4. RESULTS AND DISCUSSION

Metal sulfide nanoparticles are of great interest due to unique optical and electrical properties thus leading to wide applications. Numerous methods in literature have been reported for synthesis of these nanoparticles [96-120]. But still there is a need of simple, facile method with less tedious experimental conditions to synthesize monodispersed nanoparticles of small size. In this thesis, an easy approach for the synthesis of metal sulfide nanoparticles, in particular, zinc sulfide (ZnS) and cadmium sulfide (CdS), has been employed. Since polyethylene glycol (PEG) of molecular weight 2000 is biocompatible, biodegradable and excellent host material for nanoparticles, therefore, it is used as a capping agent. The hydroxyl (-OH) groups of PEG make particles soluble in water. The microwave irradiation method has been used for the synthesis of nanoparticles due to its many advantages like rapid heating and improvement in rate of the reaction, thus, resulting in a narrow distribution of the particle size. The nanoparticles have been characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), particle size analysis (PSA), Fourier transmission infrared spectroscopy (FTIR), UV-vis spectroscopy, fluorescence spectroscopy. The synthesized nanoparticles have been used to fabricate electrochemical sensor for hydrazine, cyanide and 2, 4, 6-trinitrotoluene (TNT) in aqueous solution using cyclic voltammetry and amperometry. An attempt has also been made to develop fluorescent sensors for cyanide and TNT using ZnS nanoparticles. The fabricated systems have been found to possess good sensitivity, lower limits of detection, reproducibility and applicability to real samples. Further, both ZnS and CdS nanoparticles have been employed as catalyst for Biginelli reaction under solvent free conditions. The excellent yields of products have been obtained. The products have been characterized using nuclear magnetic resonance (NMR) spectroscopy.

4.1. Synthesis of nanoparticles

The synthesis of metal sulfide nanoparticles has been carried out using an eco-friendly route. Metal acetate (M(OAc)₂, M = Zn, Cd) and thioacetamide (TA) have been chosen as metal ion source and sulfide ion source, respectively. TA is used instead of ionic precursors like Na₂S as sulfide ion source because it decomposes on heating and releases \( \text{H}_2\text{S} \) gas slowly, which leads to formation of small
Results and discussion

monodispersed nanoparticles of narrow size distribution [263]. PEG (27) has been used as a capping agent for the stabilization of nanoparticles because of its biocompatibility as well as biodegradability.

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{O} \\
\text{H}
\end{array}
\]

\[\text{27}\]

Figure 75. Molecular structure of PEG.

4.1.1. Optimization of conditions for the synthesis of nanoparticles

The preliminary investigation for optimization of conditions has been done by visual inspection as well as UV-vis spectroscopy. The appearance of light turbid and light yellow colour (Figure 76) has indicated the formation of ZnS and CdS nanoparticles, respectively. PEG has been used as surface protecting agent as the aqueous dispersions of nanoparticles synthesized in its presence are stable for months. However, in the absence of PEG, the particles are found to be unstable and settled down.

\[\begin{array}{c}
\text{(a)} \\
\text{(b)}
\end{array}\]

Figure 76. Indication of formation of (a) ZnS (b) CdS nanoparticles by colour change after microwave irradiating samples.

Since band gaps of both ZnS and CdS fall in UV-vis region, therefore, UV-vis spectroscopy can be used to monitor the growth of nanoparticles. Aqueous solution of PEG has been taken as reference, therefore, peaks only due to nanoparticles have been observed. The metal acetates do not show any peak in 200-600 nm range while TA
Results and discussion

shows a prominent peak at 270 nm. On microwave irradiation, the peak at 270 nm disappeared and characteristic absorption shoulders appeared at approx. 300 and 490 nm respectively for ZnS and CdS nanoparticles (Figure 77), which are attributed to exciton absorption of nanoparticles [109].

Figure 77. UV-vis spectra of thioacetamide, ZnS and CdS nanoparticles.

The experimental conditions have been optimized for the synthesis of ZnS nanoparticles using UV-vis spectroscopy. First of all, the effect of ratio of [Zn(OAc)$_2$]:TA has been investigated by keeping [Zn(OAc)$_2$] constant and varying concentration of TA (Figure 78a). The microwave irradiation time has been kept 10 s for all samples. It has been observed that absorbance increases on increasing concentration of TA and reaches maximum at [Zn(OAc)$_2$]:TA] = 2. On further increasing concentration of TA to get [Zn(OAc)$_2$]:TA] = 2.5, the absorption maximum is not changed. Thus, [Zn(OAc)$_2$]:TA] = 2 has been found to be optimum and further studies have been carried out at this ratio. After fixing the [Zn(OAc)$_2$]:TA], next step is to find out the optimum irradiation time. For this, concentration of PEG is kept constant (5 mM) and [Zn(OAc)$_2$]:[TA] has been taken as 2. Four different samples have been irradiated at different times (10, 15, 20, 25 s) and absorption spectra have been recorded (Figure 78b). After 20 s, there is no effect on the absorption spectra. Thus, the optimum time has been fixed as 20 s. Further, ideal concentration of PEG necessary for stabilization of nanoparticles has been examined. Figure 78c shows that increasing concentration of PEG from 10 to 15 mM does not cause significant changes in absorption spectrum of nanoparticles. Also, a slight blue shift has been detected on increasing concentration of PEG from 5 to 10 mM, indicating formation
Results and discussion

of smaller size nanoparticles at 10 mM concentration. Thus further studies have been carried out at these conditions. The same optimized conditions have been used for the synthesis of CdS nanoparticles thereafter.

Figure 78. Effect of (a) Zn(OAc)$_2$:TA ratio (b) microwave irradiation time (c) different concentrations of PEG on absorption spectra of ZnS nanoparticles.

4.1.2. Morphological, Structural and optical properties of PEG-Coated ZnS and CdS nanoparticles

Transmission Electron Microscopy (TEM)

The morphologies of ZnS and CdS nanoparticles have been characterized by TEM and the results are shown in Figure 79 (a and b). It is clear from the micrograph that the as-synthesized nanoparticles are monodispersed and spherical in shape. Most of the nanoparticles possess almost similar diameter. The typical diameters of the ZnS and CdS nanoparticles are approx. 11 and 15 nm, respectively.

Figure 79. TEM images of (a) ZnS (b) CdS nanoparticles.
X-ray diffraction (XRD)

To examine the crystallinity and crystal phases of nanoparticles, XRD has been recorded and the results are presented in Figure 80. Three well defined diffraction peaks have been observed for ZnS nanoparticles in the obtained XRD pattern (Figure 80a). The diffraction peaks appear at 2θ = 29°, 48.4° and 57.4° which correspond to <111>, <220>, and <311> lattice planes, respectively. This clearly confirms the cubic zinc blende structure of prepared ZnS nanoparticles (JCPDS 05-0566) [264]. The crystallite size is estimated to be 2.25 nm using Debye Scherrer’s formula (eqn 1). In the obtained patterns, no peak related with any impurity has been observed, within the resolution limit of the XRD diffractometer, which confirms the pure phase formation of prepared ZnS nanoparticles. In addition to this, the broadening in the diffraction peaks clearly confirms that the synthesized product is in nanoscale. Figure 80b exhibits typical XRD pattern of CdS nanoparticles powder sample. The peaks at 2θ = 25.2°, 26.8°, 28.5°, 43.95°, 48.3 and 52.3° corresponding to planes <100>, <002>, <101>, <110>, <103> and <112>, respectively have been observed. XRD pattern of this sample can be indexed to a hexagonal phase (JCPDS 41-1049) [265]. The estimated average crystallite size of CdS nanoparticles from XRD is 12.5 nm.

![Figure 80. XRD pattern of (a) ZnS and (b) CdS nanoparticles.](image-url)
Results and discussion

FTIR spectroscopy

Adsorption of PEG on nanoparticles has been examined by recording FTIR spectra in the range 4000-400 cm\(^{-1}\). Figure 81 depicts FTIR spectra of pure PEG and PEG coated metal sulfide nanoparticles. The peaks at 3424, 2887 and 1113.6 cm\(^{-1}\) are due to O-H, CH\(_2\) and C-O stretching, respectively. These peaks significantly shift to 3392, 2918, and 1101 cm\(^{-1}\) respectively, when PEG is adsorbed on ZnS nanoparticles. While adsorption of PEG on CdS nanoparticles shift these peaks to 3392, 2867 and 1112 cm\(^{-1}\) respectively that indicates the absorption of PEG on metal sulfide nanoparticles. Also, in the case of ZnS and CdS nanoparticles, peaks at 457 and 411 cm\(^{-1}\) correspond to Zn-S and Cd-S bonds, respectively [266, 267].

![FTIR spectra of PEG, ZnS, and CdS nanoparticles](image)

Figure 81. FTIR spectra of (a) PEG, (b) ZnS and (c) CdS nanoparticles.

