3. Materials and methods

3.1. Materials

Lead acetate (CH$_3$COO)$_2$Pb, (99.9%), copper acetate (CH$_3$COO)$_2$Cu, Sodium telluride, 1-bromododecane, 1-bromotetradecane, 1-bromohexadecane, N, N, N’, N’-tetra-methylethlenediamine (TEMED), Hydrazine hydrate, Acetone, Ethanol and Ethyl acetate were obtained from Sigma Aldrich and were used directly without any treatment. All chemicals were of analytical grade and double distilled water has been used for all preparations. Dimeric cationic surfactants such as dimethylenebis(alkyldimethylammonium bromide) (m-2-m, where m is 12, 14 and 16) were synthesized according to the method reported elsewhere (Zana et al., 1991; Wetting et al., 2001; Bai et al., 2001; Zana et al., 1998). All surfactants were used after repeated crystallization from ethyl acetate and acetone. All stabilizing/capping agents used for the controlled crystal growth of nanoparticles in the present study have been listed in table 3.1.
Table 3.1. Different twin tail surfactants used in the present study.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Abbreviation</th>
<th>IUPAC Name</th>
<th>Critical micelle Concen. (cmc)/mM</th>
<th>Mol. Wt.</th>
<th>Surfactant Structure</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>(12-2-12)</td>
<td>Dimethylene bis(dodecyl-dimethyl ammonium bromide)</td>
<td>0.84</td>
<td>614</td>
<td>[\text{N}(\text{CH}<em>2)</em>{11}\text{N}^+ + \text{(CH}<em>2)</em>{11}\text{CH}_3\text{CH}_3 \times 2\text{Br}^-]</td>
<td>(Zana et al., 1991; Wettig et al., 2001)</td>
</tr>
<tr>
<td>2.</td>
<td>(14-2-14)</td>
<td>Dimethylene bis(tetradecyl-dimethyl ammonium bromide)</td>
<td>0.16</td>
<td>670</td>
<td>[\text{N}(\text{CH}<em>2)</em>{13}\text{N}^+ + \text{(CH}<em>2)</em>{13}\text{CH}_3\text{CH}_3 \times 2\text{Br}^-]</td>
<td>(Wettig et al., 2001; Bai et al., 2001)</td>
</tr>
<tr>
<td>3.</td>
<td>(16-2-16)</td>
<td>Dimethylene bis(hexadecyl-1-dimethyl ammonium bromide)</td>
<td>0.02</td>
<td>727</td>
<td>[\text{N}(\text{CH}<em>2)</em>{15}\text{N}^+ + \text{(CH}<em>2)</em>{15}\text{CH}_3\text{CH}_3 \times 2\text{Br}^-]</td>
<td>(Zana et al., 1991; Wettig et al., 2001)</td>
</tr>
</tbody>
</table>

3.2. Synthesis of Gemini surfactants

Gemini surfactants were prepared from N, N, N’, N’-tetra-methylethylenediamine (TEMED) and corresponding alkyl bromides (1-bromododecane, 1-bromotetradecane, 1-bromohexadecane) in absolute ethanol under reflux at 75°C for 48 hours. After removal of solvent by rotary evaporation, the surfactants were recrystallized 3-4 times in acetone/ethyl acetate (1:1). The product was dried and stored in desiccators to prevent moisture absorption.

3.3. Synthesis of surfactant capped PbTe nanoparticles

The PbTe nanoparticles were synthesized by simple hydrothermal method. In detail, 10 mL of aqueous gemini surfactant i.e. (12-2-12) (1 mM), (14-2-14) (0.5 mM) and (16-2-16) (0.25 mM) solutions of a stipulated concentration containing
2.5% hydrazine was taken in a conical flask. 15 mL of 1 mM lead acetate followed by 1 M NaOH was added to it and then 10 mL of 1 mM sodium telluride solution was also added, total solution was diluted to 40 mL under constant stirring for 10 minutes. The total clear solution was further transferred into a Teflon-lined autoclave with a volume capacity of 50 mL, up to 80% capacity of total volume of the autoclave. The sealed autoclave was put into a 150 °C furnace, and the separate reactions were carried out for 8 hours and 32 hours. Subsequently the container was cooled to room temperature and a grey powder was collected by centrifuging at 4500 rpm and washed several times with distilled water and ethanol to get purified sample.

