Chapter 4  

Results and Discussion

The fourth chapter solicits the results and discussion of hydrothermally synthesized lead telluride and copper telluride semiconductor nanoparticles in the presence of cationic gemini surfactant/Twin-Tail surfactants (TTS) at 150°C for 8 and 32 hours. (12-2-12), (14-2-14) and (16-2-16), gemini surfactants has been selected as capping agents for this study. The effect of TTS on shape and size of lead telluride and copper telluride quantum dots has been evaluated with their structural, optical and electrical aspects.

Results and Discussion

4.1. Synthesis of (12-2-12) TTS capped Lead Telluride nanoparticles at 150 °C for 8h.

4.1.1. XRD Analysis

Figure 4.1.1 represents XRD spectrum of PbTe where the entire peaks pattern can be indexed to the cubic rock salt type and orthorhombic phase of PbTe. The peaks of 2 theta at 27.75°, 39.54°, 48.94°, 57.18°, 64.66° and 71.63° corresponds to (200), (220), (222), (400), (420) and (422) planes of cubic phase of PbTe respectively (Cao et al., 2010). The peaks at 23.82° and 34.15° are assigned to (111) and (221) planes of orthorhombic phase of PbTe respectively (Park et al., 2007). The average particles size has been calculated 25 nm using Scherrer formula (Borah et al., 2008).

Figure 4.1.1: XRD patterns of PbTe semiconductor quantum dots.

The resulting lead telluride nanostructures were further investigated morphologically by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Manifestations of nanocuboids morphology of aforementioned PbTe nanomaterials have been divulged through SEM (Figure 4.1.2a).

![Figure 4.1.2: (a) Scanning electron micrograph (b) EDX spectrum (c) & (d) Transmission electron micrographs at different magnifications of PbTe nanoparticles displaying cubic nanostructure.](image-url)
EDX elemental analysis specified the manifestation of lead telluride with 13:10 atomic percentage ratio of Pb:Te in PbTe (Figure 4.1.2b). TEM images of lead telluride nanostructure endorsed a cubic structures with pearl necklace arrangement (Figure 4.1.2c and 4.1.2d) with average particle size 20 ±5 nm, which is close to the calculated size from XRD. The outer diminished layer in the Figure 4.1.2d clearly demonstrates surfactant capping onto the cubic nanostructures. All the peaks were much pronounced and refer to the cubic rock salt structure. The intensity of (200) peak is much higher, thus indicating a higher growth rate on (100) facet in contrast to the (111) facets. The ratio of the growth rate in the (200) direction to that of (111) direction is used to determine the shape of fcc nanocrystals for the rock salt structure. For fcc crystal, (111) plane have higher surface energy than the (200) plane (Park et al., 2007; Li et al., 2008; Wang, 2000). Therefore, occurrence of cubic morphology in case of PbTe nanocrystals may be considered favourable for their formation because of a faster growth rate in the (111) directions.

4.1.3. Possible formation mechanism

Lead acetate and sodium telluride are expected to dissociate into their respective ions as soon as they are dissolved in water. Hydrazine will convert tellurite ions into telluride ions by following a redox reaction. Once telluride ions are produced, they will undergo neutralization with lead ions to generate lead telluride in the presence of hydrazine (Wan et al., 2009). The formation of lead telluride nanostructure in this hydrothermal process has been considered a direct combination pathway as follows (Wan et al., 2010):

\[
Pb(CH_3COO)_2 \rightarrow Pb^{2+} + 2CH_3COO^- \quad 4.1
\]

\[
Na_2TeO_3 \rightarrow 2Na^+ + TeO_3^{2-} \quad 4.2
\]

\[
TeO_3^{2-} + N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + Te^{2-} \quad 4.3
\]

\[
Pb^{2+} + Te^{2-} \rightarrow PbTe \quad 4.4
\]