UV-vis spectra

UV-vis spectroscopy is an important technique for the characterization of semiconductor nanoparticles. The absorption of nanoparticles is very much dependent upon their size. Smaller the size of nanoparticles, greater is the band gap between valence band and conduction band. Thus, small sized nanoparticles absorb at higher energy or smaller wavelengths than large sized particles. To examine the optical properties of synthesized ZnS and CdS nanoparticles, UV-vis spectra have been recorded at room-temperature. For UV-vis measurements, the synthesized products
have been ultrasonically dispersed in water. One mL of this solution is used for analysis with PEG as a reference. Figure 82 depicts typical UV-vis spectrum of synthesized nanoparticles. The well-defined absorption shoulders at 293 and 490 nm have been observed for ZnS and CdS nanoparticles, respectively (Figure 82). It is well known that the relationship between absorption coefficient and the incident photon energy of semiconductors can be obtained by using Tauc’s formula (eqn 4).

\[
(\alpha h\nu) = A(h\nu - E_g)^n
\]  

where \(\alpha\) is the absorption coefficient, \(A\) is constant, and \(n\) is equal to \(\frac{1}{2}\) for a direct transition semiconductor and 2 for indirect transition semiconductor. Using Tauc’s equation, the optical band gap (\(E_g\)) can be experimentally obtained from absorption coefficient. The calculated optical band gaps for the synthesized ZnS and CdS nanoparticles are 4.23 and 2.53 eV, respectively. The obtained optical band gaps are considerably higher and blue shifted from the bulk ZnS (3.65 eV) and CdS (2.40 eV). This is attributed to the quantum size effect of the synthesized nanostructures.

\[\text{Figure 82. UV-vis spectra of (a) ZnS and (b) CdS nanoparticles.}\]

**Photoluminescence Studies**

Due to several advantages from application point of view [268-270], photoluminescence (PL) properties of synthesized metal sulfide nanoparticles have been carried out. Figure 83a shows typical PL spectrum of ZnS nanoparticles at excitation wavelength of 320 nm. The obtained PL spectrum exhibits the appearance
of two emissions, i.e. a small band at 360 nm in the UV region and a broad band at 434 nm in the UV-vis region. The peak in the UV region has been attributed to direct band to band recombination and is called band edge emission. The visible region peak can be assigned to defect related emission [271]. Figure 83b shows PL spectra of as prepared CdS nanoparticles with the excitation wavelength at 400 nm. The peak around 535 nm (referred as green emission) and a minor emission shoulder around 575 nm (referred as yellow emission) have also been observed. The peak around 480 nm shows near band-edge emission while other peaks, which are at higher wavelength than the absorption edge indicate that the emission involving donor, acceptor and trap states [272]. The energy levels of interstitial and vacancies ions lie in between valence band and conduction band of semiconductors. These levels cause emission at lower energies (longer wavelength) compared to band edge emission (Figure 84).

**Figure 83.** PL spectra of (a) ZnS and (b) CdS nanoparticles.

**Figure 84.** Various decay routes for electron-hole recombination in metal sulfide nanoparticles.
Particle size analysis (PSA)

The particle size distribution of synthesized nanoparticles has been characterized by PSA. Figure 85 shows the typical particle size distribution graph which reveals that the average diameters of synthesized ZnS and CdS nanoparticles are approx. 7 and 11 nm, respectively. The polydispersity indices of synthesized nanoparticles have been found to be 0.19 and 0.18, which further confirm the monodispersity of synthesized nanoparticles.

Figure 85. Particle size distribution of (a) ZnS and (b) CdS nanoparticles.

The growth of nanoparticles can be well understood based on the chemical reactions involved in the synthesis process. During the reaction, M(OAc)$_2$ dissociates into metal ions (M$^{2+}$) and acetate (OAc$^{-}$) ions. The fast heating in microwave process in the presence of PEG accelerates the decomposition of TA to provide sulfide (S$^{2-}$) ions. This phenomenon can be understood through a simple chemical reaction mentioned below:

\[ \text{CH}_3\text{CSNH}_2 + \text{H}_2\text{O} \xrightarrow{\text{MW}} \text{CH}_3\text{CONH}_2 + \text{H}_2\text{S} \quad \text{(xi)} \]

\[ \text{H}_2\text{S} \rightarrow 2\text{H}^+ + \text{S}^{2-} \quad \text{(xii)} \]

The nucleation of metal sulfide (MS) occurs due to the reaction between M$^{2+}$ and S$^{2-}$ ions according to the chemical reaction mentioned below:

\[ \text{M}^{2+} + \text{S}^{2-} \rightarrow \text{MS} \quad \text{(xiii)} \]

The initially formed metal sulfide nuclei act as building blocks for the formation of final product. With time under proper reaction conditions, the concentration of metal sulfide nuclei increases which leads the formation of final products.
Results and discussion

During the reaction, PEG gets adsorbed on the surface of MS nanoparticles with their hydrophilic –OH groups spread out into water. Figure 86 illustrates a typical stabilization structure of MS nanoparticles by PEG in aqueous solution. Therefore, as a final product, MS nanoparticles have been obtained under the reaction conditions employed.

![Illustration of adsorption of PEG on nanoparticles.](image)

Conclusions

ZnS and CdS nanoparticles have been synthesized by irradiating sample in microwave for 20 s. The characterization of nanoparticles has been done by various techniques like UV-vis spectroscopy, TEM, XRD, FTIR and fluorescence spectroscopy. XRD of ZnS nanoparticles has revealed cubic zinc blende crystal structure with crystallite size 2.25 nm. However, size from TEM and PSA has been evaluated as 11 and 7 nm, respectively with good monodispersity. In UV-vis spectrum, a shoulder at 293 nm has been observed. In case of CdS, the size of nanoparticles has been found to be approx. 15 nm from TEM. Almost all the particles have been found to be of similar sizes. From XRD, the crystal structure of CdS has been observed as hexagonal with crystallite size 12.5 nm. A shoulder at 490 nm has been observed in UV-vis spectrum. The shifting of bands in FTIR suggests the adsorption of PEG on surface of nanoparticles. Thus an easy and simple one-pot approach has been developed for synthesis of monodispersed spherical nanoparticles of ZnS and CdS.
4.2. Application of nanoparticles

4.2.1. Electrochemical sensors

Electrochemical sensors based on MS nanoparticles for cyanide, hydrazine and TNT have been developed using cyclic voltammetry. In voltammetry, the current-potential behaviour at an electrode surface is investigated. A three electrode system, consisting of reference electrode, counter electrode and working electrode is used. The potential is varied and corresponding current is measured. Different compounds have different tendency to get oxidized or reduced on a given electrode at a particular potential. Thus, cyclic voltammetry can be used for quantitative as well as qualitative analysis. The current is due to electrochemical oxidation or reduction of electroactive species. The current depends linearly upon the concentration of the electroactive component [273]. The peak current also depends upon scan rate [274]. At slower scan rate of potential, the formation of diffusion layer extends far from the electrode as compared to fast scan rate. Thus, the peak current is less at slow scan rates and keeps on increasing with increasing scan rates. The mechanism of oxidation and reduction can be predicted by calculating number of electrons involved in the reaction using Randles Sevick equation (5) for reversible and modified equation (6) for a totally irreversible reaction.

\[ i_p = \left(2.99 \times 10^5\right)n^{1/2}A^{1/2}D^{1/2}C \]  
\[ (5) \]

\[ i_p = \left(2.99 \times 10^5\right)(\alpha n_\alpha)^{1/2}A^{1/2}D^{1/2}C \]  
\[ (6) \]

Where \( n \) is the number of electrons exchanged during the redox process, \( \alpha \) is charge-transfer coefficient, \( n_\alpha \) is number of electrons involved in charge transfer step, \( A \) (cm\(^2\)) is the active area of the working electrode, \( D \) (cm\(^2\) s\(^{-1}\)) is the diffusion coefficient, \( C \) (mol cm\(^{-3}\)) is the bulk concentration of electroactive species and \( v \) is the voltage scan rate (V s\(^{-1}\)). The value of \( \alpha n_\alpha \) can be calculated from equation (7)

\[ \alpha n_\alpha = 47.7\frac{mV}{(E_p - E_{p/2})} \]  
\[ (7) \]

Where \( E_p \) is peak potential and \( E_{p/2} \) represents half-peak potential (potential at which current is half of the peak current).

Conventional electrodes suffer from hindrance of electrochemical detection due to large overpotentials of some compounds. The use of modified electrodes has
Results and discussion

provided the solution of this problem, by diminishing these typically large overpotentials encountered in direct oxidation or reduction at bare electrode surfaces [275-277]. Further, the modification of conventional electrodes with nanomaterials offer advantages like high catalytic ability, large pore size, high sensitivity and lower limits of detection. In present study, Ag/AgCl electrode and Pt electrode have been used as reference and counter electrodes, respectively. We have used ZnS and CdS modified gold (ZnS/Au and CdS/Au) electrodes for the detection of cyanide, hydrazine and TNT. The investigations have shown that these nanoparticles can detect mentioned analytes upto trace levels with high sensitivity.

4.2.1.1. Cyanide detection

Cyanide is one of the rapidly acting lethal poisons due to its high toxicity in the physiological systems. Thus, an attempt has been made to detect cyanide ion in aqueous solution using cyclic voltammetry. To evaluate the cyanide sensor performance based on ZnS nanoparticles, the ZnS/Au electrode has been used for all the cyclic voltammetric and amperometric experiments. Figure 87a exhibits the CV electrochemical responses of ZnS/Au electrode towards cyanide oxidation. The CV has been measured by scanning the potential from -0.5 to +0.5 V versus Ag/AgCl at a scan rate of 50 mV s\(^{-1}\). The cyclic voltammograms of the cyanide using ZnS/Au electrode in a 0.1 M phosphate buffer solution (PBS) (pH = 10.0) with and without NaCN solution are presented. As it is clear from the CV graphs that no redox peak has been observed in the absence of cyanide solution using modified electrode; however, when a small amount of cyanide solution (1 mM) is added, under same experimental conditions and setup, a significant and enhanced anodic peak at -0.08 V and current 0.876 \(\mu\)A have been observed. The unmodified gold electrode has been found to be inefficient for electrooxidation of cyanide. The electrochemical response of cyanide is irreversible as no cathodic current is observed in the reverse sweep. Therefore, it can be concluded that the modified ZnS/Au electrode can be used as an efficient and sensitive sensor for detection of cyanide ion in aqueous solution.