3.4. Synthesis of surfactant capped Cu_{2-x}Te nanoparticles

Copper telluride nanoparticles were prepared through a reaction between copper acetate and sodium telluride in the presence of aqueous hydrazine under hydrothermal conditions. Briefly, 10 mL of aqueous gemini surfactant i.e. (12-2-12) (1 mM), (14-2-14) (0.5 mM) and (16-2-16) (0.25 mM) solution of a stipulated concentration containing 2.5% hydrazine was taken in a conical flask. 15 mL of 1 mM copper acetate followed by 1 M NaOH was added to it and then 10 mL of 1 mM sodium telluride solution was added, total solution was diluted to 40 mL under constant stirring for 10 minutes. The initial color of the solution was light yellow, then it shifted to brown and then to greenish black within 5 min and then remained the same. The total solution was further transferred into a Teflon-lined autoclave with a volume capacity of 50 mL, up to 80% capacity of total volume of the autoclave. The sealed autoclave was put into a 150 °C furnace, and two different reactions were carried for 8 hours and 32 hours. Greenish black powder was collected by centrifuging at 4500 rpm and washed several times with distilled water and ethanol.

3.5. Characterization Techniques

Numerous techniques are accessible under the broad umbrella of characterization of materials, which may be used to study nanomaterials in one way or the other. The resulting information can be processed to yield images or spectra which reveal the topographic, structural, geometric, chemical and physical details of the nanomaterials. Various techniques based on the use of photon (light and X-ray), electron and neutron probes, which are parallel with respect to their sensitivity on
different length scales, have been used. These techniques can be widely classified into three categories: (a) spectroscopic, (b) microscopic and (c) scattering techniques.

3.5.1. Spectroscopic Techniques

Optical spectroscopic techniques are widely used in the study of optical properties of different materials including nanoparticles. The different techniques are usually based on measuring absorption, scattering or emission of light that contains information about properties of materials. Most commonly used techniques include UV-visible electronic absorption spectroscopy, photoluminescence, infrared absorption and Raman scattering. These different techniques can provide different information about the nanoparticle properties of interest.

**UV-vis-Near IR Spectroscopy**

UV-vis-near IR spectroscopy offers a comparatively forthright and effective way for quantitatively characterizing both organic and inorganic nanomaterials. Furthermore, it is an ideal technique for determining the electronic properties of nanomaterials as it operates on the principle of absorption of photons that promotes the molecules to an excited state. In nanoparticle spectrum, the absorption peak width strongly depends on the chemical composition and particle size (Adachi, 1999). As a result, their spectrum is different from their bulk counterparts. For semiconductor nanoparticles, the absorption spectrum is broadened owed to quantum confinement effects and as their size reduces, there is no longer a distinct peak, rather there is a band. Moreover, the absorption peak in semiconductor nanoparticles shifts towards smaller wavelength as their size decreases. An important consequence of using UV-vis-near IR spectroscopy is that the band gap of the nanosized materials can be determined (Workman and Springsteen, 1998).

**Methodology:** The UV-visible spectra of as prepared aqueous solutions were taken by UV spectrophotometer (Systronic 2202) in the wavelength range to of 200-900 nm to determine the absorbance of copper telluride nanoparticles and near-IR spectra of lead telluride nanoparticles were recorded in the range 800-2500 nm by using UV-vis-NIR spectrophotometer (Hitachi 330). The absorption peak’s and band gap for semiconductor nanoparticles have been specifically explained in the discussion part.
Fourier Transform Infra-Red (FTIR) analysis
Infrared spectroscopy is an influential analytical technique, which support useful information about the structure of the molecules and bonding. The technique is based upon the principle that a chemical substance shows selective absorption in infrared region giving rise to absorption bands, called as IR absorption spectrum, which extends over a wide wavelength range (Smith, 1996). A molecule absorbs radiation only when the natural frequency of vibration of atoms is the same as the frequency of the incident radiation. After absorbing the correct wavelength of radiation, the molecule starts vibrating. This occurs due to absorption of energy of the IR radiation. Various bands in FTIR spectrums correspond to characteristic functional groups and bonds present in the chemical substance. FTIR spectrum of a chemical substance is thus a fingerprint for its identification (Chandra, 1981; Kalsi, 1995).

