1. INTRODUCTION

According to British Royal Society and Royal Academy of Engineering, ‘Nanotechnology is the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale’ [1]. To better visualize nanoscale, different objects are compared in Figure 1. The main reason for the great interest in nanometer-sized structures is their interesting optical, magnetic and electrical properties, which are not found in their bulk counterparts. Among several exceptional characteristics of nanomaterials, high-surface-to-volume ratio [2, 3] and quantum confinement effects [4] are the two important properties. Such effects are responsible for new improved materials which have found applications in almost every field of science e.g. in medical applications, information technologies, energy production and storage materials, manufacturing, instrumentation, environmental applications and security [5-8].

![Nanometer Scale](image)

*Figure 1. Size of various objects at nanoscale.*

- **Semiconductor nanoparticles**

Semiconductor nanoparticles have special place in various fields due to their unique optical and electronic properties which can be manipulated by controlling their size [9]. They have broad absorption spectra and size-tunable photoluminescence (PL) spectra with narrow emission bandwidths [10]. The semiconductors composed of elements of two or more different groups, are more advantageous than pure semiconductors (silicon and germanium) because of higher electron mobility, wider band gaps, low thermal noise to devices at room temperature, etc. Among various semiconductor materials, the II-VI type semiconductors are the most vital materials due to larger band gaps. Cadmium sulfide (CdS) is the one of the most studied II-VI chalcogenides. It is yellow in colour and exists in two different forms, hexagonal...
greenockite [11] and cubic hawleyite [12]. It is a direct semiconductor with a band gap of 2.42 eV [13]. CdS nanoparticles have been explored in many applications including light emitting diodes, solar cells, lasers and biological markers [14-16]. Another important metal chalcogenide, Zinc sulfide (ZnS) has also been studied extensively because of its wide band gap and high refractive index. It is a white coloured powder having band gap 3.6 eV. It can also exist in two forms, cubic form also known as zinc blende [17] and hexagonal form [18].

Due to several useful properties, both ZnS and CdS nanoparticles are widely used in electroluminescence, non-linear optical devices, light emitting diodes, flat-panel displays, electroluminescence devices, photonic crystal devices, lasers, photocatalysis etc [19-25].

Synthesis of nanoparticles

The synthesis of nanoparticles can be classified into two approaches ‘top down’ and ‘bottom up’ (Figure 2). In top down approach, the bulk material is broken down into nanosized particles e.g. lithiographic techniques [26], laser beam processing [27] and microcontact printing [28]. The bottom up approach involves building up of material from bottom, atom-to-atom, molecule to molecule or cluster to cluster e.g. chemical synthesis [29] and colloidal aggregation [30].

![Figure 2. Comparison of ‘top down’ and ‘bottom up’ approaches.](image-url)

The colloidal solutions of nanocrystals are unstable due to their high surface area. Therefore, proper surface functionalization with suitable ligand is necessary for the stability of nanocrystals. Usually small organic molecules, surfactants or polymers, which bind to the surface of the nanoparticles, are used to stabilize
nanoparticles and prevent their aggregation. The stabilization of nanoparticles is generally divided into two types. One is electrostatic stabilization (Figure 3a), which arises due to coulombic repulsions between the particles [31] and other is steric stabilization (Figure 3b), due to adsorption of large molecules on surface of nanoparticles [2]. Polar and charged molecules/ligands have been observed to provide good dispersibility to the nanoparticles in aqueous media. However, nanocrystals stabilized by hydrophobic ligands are only soluble in nonpolar organic solvents.

![Electrostatic and steric stabilization](image)

**Figure 3.** Schematic illustration of (a) electrostatic and (b) steric stabilization of nanoparticles.

There have been a number of reports for the synthesis of metal sulfide nanoparticles [32-34]. However, most of the reported methods deal with their synthesis in organic media. Hence, to make nanoparticles water soluble, phase transfer is necessary [35, 36]. The methods involving synthesis of water soluble metal sulfide nanoparticles suffer from many disadvantages like larger sizes, high polydispersity of nanoparticles, long reaction times, high temperature requirement and tedious procedures [37, 38]. Thus, inspite of many procedures available for the synthesis of metal sulfide nanoparticles, a facile procedure with the use of less toxic precursors is still required.

- **Properties of semiconductor nanoparticles**

The properties of metal sulfide nanoparticles are totally different from bulk materials and depend upon their shape and size [39]. To explore numerous applications of these nanoparticles in the field of optoelectronic devices, photovoltaics etc., it is very important to understand their properties. One of the important properties of semiconductor nanomaterials is their wider band gap as compared to bulk materials due to quantum size effects (Scheme 1). In a nanoparticle, the particle size is comparable to or smaller than the exciton diameter in bulk material. As a
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consequence, continuous energy bands split into discrete levels and the electronic excitation shifts to higher energy.