4.1.4. Williamson-Hall Methods

Williamson-Hall analysis of lead telluride NPs data have been carried out by assuming three main models i.e. Uniform deformation model (UDM), Uniform...
stress deformation model (USDM), and Uniform deformation energy density model (UDEDM). Williamson-Hall method varies with $\tan \theta$ and does not follow $1/\cos \theta$ dependency in the Scherrer equation. This major difference allows for separation of reflection broadening when both the microstructural causing small crystalline size and micro-strain transpire together (Zak et al., 2011). The strain induced in the powders due to crystal imperfection and distortion was calculated using following formula:

$$\varepsilon = \frac{\beta_{hkl}}{\tan \theta} \quad 4.5$$

where $\varepsilon$ is the root mean square value of the microstrain and assuming that the particle size & strain contribution to the line broadening are independent of each other and the observed line breadth is simply the sum of the two terms.

$$\beta_{hkl} = \beta_D + \beta_\varepsilon = \frac{k\lambda}{D \cos \theta_{hkl}} + [4 \varepsilon \tan \theta] \quad 4.6$$

where $\lambda$ is the wavelength of the radiation (1.54056 Å for CuKα radiation), $k$ is a constant equal to 0.94). Rearranging equation (4.6) gives:

$$\beta_{hkl} \cos \theta_{hkl} = \beta_D + \beta_\varepsilon = \left[ \frac{k\lambda}{D} \right] + [4 \varepsilon \sin \theta] \quad 4.7$$

Here equation 4.7 stands for Uniform Deformation Model (UDM), where it has been assumed that strain is uniform in all crystallographic directions, thus recognizing the isotropic nature of crystal, where all the material properties are independent of the direction along which they are measured (Prabhu et al., 2013). $\beta \cos \theta$ was plotted with respect to $4 \sin \theta$, while strain and particles size have been calculated from the slope and y-intercept of the fitted line respectively. The plots exhibited a negative strain for the nanoparticles which may be due to the lattice shrinkage that was observed in the calculation of the lattice parameters. The uniform deformation model analysis results for lead telluride are shown in Figure 4.1.3a. The different plot of Hall equation for lead telluride indicate positive and negative slope. Positive slope indicates the presence of tensile strain in lattice, negative slope attributed to the presence of compressive strain. The strain is manifestation of dislocation network, and the decrease of strain indicates a decrease in concentration of lattice imperfections.
For Uniform Stress Deformation Model (USDM) strain have been calculated from Hook’s law, retaining only the linear proportionality between stress and strain as given by $\sigma = \varepsilon E_{hkl}$, where $\sigma$ is the stress of the crystal and $E_{hkl}$ is the modulus of elasticity or young’s modulus. This equation is an approximation that is valid for a significantly small strain. Presuming the existence of a small strain in lead telluride nanoparticles, the Williamson-Hall equation has the form:

$$\beta_{hkl} \cos \theta = \left( \frac{k^2}{D} \right) + \left( \frac{4\varepsilon \sin \theta}{E_{hkl}} \right)$$

Young’s Modulus, $E_{hkl}$ for lead telluride has been reported 58 GPa (Vasilevskiy et al., 2012). Designated as USDM plots and drawn between $4\sin\theta/E_{hkl}$ and $\beta\cos\theta$ for lead telluride has been revealed in Figure 4.1.3b.

![Figure 4.1.3](image)

**Figure 4.1.3:** W-H analysis of lead telluride NPs capped with (12-2-12) surfactant assuming UDM (a), USDM (b) and UDEDM (c). Fit to the data, the strain is extracted from the slope and the crystalline size is extracted from the y-intercept of the fit. For SSP (d) the particle size is obtained from the slope of the linear fitted data, and the root of the y-intercept gives the strain.
The energy density of crystals was calculated from a model called Uniform Deformation Energy Density Model (UDEDM). The crystals have been assumed to retain homogenous and isotropic nature. The energy density \( u \) (energy per unit volume) for elastic system that follows Hook’s law, the energy density can be calculated from \( u = \varepsilon^2 E_{hkl}/2 \). Then equation 4.8 can be rewritten according to the energy and strain relation as below:

\[
\beta_{hkl} \cos \theta_{hkl} = \left( \frac{k^2}{D} \right) + \left( 4 \sin \theta \left( \frac{2u}{E_{hkl}} \right)^{1/2} \right)
\]