Methodology: The infrared spectrum of surfactant capped lead telluride and copper telluride nanoparticles were measured by a RZX (Perkin Elmer) and CARY 630 (Agilent) Fourier transform infrared spectrometer (FTIR) at room temperature in the range of 4000-400 cm\(^{-1}\) in the form of KBr pressed pellet method and by powdered method respectively.

Photoluminescence
Luminescence is a phenomenon in which the electronic states of a substance are excited by external energy (physical and chemical) and the excitation energy is given off as light (Yang et al., 2001). The fluorescence studies are mainly concerned with two types of spectrum, the excitation spectrum and emission spectrum. The excitation spectrum is determined by measuring the emission intensity at a fixed wavelength while varying the excitation wavelength. The emission spectrum is determined by measuring the variation in emission intensity wavelength for the fixed excitation wavelength. The difference between the excitation and emission wavelength is called as stoke’s shift. PL can be divided into two types, phosphorescence and fluorescence (Brus, 1994; Hines and Guyot-Sionest, 1996).

Photoluminescence in solid is a process in which luminescence is stimulated by the interaction of photons (electromagnetic radiations) with a material. The process is divided into two major types, namely intrinsic and extrinsic photoluminescence.
Intrinsic photoluminescence is observed in materials which contain no impurity atoms. Extrinsic photoluminescence is caused by intentionally incorporated impurities and in most cases metallic impurities or defects (Nirmal et al., 1995).

**Methodology:** The photoluminescence spectra of lead telluride and copper telluride nanoparticles were recorded by LS-55 (Perkin Elmer) at room temperature. All samples were excited at 290 nm.

**Raman Scattering**
Raman spectroscopy is based on the Raman Effect, An inelastic scattering process that was discovered by the Indian physicist Raman in 1928. The basic principle of this technique is that a monochromatic beam of light is focused onto the sample and the energy shifted fraction of the scattered light is detected. Raman scattering is used to explore the vibrational energy levels of molecules. It can instantly organize valuable information about the structure and identification of solid, liquid and gaseous substances. The technique is non-contact and non-destructive (Mlayah et al., 1994; Hayashi et al., 1989).

In Raman scattering, a photon is scattered by the molecular system. Most photons are elastically scattered (Rayleigh scattering) and have the same wavelength as the absorbing photon. But in Raman scattering, the energies of the incident and scattered photon are different because the inelastic scattering of photons by molecules. The energy of the scattered radiation is less than the incident radiation for stokes line and for the anti-stokes line. This increase or decrease in energy is related to the vibrational energy spacing in the ground electronic state of the molecule, so the wavelength of stokes and anti-stokes lines are direct measurements of the vibrational energies of the molecule (Venugopal et al., 2005; Batonneau et al., 2000).

**Methodology:** Raman scattering measurements was performed at room temperature with a lab RAM HR system in a backscattering configuration. The instrument was calibrated to same accuracy using silicon and a naphthalene standard.

**3.5.2. Microscopic Techniques**
Microscopic techniques for the characterization of nanoparticles include interaction of electron beams with the specimen, and the consecutive collection of transmitted or scattered electrons in order to create an image. This process may be carried out by scanning of a fine beam over the sample (e.g. scanning electron microscopy) or
Chapter 3

Materials and methods

by wide-field irradiation of the sample (e.g. transmission electron microscopy). Scanning probe microscopy involves the interaction of a scanning probe with the surface of the object of interest. The advantage of microscopic techniques is that it allows the direct visualization of the nanoparticles.