Spectroscopy is the most important route to understand their properties completely. Bulk metal sulfide can absorb a photon and its electron gets excited from valence band to conduction band [40]. Smaller the size of nanoparticles, more is the blue shift in the absorption spectrum due to wide band gap [41].

Scheme 1. Band gap of nanoparticles is more compared to that of bulk semiconductor.

Fluorescence is another major optical property of semiconductor nanoparticles. It originates when excited electron in conduction band relaxes back to ground state by emission of energy [42]. However, practically luminescence of nanoparticles is very complicated. If the photo-excited electron recombines with holes in the valence band, near band edge emission takes place. Apart from this, trap state emission can also occur. Trap state emission can further be divided into two types: shallow-trap and deep-trap emission [43]. The shallow level traps, lie near to conduction or valance band, however, deep traps lie further into band gap. The emission due to these defects is of lesser energy or longer wavelength (Scheme 2).

Scheme 2. (a) Typical band edge emission (b) defect related emission.
Application of nanoparticles

(i) In chemical sensing

A chemical sensor is a device which responds to a particular chemical compound and can be used in qualitative and quantitative determination of analyte. In general, a sensor consists of three major components: a receptor to provide selective/specific binding with the target analyte and a transducer component which converts the signal in readable form [44] (Scheme 3). The efficiency of a sensor is determined from factors like limit of detection, signal to noise (S/N) ratio, selectivity and response time. In past decade, nanomaterials have proven to be highly promising candidates in chemical sensing and biosensing by increasing S/N ratio due to miniaturization of sensor elements [45]. Owing to the large fraction of surface atoms, the nanoparticles exhibit enhanced sensitivity and catalytic activity.

Scheme 3. Pictorial representation of general components of a chemical sensor.

Electrochemical sensors

Electrochemical sensors provide an accurate, low-cost, fast, on-line measuring system for the detection of hazardous chemical compounds and biomaterials. Electrochemical sensors can be broadly divided into three categories – potentiometric, coulometric and voltammetric. In potentiometric sensors, the potential difference between working and reference electrode is measured that relates to concentration of analyte. Coulometric sensors measure the amount of electricity consumed or produced to convert analyte into different oxidation state. However, voltammetric techniques are the most widely employed because of sensitivity, versatility, good S/N ratio and less influence of electrical disturbances [46-49]. In voltammetry, a potential is applied between working electrode and reference electrode, and the current resulting from the reduction or oxidation of the redox-active species on the electrode surface is measured. Different analytical techniques, including linear, cyclic, stripping and
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Amperometric methods can also be employed in voltammetry. Amperometry involves measurement of current at fixed potential. The magnitude of current is directly proportional to concentration of analyte.

The nanoparticles can be used in electrochemical sensors by immobilizing them on the surface of working electrode (Scheme 4). They provide large surface area for high catalytic activity, porous property for stronger adsorption of analyte and lower the overpotential of some important electrochemical reactions. Thus, nanoparticles improve the sensitivity of existing electrochemical systems to a large extent. Owing to their unique electrical properties, semiconductor nanocrystals, in particular, have generated considerable interest in electrochemical detection. The role of nanoparticles in electrochemical sensing can be either as a catalyst for electrochemical reactions or as one of the reactants [50].

![Scheme 4. Illustration of electrochemical response of nanoparticles modified electrode towards analyte.](image)

**Fluorescence sensors**

Fluorescence has become one of the most important methodologies in sensing because of its sensitivity, ease of use, and versatility. Conventionally, organic dyes have been used as fluorescent lables, but have many disadvantages like photobleaching, limited brightness and short lifetimes. The semiconductor nanoparticles have emerged as new advanced materials for fluorescent sensing with advantages like tunable emission, narrow and symmetric fluorescence spectra, high photochemical stability, broad absorption spectra etc [51]. In semiconductor nanoparticles, on the absorption of light, the electron from the valence band get excited to the conduction band, generating localized excitons (electron-hole pairs).
The electron–hole recombination leads to release of energy in the form of emission. The optical properties of semiconductor nanoparticles can be controlled by varying the particle size, size distribution (dispersity), shape, and surface chemistry etc. The photoluminescence (PL) of nanoparticles depends highly upon the surface chemistry. Thus the presence of different analytes [5, 52] in the environment of nanoparticles can largely influence the PL of nanoparticles. The chemical or physical interaction of nanoparticles with ions or small molecules present in the nanoparticles environment can respond via changes in their PL emissions. This forms the basis for using nanoparticles as fluorescence sensors. There can be decrease in intensity or an increase of the emission or a variation of the spectral shape.