4.9

The plots of \( \beta_{hkl} \cos \theta \) versus \( 4 \sin \theta \left( 2u/E_{hkl} \right)^{1/2} \) have been constructed and the data fitted to lines. From the slope the anisotropic energy density \( u \) was calculated and the average crystalline size \( D \) from the \( y \)-intercept from the deformation stress and deformation energy density are related as \( u = \sigma^2/2E_{hkl} \). It may be noteworthy that both the above equation takes into account the anisotropic nature of elastic constant, so they are essentially different. The observations of the three interpretations for lead telluride nanoparticles are possible from the analysis of Figure 4.1.3c. The scattering of the points away from the linear expression is much less in Figure 3c in contrast to Figure 4.1.3a and Figure 4.1.3b. The crystalline size estimated from the \( y \)-intercept of the graphs from Figure 4.1.3a, b, c is 7.9 nm (UDM) and 53 nm (USDM and UDEDM) for lead telluride.

**Size-strain plot method**

Williamsons-Hall plot exhibited that line broadening was imperatively isotropic whereas owing to micro-strain contribution the diffracting domains were isotropic. Size–strain parameter may be attained from the “size-strain plot” (SSP). The data from the reflections at high level have less importance and data precision is usually lower for the same. Under the preview of this estimation, it has been assumed that profile is illustrated by strain-contour via a Gaussian function and the crystalline size by Lorentzian function (Goncalves et al., 2012). Accordingly we have

\[
(d_{hkl} \beta_{hkl} \cos \theta)^2 = \frac{k}{D} \left( d_{hkl} \beta_{hkl} \cos \theta \right) + \left( \frac{\xi}{2} \right)^2
\]

4.10
where \( k \) is constant depending on the shape of the particles. Figure 4.1.3d demonstrates the construction of plots of \( d_{hkl}^2 \beta_{hkl} \cos \theta \) versus \((d_{hkl} \beta_{hkl} \cos \theta)^2\) and the data fitted to lines. The particle size is calculated from the slope and the root of the y-intercept gives the strain.

The results obtained from Williamson-Hall method has been summarised in Table 4.1.1. It is important to note here that for PbTe nanoparticles the compressive strain is more than tensile strain. UDEDM procedure show occurrence of tensile strain only in lead telluride nanoparticles.

**Table 4.1.1: Geometric parameters of (12-2-12) capped PbTe nanoparticles.**

<table>
<thead>
<tr>
<th>NPs</th>
<th>Scherrer Method</th>
<th>Williamson-Hall Method</th>
<th>Size-Strain Plot</th>
<th>TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Size, ( D ) (nm)</td>
<td>Strain, ( \varepsilon )</td>
<td>Stress, ( \sigma ) (MPa)</td>
<td>Size, ( D ) (nm)</td>
</tr>
<tr>
<td>(12-2-12) ( \text{PbTe} )</td>
<td>25</td>
<td>7.9</td>
<td>2.6 ( \times 10^{-3} )</td>
<td>4.4 ( \times 10^{-3} )</td>
</tr>
</tbody>
</table>

Where \( T = \) Tensile Strain and \( C = \) Compressive Strain.

### 4.1.5. Optical characterization

The optical properties of lead telluride quantum dots were examined by near IR region absorption spectroscopy as shown in Figure 4.1.4a. Strong absorption peaks at 2400 nm has been encountered for lead telluride. The optical band gap energy of nanoparticles was calculated using Tauc relation:

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

where \( \alpha = \) absorption coefficient = 2.303 \( A/\ell \), \( E_g = \) optical band gap, \( B = \) band tailing parameter, \( \nu = \) is the photon energy and \( n = \frac{1}{2} \) for direct band gap.

