSs and SNPs. TEM studies on the solution showed representative spherical SNPs with average sizes 2-8 nm, particularly 2.2 nm and 4.5 nm in size range and reasonable narrow particle size distributions 0.2 nm and 0.5 nm respectively. The SNPs SPR resonance band around 420 nm was found to be broadened and little moved to the long wavelength region indicating the formation of SNPs dispersion with broad absorption around IR region. Silver complexes of these hydroxyl functionalized ILs as well as different SNPs dispersions have been tested in vitro against several gram positive and gram negative bacteria and fungus.

155 ZnO thin films were prepared on glass substrate by sol-gel dip-coating method. The structural properties were investigated by XRD, AFM. The optical properties were measured by UV-visible spectrophotometer. The XRD patterns showed that the films formed preferred orientation along c-axis which increases as a function of PVP concentration. The films gave the crystallite size of 15-18 nm calculated by Scherrer’s formula and grain size of 48-70 nm measured by AFM at different PVP concentrations. The direct optical band gap of the films was in the range of 3.80-4.08 eV.

156 The nano-sized columned β-FeOOH was prepared by Jin et al for the hydrolysis process and its electrochemical capacitance performance was evaluated in Li₂SO₄ solution. A hybrid supercapacitor based on MnO₂ positive electrode and FeOOH negative electrode in Li₂SO₄ electrolyte solution was designed. The electrochemical tests demonstrated that the hybrid
supercapacitor has an energy density of 12Wh kg$^{-1}$ and a power density of 3700 Wkg$^{-1}$ based on the total weight of the electrode active materials with a voltage range 0–1.85 V. This hybrid supercapacitor also exhibits a good cycling performance and keeps 85% of initial capacity over 2000 cycles.

157 Crystalline ZnO nanoparticles were synthesized by mechanochemical method. It involves the mechanical activation of solid-state displacement reactions at low temperatures in a ball mill. Statistical design was used to investigate the effect of main parameters (i.e. time, milling rate and calcination temperature) on ZnO crystallite size and morphology. After annealing at 400$^0$C in air, ZnO were obtained. The milled powders are analyzed by XRD, TG/DTA and TEM. The crystallite size of ZnO samples calculated from XRD is consistent with the TEM images and estimated to be less than 20 nm. The optical properties of the samples were studied by UV–visible spectrophotometer.

158 ZnO nanoparticles were formed under continuous flow using spinning disc processing (SDP). Synthetic parameters such as temperature, flow rate, disc speed, and surface texture influence the reaction kinetics and particle size in an ethanolic solution using PVP as a capping agent. SDP ensures intense mixing, accelerates nucleation and growth, and affords monodispersed ZnO nanoparticles with controlled particle size. UV-visible spectroscopy shows the formation of particles down to a size of 1.3 nm and polydispersities of approximately 10 %, as well as subnanometer clusters. Modification of the temperature and flow rate provides control of the particle size and polydispersity, albeit with the nanoparticles slowly undergoing ripening post-SDP.

159 Silver nanobars with rectangular side facets and an average aspect ratio of 2.7 have been synthesized by modifying the concentration of bromide added to a polyol synthesis. Due to their anisotropy,
nanobars and nanorice exhibit two SPR scattering light both in the visible and in the near-infrared regions. With a combination of discrete-dipole approximation calculations and single-nanoparticle spectroscopy, the effect of nanostructure aspect ratio and corner sharpness on the frequency of plasmon resonance was explored. Near-field calculations and SERS measurements on single particles were performed to show how local field enhancement changes with both the wavelength and polarization of incident light.

| 160 | The synthesis and automatic separation of solvent dispersible silver and platinum nanoparticles in 1-butyl-3-methylimidazolium bis ( triflylmethyl-sulfonyl) imide ([BMIM] [Tf 2N]) ionic liquid (IL) using oleic acid as the major capping agent was reported. | 2006 |
| 161 | The antibacterial effects of six inorganic antibacterial agents were assessed using broth dilution and agar dilution tests on six pathogenic bacteria associated with oral infectious diseases: *S. mutans* (spe.1), *S. mutans* (spe.2), *A. viscosus* *L. casei*, *S. aureus* and *C. albicans*. The results of the broth dilution test were significantly lower than those of the agar dilution test (F=38.290; P<0.01). The six inorganic agents not ably inhibited the growth of tested common oral bacteria in vitro. Among them, Longbei inorganic antibiotic powder was the strongest antibacterial agent, followed by ZnO whisker antibacterial complex (ZnOw) AT-83, IONPURE-H, basic magnesium hypochlorite, ZnO wAT-88 and Antim-AMS2. The broth dilution test appears to be more suitable for testing insoluble inorganic agents. | 2006 |
| 162 | Coating of ZnO nanoparticles on paper surface has potential technological applications. With this motivation, a simple approach of ultrasound assisted coating of paper with ZnO nanoparticles without the aid of binder was reported. SEM was used to characterize the surface morphology showing ZnO | 2006 |
nanoparticles bound to cellulose fibers. Further characterization of coated surface is performed by attenuated total reflectance-FTIR, XRD, and time-of-flight secondary ion MS in positive ion detection mode along with its imaging capability. The effect of ultrasound irradiation time on ZnO nanoparticles loading was estimated by TGA analysis. The ZnO nanoparticles coated paper was found to possess antibacterial activity against *E. coli* 11634.

