CHAPTER 2

MATERIALS AND METHODS
2.1 Chemicals used

All the Chemicals used in the experiments were Analytical reagent (AR) grade obtained from the sources given in the brackets.

Adenine (Sigma), cytosine, thymine (Sisco Research Laboratory), purine, zinc perchlorate hexahydrate (Aldrich), sodium hexametaphosphate (Qualigens), sodium sulfide (Acros), L-histidine, methyl orange, 1, 2, 4 –THB, 1, 2, 3-THB, 1, 3, 5-THB (Aldrich) and sodium dodecylsulfate (Himedia). All the reagents were used without further purification. The water used for preparing the solutions was purified through a Millipore system.

2.2 Instrumentation

2.2.1 Ultraviolet–visible (UV–Vis) absorption spectrophotometer

UV–Visible spectroscopy is an important technique to determine the bandgap of the semiconductor nanoparticles. The absorption spectra for the synthesized zinc sulfide nanoparticles and reaction mixtures were recorded on a PerkinElmer Lambda 25 spectrophotometer in the range 200-700nm.

2.2.2 Fluorescence spectrophotometer

Fluorescence spectroscopy is a useful technique to characterize materials which are fluorescent in nature. The synthesized ZnS nanoparticles have good fluorescence emission with high intensities. The fluorescence spectra were
obtained using a PerkinElmer LS 55 spectrofluorimeter and Hitachi F-4500 spectrophotometer. The samples containing ZnS and the substrate were generally excited at 320nm. The emission was monitored between 340-550 nm.

2.2.3 Fluorescence Lifetime Measurements

Semiconductor nanoparticles are characterized by a range of lifetimes which indicate different emitting states. Fluorescence lifetimes were measured on a time correlated single photon counter (TCSPC) obtained from HORIBA scientific and Photon Technology International. The fluorescence lifetimes were determined by following the decay of emission at the respective fluorescence maxima of the as-prepared ZnS nanoparticles. The excitation and emission wavelengths were chosen as desired in different experiments. The luminescence of semiconductor nanoparticles is known to decay in a multi-exponential manner [1-3]. The decay of ZnS fluorescence was found to be 3-exponential. The average emission lifetime, \( <\tau> \) has been calculated using the following relation given by James et al. for emission from solid surfaces [4].

\[
<\tau> = \frac{\Sigma a_i \tau_i^2}{\Sigma a_i \tau_i}
\]

where \( a_i \) and \( \tau_i \) denote the pre-exponential factor and the corresponding lifetime respectively. The reliability of fitting was checked by numerical value of reduced chi-square (\( \chi^2 \)) and Durbin-Watson (DW) parameter.
2.2.4 Fourier transform infrared (FTIR) spectroscopy

Infra-red spectra were recorded on a PerkinElmer BX FTIR system. The measurements were made using solid samples by removing water from colloidal solutions on a rotavapor. The spectra were recorded in the transmittance mode between 600-4000 cm\(^{-1}\).

2.2.5 Transmission electron microscopy (TEM)

The size and morphology of prepared nanoparticles were examined using TEM analysis. The TEM measurements were performed using a JEOL 100 CX transmission electron microscope operating at 100 kV and JEM-2100 transmission electron microscope operating at 200 kV. A drop of the ZnS nanoparticle solution was placed on a carbon-coated copper grid and allowed to dry at room temperature prior to measurements. The synthesized zinc sulfide nanoparticles have a wide range of size distribution depending on the synthetic conditions and are nearly spherical in shape in most cases. The sizes of sodium hexametaphosphate stabilized ZnS nanoparticles prepared at pH 7.0 range from 30-100 nm in diameter [5], while the sizes of these particles prepared at a lower pH of 3.3 were found to be smaller ranging from 4.5 to 7.0 nm in diameter (chapter 6). The sizes of the histidine-stabilized ZnS nanoparticles vary as a function of starting pH during the synthesis process, ranging from 11.2 to 12.6 nm as well as stabilizer /metal ion ratio [6]. The ZnS nanoparticles prepared in sodium dodecylsulfate micellar medium range from 7.8 to 24.4 nm in diameter and were oval in shape.
2.2.6 Powder X-ray diffraction (XRD) studies

In order to determine the phase structure of ZnS nanoparticles, X-ray diffraction measurements were carried out. The synthesized ZnS nanoparticles show two phase structures, the cubic zinc blende and the hexagonal wurtzite. The histidine- stabilized ZnS nanoparticles show peaks having 2-theta values of 26°, 48° and 53° which correspond to the (100), (110) and (103) planes of wurtzite ZnS [7] and the ZnS nanoparticles prepared in sodium dodecylsulfate micellar medium show peaks at 2-theta values of 29.2, 48.8 and 57.5° approximately which correspond to the (111), (220) and (311) crystalline phases of face centered cubic ZnS [8].

2.2.7 Light source for photocatalytic experiment

For photocatalytic activity measurements, a 200 W Hg (Xe) arc lamp (Oriel Instruments) was used as the light source. Light of wavelength longer than 320 nm was selected using a cut filter.

2.2.8 pH meter

pH measurements were performed using a digital pH meter 335. pH calibrations were carried out by using acid buffer (mixture of 0.1 M acetic acid and 0.1 M sodium acetate) and base buffer (0.05M borax).
2.3 Preparation of samples for fluorescence measurements

To sample tubes containing 10 ml colloidal ZnS nanoparticles solution, µL amounts of freshly prepared stock solution of substrate were added to obtain the desired concentration range. The sample tubes were shaken for about 15 min on a shaker. The samples were then kept undisturbed for about an hour before making the fluorescence measurements. The excitation wavelength was selected was at a wavelength (295 nm to 320 nm) so that the substrates do not absorb any light. Both steady-state and time-resolved measurements were performed by taking the solutions in a 1 cm quartz cuvette.

2.4 Preparation of reaction sample for photocatalytic experiment

The reaction mixture for measuring photocatalytic activity of the prepared ZnS nanoparticles was prepared as follows: To 8 ml of ZnS nanoparticles solution in a test tube, 2 ml of methyl orange (stock ~ 5 x 10^{-5} M) was added to obtain 1 x 10^{-5} M concentration of the dye. The reaction mixture was shaken in a water bath incubator shaker for 30 min. The sample was then allowed to stand in the dark for 2 hours in order to achieve equilibration prior to starting the photocatalytic activity measurement.
2.5 Determination of photocatalytic activity

The photocatalytic activity of the ZnS nanoparticles was evaluated by monitoring the degradation of methyl orange dye as a function of irradiation time using a Hg (Xe) arc lamp. The sample containing the photocatalyst (ZnS) and the dye was taken in a 1cm quartz cell and irradiated with light of λ > 320 nm. The concentration of methyl orange was determined at various time intervals by monitoring the absorbance at its $\lambda_{\text{max}}$ (464 nm). The degradation efficiency may be calculated using the equation

$$\text{efficiency (\%) = (1 - C_t/C_0) \times 100}$$

where $C_0$ and $C_t$ are the initial and time dependent concentrations of methyl orange.
2.6 References