The optical band gap have been determined by extrapolating the straight portion of curve between \((\alpha \nu)^2\) and \( \nu \). The optical band gap of as-prepared lead telluride sample has been appraised as 0.50 from the near-IR absorption spectrum, which is
larger than the direct band gap (lead telluride -0.32 eV) of bulk (Li et al., 2013; Tai et al., 2008) clearly indicating quantum confinement. The quantum confinement may have been arising when size of particles was comparable to Bohr exciton radius. The higher band gap can be attributed to size effect of the present nanostructure. Consequently, the increase of band gap as compared to bulk can be understood on the basis of quantum size effect which may have been arising due to very small size of NP (Figure 4.1.4b). The calculated band gaps were plotted as a function of the NP size and the band gap increases cogently with decreasing NP size.

Figure 4.1.4: (a) Near-IR spectrum of (12-2-12) capped lead telluride NPs. (b) Tauc plots for lead telluride NPs, dotted lines representing extrapolation for band gap.

4.1.6. Electrical conductivity measurements
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Lead telluride quantum dots exhibit a linear Current- Voltage (I-V) curve (Figure 4.1.5a) that is almost symmetric about the origin, indicating that the contacts are ohmic. The resistance of the samples, as calculated from the slope of the I-V curve have been found about 1-5 Ω for lead telluride. Figure 4.1.5b displays the temperature dependence of electrical resistivity for PbTe quantum dots, which varies from 64.22 ohm cm to 13.51 ohm cm at different temperature (293K-383K). Based on the resistance and size including length, width and thickness of the sample, the electrical conductivities of lead telluride have been measured to be 0.01-0.07 S cm\(^{-1}\). The observed values of resistivity agree well with the reported values (Dong et al., 2012; Zhang et al., 2010). It may be interpreted that the particle size plays a crucial role in the conductivity and the semiconductor quantum dots possess better conductivity in comparison to their bulk equivalents. The quantum confinement effect arise when the size of the quantum dots fall below the Bohr exciton radius of the material and dominates over the grain boundary defects phenomena, hence resulting better conductivity (Wang and Herron, 1991; Saravanan et al., 2011).

4.1.7. FTIR measurements

Figure 4.1.6 shows FTIR spectral studies of pure (12-2-12) surfactant as well as interactions of capping surfactant molecule with PbTe at surfactant concentration of 1 mM. In the higher frequency region IR spectrum of pure (12-2-12), lead telluride NPs show symmetric and asymmetric stretching vibrations of methylene in the alkyl chains at 2959 and 2858 cm\(^{-1}\), 2925 and 2854 cm\(^{-1}\). Scissoring mode of vibration at (δ\(_s\)(C-H)) at 1469 cm\(^{-1}\), which shifts to 1410 cm\(^{-1}\) for PbTe and ν(C-N\(^+\)) modes at 1160 and 974 cm\(^{-1}\) shift to 1110 cm\(^{-1}\) for PbTe which can be used as an indicator of the higher energies of stretching vibrations corresponding to more gauche defects. Small vibrational frequency shifts have also been detected for TTS engineered nanoparticles, indicating a high surface coverage of TTS on the nanoparticles (Bakshi et al., 2007; Naselli et al., 1985; Zhang et al., 2006).
Figure 4.1.5: (a) I-V characteristics and (b) variation of resistivity with temperature for PbTe nanoparticles.
Figure 4.1.6: FTIR spectra of (a) pure surfactants and (b) PbTe NPs synthesized with (12-2-12) surfactants.