| 163 | Using a thin film of metallic tin as catalyst, ultra small single-crystalline zinc oxide nanobelts were synthesized in large quantity using a simple solid-vapor technique. The nanobelts were shown an average width of 5.5 nm and a narrow size distribution of (1.5 nm. The nanobelts grew along the [0001] direction, with (2-11-0) top/bottom surfaces and (011-0) side surfaces. PL measurement showed a blue shift in the emission spectrum compared to that acquired from ZnO nanobelts of ~200 nm in width. These ultrafine nanobelts were predicted as good candidates for investigating size-induced electrical and optical properties of functional oxides. | 2005 |

| 164 | Ordered arrays of polystyrene nanospheres were self-assembled on glass substrate and subsequently used as templates for thin silver film deposition. Silver-polystyrene nanocomposites with periodicity given by the polystyrene spheres diameter (400 nm) were obtained and investigated by optical and electron microscope measurements. The resonant interaction of light with SPR supported by periodically structured silver polystyrene nanocomposite leads to important spectroscopic applications like molecular sensing and enhanced Raman scattering. | 2005 |

| 165 | Preparations of metal nanoparticles and conjugated polymers and oligomers nanocomposite were synthesized by chemical and electrochemical methods are described. The electronic and optical properties of these materials were discussed. | 2005 |
The LSPR nanosensor based on the optical properties of SNPs was shown to aid in the understanding of the interaction between amyloid β-derived diffusible ligands (ADDL) and the anti-ADDL antibody, molecules possibly involved in the development of Alzheimer’s disease. By varying the concentration of anti-ADDL antibody, a surface confined binding constant of $3.0 \times 10^7$ M$^{-1}$ for the interaction of ADDLs and anti-ADDLs was measured. Influences of Cr, the nanoparticle adhesion layer was shown to be the limiting factor in the sensitivity of this assay.

Bending of polar-surface-dominated (PSD) nanobelts of ZnO were explained by one of the processes: as electrostatic neutralization of the dipole moment via deformation or imbalances between surface tensions via surface-termination induced stresses. The experimental data on the structural features of nanorings and nanobows formed by bending single-crystal, PSD ZnO nanobelts. The obtained data exclusively supports the electrostatic polar charge model as the dominant mechanism for bending.

One-phase synthesis of gold and platinum nanoparticles using new thiol functionalized ionic liquids (TFILs) was described for the first time. TEM, XRD, and NMR were used for the characterization of nanoparticles. The metal nanoparticles formed using TFILs are crystalline structures with face-centered cubic packing arrangements and having small sizes (the average diameter sare 3.5, 3.1, and 2.0 nm for Au and 3.2, 2.2, and 2.0 nm for Pt, respectively) and uniform distributions (the standard deviations are 0.7, 0.5 and 0.1 nm for Au and 1.1, 0.2, and 0.1 for Pt, respectively). It Is believed that the nanoparticle size and distribution depend on the number and position of thiol groups in the IL.

The work function at the tips of individual ZnO nanobelts has been measured by an electromechanical resonant method using in-situ
transmission electron microscopy. The work function of the ZnO nanobelts is ~ 5.2 eV, which shows no significant dependence on the geometrical size. Using a ZnO nanobelt as a carrier beam, the work function of a single nanoparticle of a different material has also been measured.

Well-aligned ZnO nanorods with identical crystallographic orientation have been synthesized using a vapor transport deposition process. Orientation-ordered nanorods were found to be grow normal to the c planes of the as-deposited micrometer-sized ZnO rods on a polycrystalline Al$_2$O$_3$ substrate, and each nanorod was along [001] and enclosed by [21-1-0] facet surfaces. By controlling the growth time at high temperature, uniform lengths of aligned nanorods have been received.

1.17 Plan of work

We purpose from the literature survey and theoretical background that the applications of nanostructured silver, zinc oxide and silver loaded zinc oxide is of great importance for the future in different areas of nanotechnology.

We have synthesized silver nanoparticles, zinc oxide nanoparticles and silver zinc oxide nanocomposite. The SNPs were synthesized by three schemes, two are chemical reduction method and third is biological method. In chemical reduction method stabilizing agents such as polyvinyl alcohol and ionic liquids are used as a stabilizer and hydrazine hydrate as a reducing agent. In biological method Ocimum leaf extract is used as both stabilizing as well as reducing agent. Biological method is novel non toxic and ecofriendly method for the synthesis of SNPs because there is no use of any chemicals which are harmful to the environment. Zinc oxide is synthesized by sol-gel method. In this method also no stabilizing agents were used, synthesis is done in ethanol-water system. Silver loaded zinc oxide nanocomposite is synthesized by loading of silver ions on zinc oxide, subsequently reduced by *Ocimum* leaf extract.
Chapter 1

The antibacterial behavior of synthesized SNPs, ZnO nanoparticles and silver zinc oxide nanocomposite materials is checked for strains of different gram positive, gram negative and non ferment gram negative bacteria. All the schemes of silver nanoparticles, zinc oxide nanoparticle shows very good antibacterial activity. There is the synergetic effect on the antibacterial activity observed for the silver loaded zinc oxide nanocomposite. The photocatalytic activity of zinc oxide and silver loaded zinc oxide is checked for Rhodamine B. The incorporation of small amount of SNPs on zinc oxide increases its photocatalytic activity largely.
References

Chapter 1

Chapter 1

[70] Li YQ, Fu SY, Mai YM, Polymer, 47 (2006) 2127.
Chapter 1