Figure 87b shows the response of CdS/Au electrode with phosphate buffer and cyanide ion solution (1 mM) using CV. The electrode is inactive for buffer as no peak has been observed. Also, there is no response when unmodified gold electrode has been employed as working electrode in cyanide ion solution. However, a significant
Results and discussion

A peak appears in the same range when cyanide ion solution is treated with CdS/Au electrode. Thus, the system is active for cyanide ion detection with CdS/Au electrode.

**Figure 87.** Cyclic voltammograms of 1 mM cyanide ion using bare Au, and (a) ZnS/Au (b) CdS/Au electrodes in absence and presence of 1 mM cyanide.

**Effect of scan rates**

To get more information regarding the catalytic reactions involved in the sensing process, the modified ZnS/Au and CdS/Au electrodes have been examined at various scan rates (50, 60, 70, 80, 90 and 100 mV/s), in 0.1 M PBS buffer solution (pH=10.0), containing 1 mM NaCN solution. Figure 88 (a and b) exhibits the CV responses of the modified electrodes at various scan rates for ZnS and CdS nanoparticles, respectively. It is clear from the observed CV graphs that with increasing scan rates, the current also increases and apparently slight shifts in the anodic peak potential have been observed. Figure 89 (a and b) shows a linear relationship between the anodic peak current and square root of the scan rates ($v^{1/2}$). This is in accordance with modified Randles Sevick equation (6) which infers that the reaction involved is a diffusion controlled [274, 278, 279]. Moreover, the number of electrons involved in overall reaction ($n$) has been calculated using equation (6) for a totally irreversible reaction, which comes out to be 2. Accordingly, the mechanism for the oxidation process of cyanide at both ZnS/Au and CdS/Au electrodes can be proposed as

$$\text{CN}^- + 2 \text{OH}^- \rightarrow \text{CNO}^- + \text{H}_2\text{O} + 2 \text{e}^- \quad \text{(xiv)}$$
Results and discussion

Potential (volt) v/s Ag/AgCl

Figure 88. Effect of scan rate (50, 60, 70, 80, 90, 100 mV) on oxidation of cyanide ion using (a) ZnS/Au and (b) CdS/Au electrodes.

Figure 89. Plot of peak current vs. square root of scan rate using (a) ZnS/Au and (b) CdS/Au electrodes.

Amperometric studies

As the amperometry has a much higher current sensitivity than the cyclic voltammetry, hence the amperometric experiments have been performed under stirring. The detection of cyanide ion follows the chemical reaction mentioned in equation (viii) and finally amperometric responses have been observed. Figure 90 shows amperometric responses of ZnS/Au and CdS/Au electrodes on subsequent addition of NaCN solution (100–700 nM) at a constant potential in 0.1 M PBS solution at pH = 10.0. It is apparent that after each addition of NaCN solution, a rapid
Results and discussion

increase in the current has been observed within a response time of < 2 s in amperometric measurements. This shows the efficiency of nanoparticles as electrocatalyst for oxidation of cyanide.

Figure 90. Amperometric responses on successive addition of cyanide ion with (a) ZnS/Au electrode (b) CdS/Au electrode.

Figure 91 depicts the relationship between response current vs. NaCN concentration at constant applied potential. With increase in concentrations of NaCN solution, the response current also increases linearly with regression coefficient value 0.992 and 0.989 for ZnS/Au and CdS/Au electrodes, respectively. The limits of detection, estimated as 3*N/slope of calibration curve, where N is noise (or standard deviation in the peak current for five replicate measurements), have been found to be \(0.177 \times 10^{-6}\) and \(0.090 \times 10^{-6}\) mol L\(^{-1}\) for the fabricated sensors using ZnS/Au and CdS/Au electrodes, respectively. The fabricated sensors show the sensitivities of 79.7 and 48.4 \(\mu\)A cm\(^{-2}\) nM\(^{-1}\) for ZnS/Au and CdS/Au electrodes, respectively, as calculated from relation, sensitivity = slope of calibration curve/area of electrode. The observed limits of detection for the fabricated cyanide ion sensors are much lower than maximum value of cyanide (2.7 \(\times\) 10\(^{-6}\) mol L\(^{-1}\)) permitted by the World Health Organization (WHO) in drinking water. A brief comparison of various parameters of the fabricated ZnS/Au and CdS/Au electrodes based cyanide sensor with the previously reported cyanide sensors has been given in Table 6. It can be concluded that the fabricated cyanide sensor exhibits the highest sensitivity and lowest detection limit and hence exhibits excellent sensing performance.
Results and discussion

Figure 91. Calibration curves of the amperometric response of (a) ZnS/Au and (b) CdS/Au electrodes.

Table 6. Performance summary of the various cyanide ion electrochemical sensors based upon different working electrodes.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Electrode materials</th>
<th>Sensitivity (μA/cm²nM)</th>
<th>Limit of detection (μM)</th>
<th>Response time (s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>3,4-tetra pyridinoporhirazin atocobalt(II)</td>
<td>N.A.</td>
<td>9.1</td>
<td>N.A.</td>
<td>149</td>
</tr>
<tr>
<td>2.</td>
<td>MCPE electrode</td>
<td>N.A.</td>
<td>9.0</td>
<td>300</td>
<td>152</td>
</tr>
<tr>
<td>3.</td>
<td>Naflon coated Au electrode</td>
<td>N.A.</td>
<td>2.0</td>
<td>20</td>
<td>280</td>
</tr>
<tr>
<td>4.</td>
<td>Cytochrome c modified Au electrode</td>
<td>N.A.</td>
<td>0.5</td>
<td>N.A.</td>
<td>153</td>
</tr>
<tr>
<td>5.</td>
<td>ZnS nanoparticles</td>
<td>79.7</td>
<td>0.177</td>
<td>&lt; 2</td>
<td>This work</td>
</tr>
<tr>
<td>6.</td>
<td>CdS nanoparticles</td>
<td>48.4</td>
<td>0.09</td>
<td>&lt; 2</td>
<td>This work</td>
</tr>
</tbody>
</table>
Selectivity towards cyanide ion

In order to apply the proposed sensor for the determination of cyanide ion in real samples, specificity of sensor for cyanide ion has been investigated. The amperometric responses of some common interfering ions (Cl⁻, Br⁻, NO₃⁻, SO₄²⁻ and CO₃²⁻) have been recorded. Figure 92 exhibits the amperometric responses of ZnS/Au and CdS/Au electrodes in the presence of various interfering ions (Cl⁻, Br⁻, NO₃⁻, SO₄²⁻ and CO₃²⁻). It is clear that addition of other ions cause negligible changes to response current in amperometry. However, a significant and immediate increase in the response current has been observed in the amperometric measurements when cyanide ions are added in the solution. This phenomenon reflects the high selectivity of the fabricated sensors towards cyanide ions.

![Amperometric responses of ZnS/Au and CdS/Au electrodes](image)

**Figure 92.** Amperometric responses of (a) ZnS/Au and (b) CdS/Au electrodes in the presence of various interfering ions (Cl⁻, Br⁻, NO₃⁻, SO₄²⁻ and CO₃²⁻).

Application to real samples

Further, the proposed method has been applied to determine cyanide in industrial water containing cyanide ions. The comparison of results with procedure developed by Noroozifar et al. [281] has been given in Table 7. The results were compared by applying paired t-test in statistics. The calculated value of t according to eqn 8 is 1.12, which is less than the critical value of t = 3.18 for n-1 degrees of freedom (P= 0.05) [282]. Therefore, the null hypothesis of no difference is not rejected. Thus, there is a good agreement between the proposed method and other standard method.
Results and discussion

\[ t = \frac{d \sqrt{n}}{sd} \]  

(8)

where \( \bar{d} \) and \( sd \) are mean and standard deviation of difference in paired values.

To check the stability of the fabricated sensor, repetitive measurements have been done once a day for 3 weeks. From the several experiments, it has been observed that there is no significant change in current response for approximately 3 weeks, however, the current response decreases gradually thereafter. The obtained results indicate the excellent stability and reliability of the ZnS and CdS modified sensor for the detection of cyanide ion in aqueous solution.

<table>
<thead>
<tr>
<th>Industrial Sample</th>
<th>ZnS/Au electrode (μmol L(^{-1}))</th>
<th>CdS/Au electrode (μmol L(^{-1}))</th>
<th>Standard Method (μmol L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.46</td>
<td>2.18</td>
<td>2.24</td>
</tr>
<tr>
<td>2</td>
<td>2.18</td>
<td>2.28</td>
<td>2.34</td>
</tr>
<tr>
<td>3</td>
<td>1.59</td>
<td>1.49</td>
<td>1.37</td>
</tr>
<tr>
<td>4</td>
<td>1.45</td>
<td>1.26</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Thus ZnS/Au and CdS/Au have proved to be promising candidates for detection of cyanide in aqueous solutions. The lower limit of detection, high sensitivity and selectivity make these systems efficient for practical applications.