4.2 Synthesis of (12-2-12), (14-2-14) and (16-2-16) TTS capped Lead Telluride nanoparticles at 150 °C for 32h.

4.2.1. X-ray Analysis

Figure 4.2.1 shows the Powder X-ray diffraction patterns taken in the range 2θ = 20-80° for the lead telluride nanoparticles synthesized in the presence of twin tail surfactant at temperature 150 °C contained the peaks corresponding to the (200), (221), (220), (222), (400), (420) and (422) Bragg reflections and refers to the cubic phase of lead telluride nanoparticles (Gholamrezaei et al., 2014). Studies of materials in nanoscale need characterization of microstructures with emphasis in the particle size and microstrain. To estimate the average nanoparticle size using X-ray diffraction measurements, the Scherrer’s equation \(D=0.94\lambda/\beta \cos\theta\) is the most used method, where \(D\) is the particles size, \(\lambda\) is the wavelength of X-ray, \(\beta\) is the full width at half-maximum of the peak and \(\theta\) is the angle of diffraction. From different theta values, the average particle size for lead telluride nanoparticles with twin tail surfactants i.e. (12-2-12), (14-2-14) and (16-2-16) has been calculated to be about 29.53 nm, 32.17 nm and 39.12 nm respectively. We also present the mean
particle sizes for lead telluride nanoparticles calculated from XRD patterns by using the Williamson-Hall method and size-train plot method considering the effect of microstrain and then compare with those mean particle sizes obtained with Scherrer equation.

![XRD pattern of PbTe nanoparticles capped with different gemini surfactants.](image)

**Figure 4.2.1:** XRD pattern of PbTe nanoparticles capped with different gemini surfactants.

### 4.2.2. Transmission Electron Microscopy (TEM) analysis

Figure 4.2.2 shows transmission electron micrograph of lead telluride nanoparticles capped with different twin tail surfactants obtained at 150°C under hydrothermal conditions. TEM image shows similar morphologies in the presence of different twin tail surfactant, the smaller nanoparticles with average diameters of 50 ±15.18 nm has been observed with smallest twin tail surfactant i.e. (12-2-12) and the average diameter of lead telluride nanoparticles goes on increasing with increase in the length of twin tail surfactants. The average diameter for (14-2-14) and (16-2-16) capped nanoparticles has been found to be 65 ±18.70 nm and 85 ±18.7 nm respectively. The XRD pattern shows (200) peak with higher intensity as compare to other peaks for lead telluride nanoparticles capped with different twin tail surfactants and this intensity increased with increase in the tail length of the
surfactants. Fig. 4.2.2, d and f shows histograms of the nanoparticles that correspond to the TEM images.

Figure 4.2.2: TEM images of PbTe NPs synthesized with (a) (12-2-12) (c) (14-2-14) and (e) (16-2-16) surfactants. Histograms showing particle size distribution in (b), (d) and (f) for different surfactants respectively.
Table 4.2.1: Average particle sizes, as determined by XRD of (12-2-12), (14-2-14) and (16-2-16) capped lead telluride nanoparticles.

<table>
<thead>
<tr>
<th>NPs</th>
<th>2θ (degree)</th>
<th>FWHM</th>
<th>Average Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(12-2-12)-PbTe</td>
<td>27.71</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.25</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>39.62</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>49.08</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>57.21</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>64.77</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td></td>
<td>71.75</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>(14-2-14)-PbTe</td>
<td>27.71</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.25</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>39.62</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>49.08</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>57.21</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>64.77</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>71.75</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>(16-2-16)-PbTe</td>
<td>27.71</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.25</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td>39.62</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>49.08</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>57.21</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>64.77</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>71.75</td>
<td>0.53</td>
<td></td>
</tr>
</tbody>
</table>