**Scanning electron microscopy (SEM)/ Energy Dispersive X-ray (EDX)**

Scanning electron microscopy (SEM) are tailor to contribute in structural, chemical and morphological information about individual nanoparticles. A miraculous efficiency of SEM instruments is the formation of high-brightness electron probes. One of the attractive features of the SEM is its great flexibility in the detection system. Different signals generated from the same sample area can be controlled either independently or simultaneously and can be analyzed in parallel to yield complementary information about the sample (Wang, 2000).

In SEM, a finely focused electron beam (generally 5-20 keV) is directed onto the specific area under investigation in a high vacuum environment is used to form the images. The interaction of the electron beam with the sample yield backscattered (BSE) electrons, secondary electrons, X-rays with characteristic energies, or photons. The emitted electrons and photons can be analysed to determine the surface morphology, and chemical composition using energy dispersive X-rays. The X-rays are produced by higher energy electrons transiting to the lower energy shell left vacant by an ejected secondary electron. The energy released in this process can be emitted in the form of X-rays, which are characteristic of the source atom. These X-rays are detected by an energy-dispersive spectrometer (EDS). This crystal ejects a photoelectron on exposure to X-ray. The energy of the photoelectron is given up in the form of charge which is converted to a signal by a voltage converter. EDX analysis allows the chemical identification of areas as small as a square micrometre and typically can detect atoms that are up to a micron in depth.

**Methodology:** The synthesized lead telluride and copper telluride nanoparticles were analyzed by SEM, fine powder of sample was loaded into the instrument. The SEM graphs were obtained. The elemental analysis was also done with the EDX arrangement equipped with SEM. The SEM instrument used was Hitachi H-7500.
Transmission electron microscopy
In the characterization of nanomaterials and nanostructures Transmission Electron Microscope (TEM) is one of the most extensively used technique. The greatest advantages that TEM offers are the high magnification and its ability to contribute in both image and diffraction information from single sample. The high magnification of all TEM is a result of the small effective electron wavelength. A heated pointed filament is used to produce electrons. These electrons then pass through anode and into condenser lenses to vary the electron beam spot size. After passing through scan coils, the electron beam is passed through the sample and then an objective lens and aperture to eliminate highly scattered electrons. The beam is enlarged by using a projector lens, which then strikes on phosphor screen for viewing on photographic plate. Electrons interact with matter very strongly. Thus we can use contrast for detection. The dark areas of image represent the regions where electrons are not transmitted, and the lighter areas which are transparent to photographic film.

The TEM instruments are capable of processing images at higher resolutions than other conventional light microscopes, due to the small de Broglie wavelength of the electrons. TEM, therefore forms major analysis method in both physical and biological sciences. TEM finds uses in nanotechnology, semiconductor research, bacterial and viral research etc.

Methodology: The shape and size of lead telluride and copper telluride nanoparticles were characterized by transmission electron microscopy (TEM). The samples were prepared by mounting a drop of a solution on a carbon coated Cu grid and allowing it to dry in air. The samples will be observed with the help of a Hitachi H-7500 and TECNAI 200 kV TEM (Fei, Electron Optics) transmission electron microscope operating at 120 kV. The system will be fitted with an intensified video camera to assist in alignment and a slow scan CCD camera. Final images can be recorded on CCD.

3.5.3. Scattering Techniques
Scattering techniques constitute powerful probes for characterizing nanoparticles. Different techniques based on different radiations (light, X-ray and neutron) have been extensively used. The important techniques used are X-ray diffraction, light scattering and small-angle scattering. In each of these techniques the radiation
(light, X-ray or neutron) is scattered by a sample and the resulting scattering pattern is analysed to provide information about the structure (shape and size), interaction, ordering in the sample. These techniques can be utilized over a wide range of length scales 1 to 1000 nm. Since most of the measurements are performed in solution, these techniques provide unique structural information under different conditions. Furthermore, it is also feasible to invest structural evolutions. These techniques are often used as a complementary tool with each other, providing scheduled information about the system.