4.2.1.2. Hydrazine detection

The neurotoxin and mutagenic nature of hydrazine, its high solubility in water and use in many industries have raised concern about ground water contamination [54]. This motivated different research groups for developing systems for its detection in aqueous solutions. In this work, hydrazine has been detected electrochemically using ZnS/Au and CdS/Au electrodes. The CV responses of the hydrazine using ZnS/Au electrode in a 0.1 M phosphate buffer solution (PBS) of pH 7.0 with 1 mM hydrazine and without hydrazine, at a scan rate of 50 mV s\(^{-1}\) have been depicted in Figure 93a. It is apparent from the obtained CV graph that in the absence of hydrazine, the ZnS/Au electrode does not show any redox peak in the potential range of -0.1 to 0.8 V. However, on the other hand, when used in the presence of hydrazine...
Results and discussion

at the same experimental conditions and a significant enhancement in anodic peak at potential +0.21 V and current 6.9 μA have been observed. The electrochemical response of hydrazine is irreversible as no cathodic current is observed in the reverse sweep. These observations conclude that the synthesized ZnS nanoparticles are effective mediator for efficient detection of hydrazine. Figure 93b shows CV of buffer and 1.0 mM hydrazine in 0.1 M PBS (pH = 7.0) at CdS/Au electrode. No redox peak has been observed in the absence of hydrazine indicating that the modified electrode is non-electroactive in the selected potential region. However, after injecting 1 mM hydrazine into the PBS, a remarkable oxidation peak at about 0.43 V is observed. In both cases, hydrazine does not show any response with bare electrode. Thus ZnS and CdS nanoparticles are excellent electron mediators between gold electrode and hydrazine.

![Graph showing cyclic voltammetric sweep curve.](image)

Figure 93. Cyclic voltammetric sweep curve for the 1 mM hydrazine using bare Au, and (a) ZnS/Au (b) CdS/Au electrodes in absence and presence of 1 mM hydrazine.

Effect of scan rates

Figure 94 (a and b) depicts the CV curves obtained in PBS solution containing 1.0 mM hydrazine at different scan rates with ZnS/Au and CdS/Au electrodes. The scan rates used for ZnS/Au electrode are 50, 60, 70, 80, 90 and 100 mV s⁻¹. For CdS/Au electrode, the scan rate has been varied as 50, 55, 60, 65, 70, 75, 80, 85 and 90 mV s⁻¹. The plots of peak current v/s square root of the scan rate are demonstrated in Figure 95 (a and b) for ZnS/Au and CdS/Au electrodes respectively. An excellent linearity has been obtained between the square root of the scan rate and the peak current in both cases, indicating that the electrocatalytic oxidation kinetics is mainly
Results and discussion

diffusion-controlled. To depict the mechanism of electrooxidation of hydrazine, number of electrons involved (n) can be calculated from eqn 6 for a totally irreversible reaction. The estimated total number of electrons involved in oxidation process has been found to be 2. Accordingly, the mechanism for the oxidation process of hydrazine can be proposed as:

\[
N_2H_4 + 5/2 OH^- \rightarrow 1/2 N_3^- + 1/2 NH_3 + 5/2 H_2O + 2e^- \quad \text{(xv)}
\]

Figure 94. Effect of scan rate on CVs of 1 mM hydrazine using (a) ZnS/Au and (b) CdS/Au electrodes.

Figure 95. Plot of peak current vs. square root of scan rate using (a) ZnS/Au and (b) CdS/Au electrodes.
Amperometric studies

Further studies on the sensitivity have been performed by monitoring the amperometric response of the modified electrodes to hydrazine. On successive addition of hydrazine (concentration varies from 100 to 1000 nM with an increment of 100 nM at each step) to the 0.1 M PBS, current response has been examined at a fixed potential (Figure 96). The relationship between response current and concentrations of hydrazine is depicted by the calibration curve in Figure 97. The current is linear to the concentration of hydrazine with a correlation coefficient of 0.995 and 0.9933 for ZnS/Au and CdS/Au electrodes respectively. From slope of calibration curve, the sensitivity of ZnS nanoparticles based hydrazine sensor has been found to be 89.3 μA cm⁻² μM⁻¹. In addition, the calculated limit of detection estimated based on signal to noise ratio (S/N), is found to be 1.07 μM. The sensitivity obtained with CdS/Au electrode is 89 μA cm⁻² μM⁻¹ and the limit of detection is estimated to be 0.061 μM at a signal-to-noise ratio of 3.

Figure 96. Amperometric responses for detection of hydrazine using (a) ZnS/Au and (b) CdS/Au electrodes.

Table 8 presents the comparison of fabricated sensors with previous electrochemical sensors for hydrazine based on the utilization of nanomaterials as efficient electron mediators such as ZnO nanorods [283], ZnO nanonails [284], SWCNT and catechine hydride [285], C@ZnO nanorods [286], high-aspect ratio ZnO nanowires [287], carbon nanotubes powder [288], nanoporous gold nanoparticles modified titanium electrode [289], caffeic acid modified GCE [290], bismuth hexacyanoferate-modified carbon ceramic electrodes [291], nickel hexacyaniferrate
Results and discussion

[292], carbon nanotubes-wired ZnO nanoflowers [293], Ru-complex films [170] and so on. It is clear from Table 8 that the fabricated hydrazine sensors exhibit high sensitivities and low limits of detection as compared to other fabricated hydrazine sensors reported in the literature [283-293].

![Figure 97. Calibration curves for (a) ZnS/Au electrode (b) CdS/Au electrode.](image)

### Table 8. Performance summary of the hydrazine chemical sensors reported in the literature constructed based on the utilization of various nanomaterials as working electrodes.

<table>
<thead>
<tr>
<th>Electrode Materials</th>
<th>Sensitivity ($\mu$A/cm$^2$/(\mu)M)</th>
<th>Detection Limit ((\mu)M)</th>
<th>Response time (s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO nanorods</td>
<td>4.76</td>
<td>2.2</td>
<td>&lt; 10</td>
<td>283</td>
</tr>
<tr>
<td>ZnO nanonails</td>
<td>8.56</td>
<td>0.2</td>
<td>&lt; 5</td>
<td>284</td>
</tr>
<tr>
<td>SWCNT and catechine hydrate</td>
<td>0.183</td>
<td>2.0</td>
<td>......</td>
<td>285</td>
</tr>
<tr>
<td>C@ZnO nanorods</td>
<td>9.4</td>
<td>0.1</td>
<td>&lt; 4</td>
<td>286</td>
</tr>
<tr>
<td>High-aspect ratio ZnO NWs</td>
<td>12.7</td>
<td>0.084</td>
<td>&lt; 5</td>
<td>287</td>
</tr>
<tr>
<td>Carbon nanotube powder</td>
<td>0.9944</td>
<td>N.A</td>
<td>&lt; 3</td>
<td>288</td>
</tr>
<tr>
<td>Nanoporous gold nanoparticles modified</td>
<td>1.117</td>
<td>42</td>
<td>......</td>
<td>289</td>
</tr>
</tbody>
</table>
## Results and discussion

<table>
<thead>
<tr>
<th>Electrode Type</th>
<th>Response Current (nA)</th>
<th>Selectivity (pM)</th>
<th>Application</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium electrode</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caffeic Acid modified GCE</td>
<td>3.6</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bismuth hexacyanoferate-modified Carbon Ceramic Electrodes</td>
<td>4.2</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel hexacyanoferate</td>
<td>0.26</td>
<td>2.28</td>
<td>&lt; 3</td>
<td></td>
</tr>
<tr>
<td>Carbon nanotube-wired</td>
<td>3.49</td>
<td>0.18</td>
<td>&lt; 3</td>
<td></td>
</tr>
<tr>
<td>ZnO nanoflower</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru-complex films</td>
<td></td>
<td>8.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnS nanoparticles</td>
<td>89.3</td>
<td>1.07</td>
<td>&lt; 2</td>
<td>This work</td>
</tr>
<tr>
<td>CdS nanoparticles</td>
<td>89</td>
<td>0.061</td>
<td>&lt; 2</td>
<td>This work</td>
</tr>
</tbody>
</table>

### Selectivity studies

The selectivity of fabricated sensors towards oxidation of hydrazine has also been evaluated. The amperometric response of some common interferents of hydrazine, such as ammonia (NH$_3$), hydroxylamine (NH$_2$OH), nitrate ion (NO$_3^-$) and nitrite ion (NO$_2^-$) has been monitored at fixed potential with both ZnS/Au and CdS/Au electrodes (Figure 98). The response current shows comparatively negligible changes on addition of ions/compounds other than hydrazine. However, on addition of hydrazine, the response current shows significant increase in both the cases. This shows high selectivity of ZnS/Au and CdS/Au electrodes for hydrazine.

### Application to real samples

Further, to increase the practical utility of developed system, some real samples have been analyzed. For this, three samples of hydrazine with different concentrations of 6.5 μM, 55.5 μM and 0.05 mM have been prepared. The above method has been applied to determine concentration of hydrazine in these samples. Table 9 lists the detected concentrations. Comparison of data depicts good agreement with known values. Therefore, the proposed sensor can be applied to determine very low concentrations of hydrazine accurately.
Results and discussion

Figure 98. Amperometric responses of (a) ZnS/Au and (b) CdS/Au electrode in the presence of various interfering compounds.

Table 9. Analysis of various samples

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Actual concentration</th>
<th>ZnS/Au electrode</th>
<th>CdS/Au electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>6.50 μM</td>
<td>6.12 μM</td>
<td>6.36 μM</td>
</tr>
<tr>
<td>2.</td>
<td>55.50 μM</td>
<td>54.89 μM</td>
<td>54.65 μM</td>
</tr>
<tr>
<td>3.</td>
<td>0.05 mM</td>
<td>0.047 mM</td>
<td>0.047 mM</td>
</tr>
</tbody>
</table>

Using ZnS and CdS nanoparticles, efficient electroanalytical systems for detection of hydrazine in aqueous solutions have been fabricated. The systems have been found to exhibit high sensitivity, low limit of detection, reproducibility and selectivity for hydrazine etc. Moreover, the developed sensors have been applied for analysis of real samples. Thus ZnS/Au and CdS/Au electrodes represent promising materials for detection of hydrazine upto trace levels.