4.2.3. FTIR analysis

To prove whether the lead telluride nanoparticles are indeed capped by twin tail surfactants, FTIR measurements were performed. In FTIR measurements, lead telluride capped by twin tail surfactants were compared with the corresponding pure twin tail surfactants. Fig 4.2.3a and 4.2.3b shows the representative FTIR spectra of pure (12-2-12), (14-2-14), (16-2-16) and twin tail surfactants capped lead telluride nanoparticles respectively. It is well known that the symmetric and asymmetric stretching vibrations of methylene can be used as an indicator of the ordering of the alkyl chains and higher energies of stretching vibrations correspond to more gauche defects. The symmetric and asymmetric stretching vibrations of methylene of pure surfactants are located at 2854, 2858, 2922, 2925 and 2959 cm\(^{-1}\) which shifts to 2851, 2922 and 2954 cm\(^{-1}\) for (12-2-12) capped nanoparticles, 2850 and 2916 cm\(^{-1}\) for 14-2-14 capped nanoparticles and 2841 and 2923 cm\(^{-1}\) for (16-2-16) capped nanoparticles. The slight shift to lower frequency Scissoring mode of vibrations (\(\delta s(C-H)\)) at 1469 cm\(^{-1}\) for pure twin tail surfactants shifts to 1409 and
1449 cm\(^{-1}\) for (12-2-12) and (14-2-14) capped lead telluride NPs respectively. In the low wave number region, the intensities of \(\nu(C-N^+)\) stretching modes for pure twin tail surfactant appeared at 1160, 1056, 1042, 984, 974 and 972 cm\(^{-1}\). These peaks shifted to 1123, 970 and 843 cm\(^{-1}\), 1175, 1056 and 843 cm\(^{-1}\) and 1025 cm\(^{-1}\) for (12-2-12), (14-2-14) and (16-2-16) capped lead telluride nanoparticles respectively (Naselli et al., 1985; Jain et al., 2014).

Table 4.2.2: Peak assignment of different gemini surfactants in the absence and presence of PbTe nanoparticles.

<table>
<thead>
<tr>
<th>Peak assignment</th>
<th>(12-2-12) PbTe</th>
<th>(14-2-14) PbTe</th>
<th>(16-2-16) PbTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_{\text{asym}}) (C-H)</td>
<td>2959</td>
<td>2954</td>
<td>2959</td>
</tr>
<tr>
<td>(\nu_{\text{sym}}) (C-H)</td>
<td>2858</td>
<td>2851</td>
<td>2854</td>
</tr>
<tr>
<td>(\delta) (C-H)</td>
<td>1469</td>
<td>1409</td>
<td>1469</td>
</tr>
<tr>
<td>(\nu) (C-N(^{+}))</td>
<td>1160</td>
<td>1123</td>
<td>1160</td>
</tr>
<tr>
<td></td>
<td>974</td>
<td>970</td>
<td>984</td>
</tr>
</tbody>
</table>

4.2.4. Possible reaction mechanism

It is extensively accepted that the formation of nanoparticles is mainly attained through two stages, first is nucleation and second growth. In the solution phase synthesis of nanoparticles, nucleation is mainly referred to the formation of seeds with a stable structure and well-defined crystallinity, the shape of NPs is primarily determined by the minimization of surface energy (Quan et al., 2008). The reaction mechanism for the formation of lead telluride nanoparticles are same as mentioned in section 4.1 equation number 4.1, 4.2, 4.3 and 4.4.

4.2.5. Williamson-Hall Methods

A simple method to separate the contribution of particle size and microstrain to the line broadening in the XRD patterns is the Williamson-Hall (WH) plotting. For this work we present the mean particles sizes for (12-2-12), (14-2-14) and (16-2-16) capped lead telluride nanoparticles calculated from XRD patterns by using the W-H plot and size-strain plot method. Williamson-Hall analysis of lead telluride nanoparticles have been carried out by assuming three main models i.e. Uniform deformation model (UDM), Uniform
stress deformation model (USDM), and Uniform deformation energy density model (UDEDM). This method varies with $\tan \theta$ and does not follow $1/\cos \theta$ dependency in the Scherrer equation. This basic difference was that both microstructure caused small crystallite size and microstrain occur together from the reflection broadening (Zak et al., 2011).

Figure 4.2.3: FTIR spectra of (a) pure surfactants and (b) PbTe NPs synthesized with (12-2-12), (14-2-14) and (16-2-16) surfactants.
This analysis supposes that the particle size (D) and microstrain (ε) contribute to the line broadening with lorentzian profiles. Crystal imperfections and distortion of strain-induced peak broadening are related by equation 4.5. The particle size & strain contribution to the line broadening are independent of each other and the observed line breadth is simply the sum of the two terms shown in equation 4.6.