The present course of work deals with the fabrication of electrochemical as well as fluorescence sensors for some hazardous compounds using metal sulfide nanoparticles. A hazardous compound means a substance which is flammable, combustible, explosive, corrosive, or reactive and whose overexposure results in acute and chronic health effects. Among numerous known hazardous chemical compounds, cyanide, hydrazine and 2, 4, 6-Trinitrotoluene (TNT) are very important because of their high toxicity, adverse health effects and threat to national security. Cyanide has received a significant attention due to its high toxicity to mammals causing death in a matter of minutes [53]. The accidental cyanide release from various industries in waste water or rivers may lead to serious contamination of groundwater and even drinking water [53]. Hence, there is need to develop some analytical methods which can detect very low concentrations of cyanide.

Hydrazine has been widely used in many industries, as rocket fuel, emulsifiers, catalysts, weapons for mass destruction, corrosion inhibitors, insecticides and plant growth regulators [54]. It has been classified as human carcinogen by Environmental Protection Agency (EPA). It has also been known as neurotoxin. The neurotoxin and carcinogenic nature of hydrazine as well as its high solubility in water raises concern for ground water contamination and generates interest among researchers for developing simple, economic and sensitive methods for its detection in aqueous solutions [55-57].

TNT, being a high energy explosive, not only poses a risk to national security but also detrimental for human health as well as aquatic life. Exposure to TNT can lead to abnormal liver function, serious effects on reproductive system, anemia,
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cataracts and cancer [58]. Thus, a significant research is being done developing methods for fast, simple, sensitive, and reliable detection of TNT [59, 60].

(ii) As catalyst in organic reactions

The semiconductor-metal nanocomposites as catalysts in organic reactions have been widely explored in literature [61-64]. The semiconductors can result into positively or negatively charged metal nanoparticles either by withdrawing electrons from or donating electrons to the metal nanoparticles, respectively. The charged metal nanoparticles can then catalyze different organic transformations. However, the semiconductor nanoparticles alone have not been explored much. Recently few groups have explored the role of semiconductor nanoparticles in organic catalysis [65, 66].

Biginelli reaction is an important organic reaction which is used for synthesis of dihydropyrimidinones (4) (DHPM). The medicinal and pharmaceutical importance of DHPM [67-70] has attracted the interest of synthetic chemists in Biginelli reaction [71, 72]. Biginelli reaction involves acid catalyzed cyclocondensation of aldehydes, alpha–beta keto esters, and urea/thiourea to give DHPM. The one pot multiple component Biginelli reaction was first studied and reported by P. Biginelli in 1893 [73] in the presence of HCl at elevated temperatures (Scheme 5). DHPM, also called Biginelli compounds, have been used as antihypertensive and anticancer drugs, antiviral and antibacterial reagents and calcium channel modulators [67-70].

\[ \text{Scheme 5. Classical Biginelli reaction.} \]

Proposed work plan

In the present work, the synthesis of water soluble metal sulfide viz. ZnS and CdS, nanoparticles has been carried out by microwave irradiation method. Polyethylene glycol (PEG) has been used as capping agent due to its biocompatible
and biodegradable nature. PEG also helps in making nanoparticles hydrophilic. The nanoparticles have been characterized by various techniques like ultraviolet-visible (UV-vis) spectroscopy, transmission electron microscopy (TEM), fluorescence spectroscopy, particle size analysis (PSA), fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) studies.

Further efforts have also been made to explore the use of synthesized nanoparticles in electroanalytic applications. Both ZnS and CdS nanoparticles have been employed to fabricate electrochemical sensors for the detection of cyanide ion, hydrazine and TNT in aqueous solutions. Cyclic voltammetry and amperometry have been used for electrochemical detection. The systems have been found to be reproducible, selective with low detection limits and have been tested on real samples. Further, ZnS nanoparticles have also been used in optical detection of cyanide and TNT in aqueous solutions. The mechanisms for variation in PL intensity on addition of cyanide ion and TNT have also been investigated. The low detection limits with good sensitivity and reproducibility make these nanoparticles suitable for practical applications.

The applications of ZnS and CdS nanoparticles have also been explored for the catalysis of Biginelli reaction. The reaction has been catalyzed using microwave irradiation and good yields of products have been obtained. The products have been characterized by $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectroscopy. Further, the nanoparticles have been recycled and reused for four times and good yields have been obtained in all cases.