4.2.1.3. TNT detection

A significant research is being done in developing methods for fast, simple, sensitive, and reliable detection of high energy explosive TNT, which is also detrimental for human health as well as aquatic life. In this section, an attempt has been made to detect TNT with ZnS/Au and CdS/Au electrodes. However, the effort to
detect TNT with ZnS/Au electrode has been unsuccessful. The reason for this is still under investigation. The electrocatalytic activity of CdS/Au electrode towards TNT reduction has been examined in the potential range from -0.85 to -0.1 V versus Ag/AgCl, at a scan rate of 50 mV s\(^{-1}\). All the experiments have been carried out at room temperature at pH 7.4. Figure 99 shows that modified gold electrode does not give any peak in buffer alone in the applied voltage range. However, three prominent peaks (Table 10) have been observed in the presence of TNT (1 mM) corresponding to the reduction of three nitro groups of TNT. The bare gold electrode does not show any response towards TNT. Thus CdS/Au electrode can be used for detection of TNT and CdS nanoparticles act as electron mediators for reduction of TNT. The process is irreversible as no anodic peak has been observed in forward scan.

![Cyclic Voltammetric sweep curve](image)

**Figure 99.** Cyclic Voltammetric sweep curve in absence and presence of 1mM TNT at 50 mVs\(^{-1}\) scan rate in phosphate buffer (pH 7.4).

**Table 10.** The three peaks corresponding to reduction of three nitro groups of TNT.

<table>
<thead>
<tr>
<th>Peaks</th>
<th>Potential (V)</th>
<th>Cathodic Current (I(_p)) ((\mu)A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-0.692</td>
<td>-30.114</td>
</tr>
<tr>
<td>b</td>
<td>-0.432</td>
<td>-13.931</td>
</tr>
<tr>
<td>c</td>
<td>-0.200</td>
<td>-2.219</td>
</tr>
</tbody>
</table>
**Results and discussion**

**Effect of scan rates**

For depicting the mechanism of reaction, the effect of scan rate (v) has been examined. Figure 100 shows the cyclic voltammograms of TNT with CdS/Au electrode at different scan rates. The peak current has been found to increase with increase in scan rate. The plot of peak current versus square root of scan rate ($v^{1/2}$) yields a straight line in the range of 50-200 mV/s (Figure 101), which indicates that the reduction of TNT is diffusion controlled.

![Figure 100. Cyclic voltammograms of TNT in phosphate buffer (pH 7.4) at different scan rate (50 to 200 mVs⁻¹).](image1)

![Figure 101. Plot of cathodic current versus square root of scan rate for peaks a, b and c](image2)
Results and discussion

The number of electrons involved in the reduction of TNT, calculated from the eqn 6, are estimated to be 6 for each peak. Further, on the basis of number of electrons involved, proposed mechanism of reduction process for one peak has been given below. Similar mechanism is applicable for other two peaks.

\[
\begin{align*}
\text{ONO}_2 + 2e^- + 2H^+ &\rightarrow \text{NO}_2^- + H_2O \\
\text{NO}_2^- + H_2O &\rightarrow \text{NO}_3^- + 2H^+
\end{align*}
\]

Amperometric studies

Amperometric studies have been performed under stirred conditions. Figure 102a shows that with increase in concentration of TNT, at a constant potential, response current also increases rapidly with a response time of < 2s. The plot between response current and concentration of TNT yields a straight line (Figure 102b). The fabricated sensor shows the sensitivity, calculated from slope of calibration curve/area of electrode, of 47.8 µA cm² µM⁻¹. The detection limit has been calculated according to the equation: detection limit=3*Noise/slope of calibration curve. The estimated limit of detection for the fabricated sensor has been calculated as 1.045 nM. Table 11 represents the comparison of developed system with previous reported sensors for TNT.

![Amperometric response and calibration curve](image)

**Figure 102.** (a) Amperometric response of the CdS/Au electrode with successive addition of TNT into 0.01M PBS buffer solution (pH 7.4). (b) Calibration curve (a plot of current versus concentration).
Results and discussion

Table 11. Comparison of various sensors for detection of TNT

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Electrode Materials</th>
<th>Limit of detection (M)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N-(3-pyrrol-1-ylpropyl)-4,4’-bipyridine</td>
<td>$2 \times 10^{-6}$</td>
<td>209</td>
</tr>
<tr>
<td>2</td>
<td>Mercury-gold amalgam electrode</td>
<td>$7 \times 10^{-6}$</td>
<td>294</td>
</tr>
<tr>
<td>3</td>
<td>CdS nanoparticles</td>
<td>$1.045 \times 10^{-9}$</td>
<td>This work</td>
</tr>
</tbody>
</table>

Selectivity studies

To check the selectivity of proposed sensor, common interferents of TNT like nitrobenzene (NB) and 2,4-dinitrotoluene (DNT) have been selected. Figure 103 shows the response current on addition of NB, DNT and TNT. The system shows no or negligible response on addition of NB or DNT, however, significant cathodic peak current is observed when TNT is added to system. This indicates the selectivity of the fabricated system for TNT.

![Figure 103](image.png)

Application to real samples

To increase the analytical usefulness of fabricated system, the detection of TNT has been done in various water samples. Unspiked tap water, river water and lake water have been tested for determination of TNT by employing above method. All the three samples have shown no signs of TNT presence. Then the samples have been spiked with TNT (1 mM) and concentrations of TNT in all samples have been
determined using above method. The concentration of TNT in tap, river and lake water have been found to be 0.961, 0.963 and 0.979 mM, respectively. Thus, the proposed method can detect TNT with good accuracy.

**Conclusions**

In this section, the electroanalytical applications of synthesized ZnS and CdS nanoparticles have been explored. The electrochemical detection of cyanide and hydrazine has been carried out using ZnS/Au and CdS/Au electrodes. CdS nanoparticles have further been used for detection of TNT. The nanoparticles have been found to catalyze the electrooxidation or reduction of species involved therein. The detection has been made up to trace levels. The fabricated systems have proven to be better than previously reported detection methods in terms of limits of detection, sensitivities and response times. These systems have been employed to real samples, which makes them highly promising and fruitful for practical applications. In all cases, CdS nanoparticles have been proven to be more efficient than ZnS nanoparticles for electrochemical detection of different analytes.
4.2.2. Fluorescent sensors

Photoluminescence (PL) is a very useful characteristic of ZnS nanoparticles. The presence of different analytes can affect the PL of ZnS nanoparticles due to the changes on the surface charges. The chemical/physical interactions between ions/molecules and surface of nanoparticles may affect the efficiency of core electron-hole recombination and hence the luminescent emission. Thus, by examining the changes in the luminescence properties, presence of analyte can be detected. Keeping in view of excellent optical transmission properties and high-refractive index, the as-synthesized ZnS nanoparticles have been used as fluorescent sensor for the efficient detection of cyanide ions and TNT.

CdS nanoparticles have also been employed for fluorescence detection of cyanide and TNT, but the results are not effective. In literature, there are many reports in which CdS nanoparticles have been used in PL detection of many compounds [140-142]. However, in our case, the fluorescence sensing with CdS nanoparticles has not been successful. The intensity of synthesized CdS is quite low, due to which it is very difficult to monitor the systems.

4.2.2.1. Detection of Cyanide ion

To explore sensing capabilities of synthesized ZnS nanoparticles to cyanide ion in aqueous solutions, the PL spectra of ZnS nanoparticles have been examined in the presence of cyanide. The effect of concentration variation of cyanide on PL of ZnS nanoparticles has been depicted in Figure 104.

![Figure 104. Effect of cyanide ion concentration on PL spectra of ZnS nanoparticles.](image)
The intensity of band edge emission of ZnS nanoparticles remains unaltered in the presence of cyanide ions. However, the defect related emission quenches on increasing concentration of cyanide ion. The changes in the charge on the surface of nanoparticles, caused by the chemical or physical interaction between ions or small molecules present in the nanoparticles environment, can respond via changes in their PL emissions. The band edge emission corresponds to recombination of exciton-hole pair and depends upon size of nanoparticles [52]. Thus, the change in surface charge does not alter this emission and only defect related peak at 434 nm gets affected by the presence of cyanide ion. Figure 105 presents the PL data as a function of relative PL intensity, $I_0/I$ ($I$ and $I_0$ are the PL intensity at 434 nm in the presence and absence of cyanide ion, respectively), vs. the concentration of cyanide ion. A good linear correlation has been found over the concentration range from 5 to 200 μM ($R^2 = 0.99$). The calibration equation is as follows:

$$I_0/I = 1.4997 + 0.0024[CN^-]$$

where $[CN^-]$ is concentration of cyanide ion in μM.

The relative standard deviation (RSD) for five replicate measurements of a solution containing 5 μM cyanide ions has been estimated to be 0.69%. The limit of detection, calculated following the $3\sigma$ IUPAC criteria has been observed as 1.293 μM. The sensing results have been found to be highly reproducible as clear from RSD value. This technique is very effective as even a trace amount of cyanide ion can also lead to noticeable decrease in PL intensity.