The UDM, where the strain was assumed to be uniform in all crystallographic directions, thus considering the isotropic nature of the crystal, where all the material properties are independent of the direction along which they are measured. \( \beta \cos \theta \) was plotted with respect to \( 4 \sin \theta \) for the peaks of lead telluride NPs with different twin tail surfactants. The graph can be fitted by a linear function that provides the strain value from the slope and the particle size from the intercept with the axis. The slope can be positive and negative. The positive slope indicates the presence of tensile strain in lattice and negative slope attributed to the presence of compressive strain. The strain is manifestation of dislocation network, and the decrease of strain indicates a decrease in concentration of lattice imperfections. The uniform deformation model analysis results for lead telluride NPs with varied twin tail surfactants are shown in Figure 4.2.4.

In Uniform Stress Deformation Model (USDM), a generalized Hook’s law refers to the strain, keeping only the linear proportionality between stress and strain as given by \( \sigma = \varepsilon E_{hkl} \), where \( \sigma \) is the stress of the crystal and \( E_{hkl} \) is the modulus of elasticity or young’s modulus. This equation is an approximation that is valid for a significantly small strain. Presuming the existence of a small strain in lead telluride NPs, Hook’s law can be used (equation 4.8).

Young’s Modulus, \( E_{hkl} \) for lead telluride has been reported 58 GPa (Vasilevskiy et al., 2012). The USDM plots were drawn with \( 4 \sin \theta / E_{hkl} \) on x-axis and \( \beta \cos \theta \) on y-axis for lead telluride NPs with different surfactants in Figure 4.2.5.
Figure 4.2.4: W-H analysis of lead telluride NPs capped with (a) (12-2-12), (b) (14-2-14) and (c) (16-2-16) surfactants assuming UDM. Fit to the data, the strain is extracted from the slope and the crystalline size is extracted from the y-intercept of the fit.

There is another model that can be used to determine the energy density of a crystal called the uniform deformation energy density model (UDEDM). The crystals have been assumed to have a homogeneous and isotropic nature. The energy density $u$ (energy per unit volume) for elastic system that follows Hook’s law, the energy density can be calculated from $u = \varepsilon^2 E_{hkl}/2$ (equation 4.9).

The uniform deformation energy density model (UDEDM) can be calculated from the slope of the line plotted between $\beta_{hkl} \cos \theta$ versus $4\sin \theta (2u/E_{hkl})^{1/2}$. The anisotropic energy density $u$ was calculated from the slope of these lines and crystalline size $D$ from the y-intercept.
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Results and discussion

Figure 4.2.5: W-H analysis of lead telluride NPs capped with (a) (12-2-12), (b) (14-2-14) and (c) (16-2-16) surfactants assuming USD. Fit to the data, the strain is extracted from the slope and the crystalline size is extracted from the y-intercept of the fit.

Figure 4.2.6: W-H analysis of lead telluride NPs capped with (a) (12-2-12), (b) (14-2-14) and (c) (16-2-16) surfactants assuming UDEM. Fit to the data, the strain is extracted from the slope and the crystalline size is extracted from the y-intercept of the fit.
The observations of the three interpretations for lead telluride nanoparticles are possible from the analysis of Figures 4.2.4, 4.2.5 and 4.2.6 because the scattering of the points away from the linear expression is much less in Figure 4.2.6 in contrast to Figure 4.2.4 and 4.2.5. The crystalline size estimated from the y-intercept of the graphs from Figure 4.2.4-4.2.6 is 12 nm (UDM), 53 nm (USDM) and 96 nm (UDEDM) for (12-2-12) capped lead telluride NPs. For (14-2-14) capped NPs crystalline size is 18.1 nm (UDM), 17.9 nm (USDM) and 57 nm (UDEDM) While for (16-2-16) capped lead telluride NPs, crystalline size was found to be 49.6 nm (UDM), 46.6 nm (USDM) and 64.2 nm (UDEDM).