**X-Ray Diffraction**

X-ray diffraction is most extensively used technique for the characterization of the materials. A lot of information can be extracted from the XRD data. This is a convenient technique for all forms of samples that is powder, bulk as well as thin films. Using XRD technique, we can get the information regarding the crystal structure, nature of the phase present, lattice parameter and crystalline size of a particular material. From the position and shape of the line, we can obtain information regarding the unit cell parameter and microstructural parameters (grain size, microstrain etc.) respectively. The change in lattice parameter with respect to bulk gives the idea about the nature of strain present in the system (Friedrich et al., 1912).

X-ray diffraction and of the exact requirement for the appearance of intensity maxima was presented by W. L. Bragg in 1912. He realized that when X-rays infringe on a crystal, some are reflected from the atoms in the top layer whereas others penetrate this layer and are reflected off the next layer, and so on (Liu et al., 1995). Analysis shows that the resultant reflected rays are only in phase for certain angles of incidents of the X-ray upon the crystals. The path difference between two waves is given by

\[
2\lambda = 2d \sin \theta \quad 3.1
\]

For constructive interference, the path difference between these waves must be an integral number of wavelengths. Bragg equation was raised (above equation) in which \(d\) is the separation between the planes, \(\theta\) is the angle of incidence and \(\lambda\) is the wavelength of the X-rays:

\[
2d \sin \theta = n\lambda \quad 3.2
\]

Where \(n\) is an integer corresponding to the order of diffraction.
X-ray diffraction analysis is used for the structural identification and broadening of the diffraction peaks caused by the finite size effect are used for estimating the average crystalline size d using Scherrer’s formula as (Krivoglaz, 1969).

\[ d = \frac{0.9\lambda}{\beta \cos \theta} \]  

Where, \( \lambda \) is the wavelength of X-ray used, \( \beta \) is the full width half maximum.

**Methodology:** X-ray diffraction analysis for lead telluride and copper telluride nanoparticles were performed by using manganese filtered Cu Kα radiation at 298 K was used. The instrument was equipped with graphite monochromator and operated at 40 kV and 30 mA. The XRD instrument used were Panalytical XPERT PRO X-Ray Diffractometer and Bruker D8 venture.

### 3.5.4. Electrical Conductivity studies

The DC conductivity studies of synthesized lead telluride and copper telluride nanoparticles was done using Keithley 2611 source meter with voltage range -10 to +10 V. Variation of DC conductivity with temperature was also studied with help of temperature control attached to Keithley Sourcemeter. Conductivity was measured with temperature in 290-473 K range during heating cycle using a temperature controller.

The characteristic I-V (Current-Voltage) curve is obtained using values of current (I) and voltage (V). The DC conductivity will be calculated by formula (Yi, 2008)

\[ \sigma = \frac{I}{VtA} \]  

Where, \( \sigma \) = conductivity, \( I/V \) is the slope of I-V curve taken, t is the thickness of the pellet and A is the area of the pellet.

**Methodology:** Synthesized sample of lead telluride and copper telluride nanoparticles were converted into pellets of 0.1 cm in thickness and having a diameter of 1.2 cm by applying a pressure of 4 Ton for 5 minutes. Fine quality silver paint was applied on both sides of pellet for good electrical contacts. The electrical conductivity measurements were carried out by two probe method using Keithley source meter.
3.5.5. Electrochemical studies

**Cyclic voltammetry**

CV has been proven as an effective technique for the characterization of semiconductors in determining their electrochemical band gaps as well as the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (Liu et al., 2014; Bae et al., 2004). In CV traces the peaks for different NPs related to their oxidation and reduction processes separated by a gap in terms of the potential (V). This is indicative of an energy gap between the band edges of the nanoparticles.

**Methodology:** Cyclic voltammetry was commenced at room temperature by using a three-electrode cell arrangement. Gold was used as the working electrode; Pt wire was as the counter electrode and Ag/Ag⁺ was as the reference electrode. The electrolyte was prepared by dissolving tetrabutyl ammonium perchlorate (TBAP) in acetonitrile (0.05 M). The scan rate was fixed at 100 mV/s. The electrochemical measurements for band gap studies were performed using Bio-Logic SP-200, in a conventional three electrode cell.