![Figure 105. $I_0/I$ plotted against concentration of cyanide ion, where $I_0$ and $I$ are the PL intensities of the ZnS nanoparticles at 434 nm in the absence and presence of cyanide ion respectively.](image-url)
Results and discussion

Proposed mechanism for PL quenching

The concentration dependence of the luminescence intensity has shown the binding of cyanide ions to the surface of the ZnS nanoparticles. The positive zeta potential value of +19.7 mV of ZnS nanoparticles indicates that the surface of nanoparticles is positively charged, i.e. the surface is rich in Zn$^{2+}$ ions. Thus, the negatively charged cyanide ions can bind to positively charged Zn$^{2+}$ ions on the surface which leads to quenching in PL emission of ZnS nanoparticles. The binding of cyanide ions to Zn$^{2+}$ ions is supported by zeta potential value of ZnS nanoparticles in the presence of cyanide ions (-5.2 mV) which indicates that the negatively charged cyanide anions are adsorbed on positively charged ZnS nanoparticles. This is further supported by FTIR spectra. Figure 106 (a and b) shows FTIR spectra of pure cyanide in solid form and of aqueous solution of ZnS nanoparticles containing cyanide ions respectively. The characteristic vibration of –C≡N group in pure cyanide is at 2080 cm$^{-1}$, which has shifted to 2140 cm$^{-1}$ when cyanide is added to ZnS solution. The change in frequency is due to binding of cyanide ion to Zn$^{2+}$ ions. The shift of frequency to higher value is attributed to kinematic coupling i.e. bridged complex formation between Zn$^{2+}$ ions and cyanide ions. Thus, the motion of cyanide ion is constrained by second Zn$^{2+}$ ion. This mechanical constraint upon cyanide ion has shifted its frequency to higher value [295].

Figure 106. FTIR spectrum of (a) pure NaCN (b) aqueous solution of ZnS nanoparticles containing cyanide ions.

Selectivity and interference studies

To investigate the selectivity and specificity of the fabricated luminescence sensors towards cyanide ion, the luminescence response of this sensing system with
other anions, under the same conditions, have been evaluated. Various ions such as F\(^{-}\), Cl\(^{-}\), Br\(^{-}\), I\(^{-}\), NO\(_3\)^{-}, S\(^2\)^{-}, SO\(_4\)^{2-}, CO\(_3\)^{2-} and HCO\(_3\)^{-} have been chosen for these experiments. The concentration of S\(^2\) ions is determined gravimetrically by trapping with AgNO\(_3\) and weighing mass of Ag\(_2\)S formed. The concentration of all ions (except sulfide ion) has been taken as $5 \times 10^{-6}$ M. Figure 107 exhibits the relative PL intensity ($I_0/I$) of ZnS nanoparticles solution in presence of various anions ($5 \times 10^{-6}$ M). It is clear that the relative PL intensity for the cyanide ion is exceptionally high as compared to other anions. In other words, the influence of other anions is almost negligible as compared to cyanide ion in the sensing system. Thus, the observed results confirm that the fabricated luminescence sensor exhibits good selectivity toward cyanide ion.

![Figure 107. $I_0/I$ of ZnS nanoparticles solution in presence of various anions ($5 \times 10^{-6}$ M) (the concentration used for sulfide ion is $4.7 \times 10^{-6}$ M).](image)

In order to further verify the performance of fabricated cyanide ion luminescence sensor, the PL intensity has been recorded in the presence of other competing ions (F\(^{-}\), Cl\(^{-}\), Br\(^{-}\), I\(^{-}\), NO\(_3\)^{-}, S\(^2\)^{-}, SO\(_4\)^{2-}, CO\(_3\)^{2-} and HCO\(_3\)^{-}). Figure 108 exhibits $I_0/I$ values of ZnS nanoparticles solution in presence of cyanide ions ($5.00 \times 10^{-6}$ M) with coexistence of other anions ($1.00 \times 10^{-4}$ M) at pH = 10. There are negligible changes in the PL intensities in the presence of coexisting ions, which further confirms the high selectivity of the fabricated luminescence sensor toward cyanide ion. Therefore, it can be concluded that other ions do not affect the ability of proposed sensor to detect cyanide ion.
Results and discussion

Figure 108. $I_0/I$ of ZnS nanoparticles solution in presence of cyanide ion ($5 \times 10^{-6}$ M) with coexistence of other anions ($1 \times 10^{-4}$ M) at pH 10 (the concentration used for sulfide ion is $0.91 \times 10^{-6}$ M).

Analysis of real samples

Further, the above method has also been used to analyze spiked real samples. Figure 109 shows negligible effect on $I_0/I$ values in PL of nanoparticles on addition of real samples like tap water, river water (collected from Ghagar river, Chandigarh, India) and blood serum to aqueous solution of nanoparticles. However, the PL intensity shows a significant change for samples spiked with cyanide ions ($5.00 \times 10^{-6}$ M). Thus the fabricated sensor can be applied to real world samples.

Figure 109. Relative PL intensity ($I_0/I$) of ZnS nanoparticles solution on addition of different samples and samples spiked with cyanide ions ($5 \times 10^{-6}$ M) at pH 10.
4.2.2.2. Detection of TNT

An attempt has been made to fabricate a luminescent sensor for the detection of explosive TNT using ZnS nanoparticles. Here, ZnS nanoparticles show a broad peak from 360-420 nm at excitation of 320 nm. Thus, the luminescence is associated primarily with surface defects with minor contribution from band edge emission. To develop a luminescent sensor for TNT, effect of TNT on PL of ZnS nanoparticles has been studied. Firstly, the synthesized ZnS nanoparticles are dried and re-dispersed in phosphate buffer of pH = 7.0 (10mg/50mL). The stock solution of TNT (125 ppm) has also been prepared in phosphate buffer. Different samples have been prepared using these two stock solutions to get final concentrations of ZnS (0.1 mg/mL) and TNT (ranging from 0.25 ppm to 25 ppm). The PL spectra of various samples have been recorded at excitation wavelength 320 nm and the results are depicted in Figure 110. It is observed that on increasing concentration of TNT, the PL of nanoparticles is quenched. Thus, the system can be used to detect TNT in aqueous solutions.

![Figure 110. Effect of TNT on PL of as synthesized aqueous solutions of ZnS nanoparticles.](image)

Figure 110 shows the plot of \( I_0/I \) (\( I \) and \( I_0 \) are the PL intensities in the presence and absence of TNT respectively) vs. the concentration of TNT. The system tolerated good linear range over from concentration 5 to 200 μM (\( R^2 = 0.996 \)). The calibration equation has been calculated as follows:

\[
I_0/I = 0.99 + 0.01216[TNT] \tag{10}
\]
Results and discussion

where [TNT] is concentration of TNT in ppm. The relative standard deviation (RSD) is about 0.020%. The limit of detection has been calculated as 4.86 ppm using 3σ IUPAC criteria.

Figure 111. $I_0/I$ plotted against concentration of TNT, where $I_0$ and $I$ are the PL intensities of the ZnS nanoparticles in the absence and presence of TNT, respectively.

Proposed mechanism for PL quenching

The PL of ZnS nanoparticles may be quenched by TNT due to charge transfer from conduction band or defect states of ZnS nanoparticles to lowest unoccupied molecular orbital (LUMO) of TNT [296]. Figure 112 shows the pictorial representation of charge transfer from photoexcited ZnS nanoparticles to electron deficient TNT.

Figure 112. Schematic illustration for quenching mechanism through electron transfer process.
**Selectivity and interference studies**

To determine the selectivity of proposed system for TNT, the effect of other nitroaromatic compounds like 2, 4-dinitrotoluene (DNT) and nitrobenzene (NB) has also been investigated. Figure 113a shows relative intensities i.e. $I_0/I$ values in the presence of different compounds. The system exhibits excellent selectivity for TNT. This is due to the fact that DNT with two nitro groups and NB with one nitro group have very less electron accepting tendency as compared to TNT. Thus quenching efficiency of TNT is much higher, which leads to selectivity of system towards TNT. The presence of other compounds also does not interfere with performance of sensor as depicted from interference studies shown in Figure 113b.

**Figure 113.** (a) $I_0/I$ of ZnS nanoparticles solution in presence of TNT, DNT and NB. (b) $I_0/I$ of ZnS nanoparticles solution in presence of TNT with coexistence of other compounds.

**Detection of TNT in real samples**

For increasing the utility of proposed system, some spiked real samples have been analyzed. For this, firstly, unspiked samples have been added to solution of ZnS nanoparticles, and PL has been recorded. Thereafter, water samples have been spiked with TNT (1 μM) and Effect of addition of spiked samples on PL of ZnS nanoparticles has been studied. The relative intensities ($I_0/I$) with the addition of spiked as well as unspiked samples are shown in Figure 114. The unspiked samples have no effect on PL of ZnS nanoparticles. However, on addition of spiked samples,
Results and discussion

high $I_0/I$ values have been observed. Thus proposed system can be employed to detect TNT in real samples.

![Graph showing PL intensity of ZnS nanoparticles solution on addition of different samples and samples spiked with TNT (1 X 10^{-6} M) at pH 7.0.]

**Figure 114.** Relative PL intensity ($I_0/I$) of ZnS nanoparticles solution on addition of different samples and samples spiked with TNT (1 X 10^{-6} M) at pH 7.0.

Conclusions

ZnS nanoparticles have been used for the detection of cyanide and TNT by PL studies. The addition of cyanide and TNT to ZnS nanoparticles, even in trace amounts, has caused the quenching of PL intensity of ZnS nanoparticles. The limits of detection for cyanide and TNT have been calculated as 1.293 µM and 4.86 ppm, respectively. An attempt has been made to investigate the mechanism for PL quenching by cyanide and TNT. The adsorption of cyanide on surface of ZnS nanoparticles and electron transfer from ZnS to TNT have been suggested as possible reasons for PL quenching. The methods are facile, sensitive, reproducible and effective for detection of TNT and cyanide in real samples. With CdS nanoparticles, the systems could not be studied because of low PL intensity of CdS nanoparticles.
Results and discussion

4.2.3. Catalysis of Biginelli reaction

In recent years, the nanoparticles have emerged as efficient catalysts for various organic reactions [297-299]. The nanoparticles offer many advantages over conventional catalysts e.g. high yields, no side reactions, recovery of catalyst, mild conditions, green solvents like water etc [300]. The solvent-free organic reactions are much attracted field these days due to environmental concern. We have attempted the scope of synthesized metal sulfide (MS) nanoparticles as catalyst for Biginelli reaction under solvent-free conditions using microwave irradiation method (Scheme 18). The reaction takes place in few minutes and good yields of products have been obtained.

![Scheme 18. Model reaction for Biginelli reaction.](image)

In the initial studies, benzaldehyde (1a) (1.06 g, 10 mmol), Urea (3a) (0.72 g, 12 mmol) and ethylacetoacetate (2) (1.30 g, 10 mmol) have been mixed thoroughly alongwith ZnS nanoparticles (10 mg) and irradiated for 3 min in microwave. After workup, the corresponding DHPM product 4a has been isolated in 67% yield and characterized by $^1$H and $^{13}$C NMR spectroscopy. The $^1$H NMR showed a broad singlet at $\delta$ 9.21 corresponding to -NH proton, a broad singlet at $\delta$ 7.75 for other -NH proton, a multiplet at $\delta$ 7.34-7.30 corresponding to two aromatic protons, a three proton multiplet at $\delta$ 7.26-7.22 for aromatic protons, a one proton doublet at $\delta$ 5.15 for ArCHNH, a quartet at $\delta$ 3.96 for OCH$_2$CH$_3$, a three proton singlet at $\delta$ 2.26 for -CH$_3$ protons and a three proton triplet at $\delta$ 7.07 for OCH$_2$CH$_3$ protons. To optimize the reaction conditions, benzaldehyde (1a), urea (3a) and ethylacetoacetate (2) have been selected to carry out the model reaction with different catalyst loading. In the optimization studies, no product has been obtained without any catalyst (Table 12, entry 1). However, with 10 mg of catalyst loading, around 63-67 % yields have been obtained (Table 12, entries 2, 3). Doubling the amount of catalysts from 10 to 20 mg
Results and discussion

have further increased the yields of corresponding DHPM product (Table 12, entries 4, 5). Best yields have been achieved with 40 mg catalyst loading (Table 12, entries 8, 9). However, further increase in the catalyst loading does not alter the yield of the reaction (Table 12, entries 10, 11).

Table 12. Variation of amount of catalyst and yields obtained.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Amount of Nanoparticles (mg)</th>
<th>Time (min)/Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nil</td>
<td>-</td>
<td>3/Nil 217</td>
</tr>
<tr>
<td>2</td>
<td>ZnS</td>
<td>10</td>
<td>3/67</td>
</tr>
<tr>
<td>3</td>
<td>CdS</td>
<td>10</td>
<td>3/63</td>
</tr>
<tr>
<td>4</td>
<td>ZnS</td>
<td>20</td>
<td>3/77</td>
</tr>
<tr>
<td>5</td>
<td>CdS</td>
<td>20</td>
<td>3/77</td>
</tr>
<tr>
<td>6</td>
<td>ZnS</td>
<td>30</td>
<td>3/83</td>
</tr>
<tr>
<td>7</td>
<td>CdS</td>
<td>30</td>
<td>3/83</td>
</tr>
<tr>
<td>8</td>
<td>ZnS</td>
<td>40</td>
<td>2.3/93</td>
</tr>
<tr>
<td>9</td>
<td>CdS</td>
<td>40</td>
<td>2.3/92</td>
</tr>
<tr>
<td>10</td>
<td>ZnS</td>
<td>50</td>
<td>2.3/93</td>
</tr>
<tr>
<td>11</td>
<td>CdS</td>
<td>50</td>
<td>2.3/92</td>
</tr>
</tbody>
</table>

To explore the substrate scope, different aldehydes containing electron withdrawing and electron releasing groups have been made to react with other components and the results are shown in Table 13. The reaction works well for all the aldehydes used, giving good yields.
Table 13. Evaluation of substrate scope for the synthesis of various DHPM’s.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>1</th>
<th>3</th>
<th>Time (min)</th>
<th>4</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZnS</td>
<td>1a (R = H)</td>
<td>3a</td>
<td>2.3</td>
<td>4a (R = H; X = O)</td>
<td>93</td>
</tr>
<tr>
<td>2.</td>
<td>CdS</td>
<td>1a (R = H)</td>
<td>3a</td>
<td>2.3</td>
<td>4a (R = H; X = O)</td>
<td>92</td>
</tr>
<tr>
<td>3.</td>
<td>ZnS</td>
<td>1a (R = H)</td>
<td>3b</td>
<td>2.9</td>
<td>4b (R = H; X = S)</td>
<td>96</td>
</tr>
<tr>
<td>4.</td>
<td>CdS</td>
<td>1a (R = H)</td>
<td>3b</td>
<td>2.7</td>
<td>4b (R = H; X = S)</td>
<td>94</td>
</tr>
<tr>
<td>5.</td>
<td>ZnS</td>
<td>1b (R = 4-OCH₃)</td>
<td>3a</td>
<td>2.6</td>
<td>4c (R = 4-OCH₃; X = O)</td>
<td>96</td>
</tr>
<tr>
<td>6.</td>
<td>CdS</td>
<td>1b (R = 4-OCH₃)</td>
<td>3a</td>
<td>2.6</td>
<td>4c (R = 4-OCH₃; X = O)</td>
<td>96</td>
</tr>
<tr>
<td>7.</td>
<td>ZnS</td>
<td>1b (R = 4-OCH₃)</td>
<td>3b</td>
<td>2.5</td>
<td>4d (R = 4-OCH₃; X = S)</td>
<td>95</td>
</tr>
<tr>
<td>8.</td>
<td>CdS</td>
<td>1b (R = 4-OCH₃)</td>
<td>3b</td>
<td>2.7</td>
<td>4d (R = 4-OCH₃; X = S)</td>
<td>94</td>
</tr>
<tr>
<td>9.</td>
<td>ZnS</td>
<td>1c (R = 4-Cl)</td>
<td>3a</td>
<td>2.4</td>
<td>4e (R = 4-Cl; X = O)</td>
<td>90</td>
</tr>
</tbody>
</table>
Results and discussion

<table>
<thead>
<tr>
<th></th>
<th>Catalyst</th>
<th>R (Substrate)</th>
<th>Substrate</th>
<th>R (Product)</th>
<th>X</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.</td>
<td>CdS</td>
<td>4-Cl</td>
<td>3a</td>
<td>2.5</td>
<td>4e (R = 4-Cl; X = O)</td>
<td>95</td>
</tr>
<tr>
<td>11.</td>
<td>ZnS</td>
<td>4-Cl</td>
<td>3a</td>
<td>2.3</td>
<td>4f (R = 3-Cl; X = O)</td>
<td>96</td>
</tr>
<tr>
<td>12.</td>
<td>CdS</td>
<td>4-Cl</td>
<td>3a</td>
<td>2.4</td>
<td>4f (R = 3-Cl; X = S)</td>
<td>92</td>
</tr>
<tr>
<td>13.</td>
<td>ZnS</td>
<td>4-CH₃</td>
<td>3b</td>
<td>2.4</td>
<td>4g (R = 4-CH₃; X = S)</td>
<td>94</td>
</tr>
<tr>
<td>14.</td>
<td>CdS</td>
<td>4-CH₃</td>
<td>3b</td>
<td>2.4</td>
<td>4g (R = 4-CH₃; X = S)</td>
<td>95</td>
</tr>
<tr>
<td>15.</td>
<td>ZnS</td>
<td>4-NO₂</td>
<td>3a</td>
<td>3.2</td>
<td>4h (R = 4-NO₂; X = O)</td>
<td>85</td>
</tr>
<tr>
<td>16.</td>
<td>CdS</td>
<td>4-NO₂</td>
<td>3a</td>
<td>3.2</td>
<td>4h (R = 4-NO₂; X = O)</td>
<td>86</td>
</tr>
<tr>
<td>17.</td>
<td>ZnS</td>
<td>2-OCH₃</td>
<td>3a</td>
<td>3.1</td>
<td>4i (R = 2-OCH₃; X = O)</td>
<td>83</td>
</tr>
<tr>
<td>18.</td>
<td>CdS</td>
<td>2-OCH₃</td>
<td>3a</td>
<td>3.1</td>
<td>4i (R = 2-OCH₃; X = O)</td>
<td>83</td>
</tr>
</tbody>
</table>

The catalysts have been recycled for four cycles and no significant decrease in yield has been observed even after fourth cycle. The mechanism of reaction (Scheme 19) involves the condensation of urea (3a) and benzaldehyde (1a) via standard nucleophilic addition, which leads to formation of N-(1-hydroxybenzyl)-urea (33) [301]. The iminium ion 34 is intercepted by the enol tautomer of ethyl acetoacetate (35), to give 36, which on cyclization followed by dehydration yields Biginelli product 4a.
Results and discussion

Scheme 19. Proposed mechanism for Biginelli reaction catalysed by ZnS/CdS nanoparticles.

Spectroscopic data (\(^1\)H and \(^{13}\)C NMR) of Biginelli reaction products (4a-i).

Ethyl-6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4a).

White solid, \(^1\)H NMR (DMSO-\(d_6\), 400 MHz): \(\delta\) 9.21 (br s, 1H, -NH), 7.75 (br s, 1H, -NH), 7.34-7.30 (m, 2H, Ar-H), 7.26-7.22 (m, 3H, Ar-H), 5.15 (d, \(J = 3.2\) Hz, 1H, ArCHNH), 3.96 (q, \(J = 7.0\) Hz, 2H, -OCH\(_2\)CH\(_3\)), 2.26 (s, 3H, -CH\(_3\)), 1.07 (t, \(J = 7.1\) Hz, 3H, -OCH\(_2\)CH\(_3\)).

\(^{13}\)C NMR (DMSO-\(d_6\), 100 MHz): \(\delta\) 165.31, 152.14, 148.31, 144.82, 128.35, 127.23, 126.22, 99.24, 59.16, 53.93, 17.74, 14.02.

Ethyl-6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4b).

Pale yellow solid, \(^1\)H NMR (DMSO-\(d_6\), 400 MHz): \(\delta\) 10.34 (br s, 1H, -NH), 9.66 (d, \(J = 1.8\) Hz, 1H, -NH), 7.37-7.33 (m, 2H, Ar-H), 7.29-7.27 (m, 1H, Ar-H), 7.25-7.21 (m,
Results and discussion

2H, Ar-H), 5.18 (d, J = 3.6 Hz, 1H, ArCHNH), 3.98 (q, J = 6.8 Hz, 2H, -OCH2CH3), 2.30 (s, 3H, -CH3), 1.12-1.06 (m, 3H, -OCH2CH3); 13C NMR (DMSO-d6, 100 MHz): δ 174.17, 165.09, 144.99, 143.45, 128.54, 127.66, 126.35, 100.68, 59.57, 54.01, 17.13, 13.97.

Ethyl-4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4c).

1H NMR (DMSO-d6, 400 MHz): δ 9.16 (br s, 1H, -NH), 7.68 (br s, 1H, -NH), 7.14 (d, J = 8.6 Hz, 2H, Ar-H), 6.86 (d, J = 8.6 Hz, 2H, Ar-H), 5.09 (d, J = 3.0 Hz, 1H, ArCHNH), 3.95 (q, J = 7.0 Hz, 2H, -OCH2CH3), 3.72 (s, 3H, -OCH3), 2.24 (s, 3H, -CH3), 1.08 (t, J = 7.1 Hz, 3H, -OCH2CH3).

13C NMR (DMSO-d6, 100 MHz): δ 165.34, 158.40, 152.13, 147.98, 137.01, 127.36, 113.66, 99.53, 59.12, 55.01, 53.29, 17.72, 14.06.

Ethyl-4-(4-methoxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4d).

1H NMR (DMSO-d6, 400 MHz): δ 10.30 (br s, 1H, -NH), 9.60 (d, J = 2 Hz, 1H, -NH), 7.15-7.12 (m, 2H, Ar-H), 6.91-6.89 (m, 2H, Ar-H), 5.12 (d, J = 3.6 Hz, 1H, ArCHNH), 3.97 (q, J = 7.1 Hz, 2H, -OCH2CH3), 3.72 (s, 3H, -OCH3), 2.29 (s, 3H, -CH3), 1.09 (t, J = 7.1 Hz, 3H, -OCH2CH3).

13C NMR (DMSO-d6, 100 MHz): δ 173.98, 165.13, 158.70, 144.71, 135.67, 127.59, 113.83, 100.92, 59.52, 55.05, 53.41, 17.10, 13.99.

Ethyl-4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4e).

1H NMR (DMSO-d6, 400 MHz): δ 9.25 (br s, 1H, -NH), 7.78 (br s, 1H, -NH), 7.38 (d, J = 8.4 Hz, 2H, Ar-H), 7.24 (d, J = 8.4 Hz, 2H, Ar-H), 5.15 (d, J = 3.2 Hz, 1H, ArCHNH), 3.95 (q, J = 7.0 Hz, 2H, -OCH2CH3), 2.25 (s,
Results and discussion

$^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 8.94 (br s, 1H, -NH), 7.36 (br s, 1H, -NH), 7.27-7.18 (m, 1H, Ar-H), 7.17-7.12 (m, 3H, Ar-H), 5.20 (d, $J = 2.4$ Hz, 1H, ArCHNH), 4.02-3.92 (m, 2H, -OCH$_2$CH$_3$), 2.26 (s, 3H, -CH$_3$), 1.18-1.08 (m, 3H, -OCH$_2$CH$_3$).

$^{13}$C NMR (DMSO-$d_6$/CDCl$_3$, 100 MHz): $\delta$ 165.22, 152.33, 148.14, 146.59, 133.29, 129.40, 126.92, 126.39, 124.56, 99.00, 59.16, 56.66, 54.00, 17.88, 13.77.

Ethyl-6-methyl-4-(4-methylphenyl)-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4g).

$^1$H NMR (DMSO-$d_6$/CDCl$_3$, 400 MHz): $\delta$ 10.03 (br s, 1H, -NH), 9.40 (br s, 1H, -NH), 7.10 (d, $J = 7.9$ Hz, 2H, Ar-H), 7.04 (d, $J = 8.0$ Hz, 2H, Ar-H), 5.17 (d, $J = 3.3$ Hz, 1H, ArCHNH), 3.96 (q, $J = 7.1$ Hz, 2H, -OCH$_2$CH$_3$), 2.28 (s, 3H, -CH$_3$), 2.25 (s, 3H, -CH$_3$), 1.13-1.07 (m, 3H, -OCH$_2$CH$_3$).

$^{13}$C NMR (DMSO-$d_6$/CDCl$_3$, 100 MHz): $\delta$ 174.14, 165.12, 144.39, 140.51, 136.69, 128.68, 126.30, 101.05, 59.33, 54.02, 20.65, 17.18, 13.83.

Ethyl-6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4h).

$^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 9.36 (br s, 1H, -NH), 8.20 (d, $J = 8.7$ Hz, 2H, Ar-H), 7.90 (br s, 1H, -NH), 7.50 (d, $J = 8.7$ Hz, 2H, Ar-H), 5.28 (d, $J = 3.2$ Hz, 1H, ArCHNH), 3.96 (q, $J = 7.0$ Hz, 2H, -OCH$_2$CH$_3$), 2.27 (s, 3H, -CH$_3$), 1.07 (t, $J = 7.1$ Hz, 3H, -OCH$_2$CH$_3$).
Results and discussion

$^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta$ 165.02, 151.95, 151.75, 149.35, 146.67, 127.62, 123.78, 98.15, 59.37, 53.65, 17.83, 13.98.

**Ethyl-4-(2-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4i).**

$^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 9.12 (br s, 1H, -NH), 7.27 (br s, 1H, -NH), 7.25-7.21 (m, 1H, Ar-H), 7.06-7.04 (m, 1H, Ar-H), 6.97 (d, $J$ = 8.0 Hz, 1H, Ar-H), 6.89-6.85 (m, 1H, Ar-H), 5.49 (d, $J$ = 2.8 Hz, 1H, ArCHNH), 3.94-3.89 (m, 2H, -OCH$_2$CH$_3$), 3.79 (s, 3H, -OCH$_3$), 2.28 (s, 3H, -CH$_3$), 1.01 (t, $J$ = 7.0 Hz, 3H, -OCH$_2$CH$_3$).

$^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta$ 165.32, 156.48, 152.16, 148.81, 131.57, 128.64, 127.05, 120.11, 111.08, 97.55, 58.95, 55.33, 48.84, 17.67, 13.98.

Conclusions

ZnS and CdS nanoparticles have been found to be efficient catalysts for Biginelli reaction. The products have been obtained in good yields. The characterization of products has been done using NMR spectroscopy. The reaction works well for various substrates containing electron withdrawing and releasing groups. The catalysts have been recycled for three to four times and reused. No significant decrease in yields has been observed on reusing catalyst for fourth time. Thus the synthesized nanoparticles can be used as efficient catalyst for Biginelli reaction. Both ZnS and CdS are almost equally efficient for catalyzing Biginelli reaction.
Results and discussion

Figure 115. $^1$H NMR of 4a.

Figure 116. $^{13}$C NMR of 4a.
Results and discussion

Figure 117. $^1$H NMR of 4b.

Figure 118. $^{13}$C NMR of 4b.
Results and discussion

Figure 119. $^1$H NMR of 4c.

Figure 120. $^{13}$C NMR of 4c.
Results and discussion

Figure 121. $^1$H NMR of 4d.

Figure 122. $^{13}$C NMR of 4d.
Results and discussion

Figure 123. $^1$H NMR of 4e.

Figure 124. $^{13}$C NMR of 4e.


Results and discussion

Figure 125. $^1$H NMR of 4f.

Figure 126. $^{13}$C NMR of 4f.
Results and discussion

Figure 127. $^1$H NMR of 4g.

Figure 128. $^{13}$C NMR of 4g.
Results and discussion

Figure 129. $^1$H NMR of 4h.

Figure 130. $^{13}$C NMR of 4h.
Results and discussion

Figure 131. $^1$H NMR of 4i.

Figure 132. $^{13}$C NMR of 4i.