**Size-strain plot method**

Williamsons-Hall plot showed that line broadening was imperatively isotropic. This indicates that the diffracting domain was isotropic and there was also a microstrain contribution. Size-strain parameter may be attained from the “size-strain plot” (SSP). The data from the reflections at high level have less importance and data precision is usually lower for the same. Under the preview of this estimation, it has been assumed that profile is illustrated by strain-contour via a Gaussian function and the crystalline size by Lorentzian function (equation 4.10) (Singh and Bedi, 2011).

Figure 4.2.7 demonstrates the construction of plots of $d_{hkl}^2 \beta_{hkl} \cos \theta$ versus $(d_{hkl}^2 \beta_{hkl} \cos \theta)^2$ and the data fitted to lines. The particle size is calculated from the slope and the root of the y-intercept gives the strain.
Figure 4.2.7: Size-strain plots of (a) (12-2-12), (b) (14-2-14) and (c) (16-2-16) capped lead telluride NPs. The particle size is obtained from slope of the linear fitted data, and the root of the y-intercept gives the strain.

Table 4.2.3: Geometric parameters of (12-2-12), (14-2-14) and (16-2-16) capped PbTe nanoparticles

<table>
<thead>
<tr>
<th>NPs</th>
<th>Scherrer Method</th>
<th>Williamson-Hall Method</th>
<th>Size-Strain Plot</th>
<th>TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UDM</td>
<td>USDM</td>
<td>UDEDMS</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Size, D (nm)</td>
<td>Strain, ε T C</td>
<td>Size, D (nm)</td>
<td>Strain, ε T C</td>
</tr>
<tr>
<td>(12-2-12) - PbTe</td>
<td>29.53</td>
<td>4.2 x 10⁻³ &amp; 1.8 x 10⁻³</td>
<td>53</td>
<td>1.02 x 10⁻²</td>
</tr>
<tr>
<td>(14-2-14) - PbTe</td>
<td>32.17</td>
<td>NA</td>
<td>17.9</td>
<td>1.74 x 10⁻²</td>
</tr>
<tr>
<td>(16-2-16) - PbTe</td>
<td>39.12</td>
<td>-4 x 10⁻³ &amp; -8 x 10⁻³</td>
<td>46.6</td>
<td>1.76 x 10⁻²</td>
</tr>
</tbody>
</table>

Where T= Tensile Strain and C= Compressive Strain.

4.2.6. Optical properties of PbTe nanoparticles

The near IR region absorption spectra of twin tail surfactants capped PbTe nanoparticles are presented in Figure 4.2.8. Absorption peaks for lead telluride nanoparticles have been encountered in the range from 1200nm- 2800nm. The role of the capping agent is very important to nanoparticle synthesis, during nucleation, growth and stabilization of the nanoparticles. We observed an increase in particle size as we increase the tail length of twin tail surfactants, on the basis of critical micelles concentration range (16-2-16) has been found to be more hydrophobic in contrast to (14-2-14) and (12-2-12) surfactants, which results admirable capping ability and a stronger liquid-solid interfacial adsorption. With increase in hydrophobicity of surfactants from (12-2-12) to (16-2-16) therefore lead to an increase in size of lead telluride nanoparticles.
Figure 4.2.8: Near-IR spectrum of (12-2-12), (14-2-14) and (16-2-16) capped lead telluride NPs

The ability to control particle size is of fundamental interest to prepare high quality lead telluride nanoparticles and to characterize their optical properties. Understanding size effects in such a system provides the possibility of tuning its prodigious properties for specific applications. Quantum confinement effects are clearly observed as shown by the red shift of the respective peaks. The appearance of well-defined peaks in absorption spectra demonstrates the high quality of the synthesized samples. The optical band gap energy of nanoparticles was calculated using the Tauc relation (equation 4.11) (Tauc et al., 1996).

The optical band gap is determined by extrapolating the straight portion of curve between $(\alpha hv)^2$ and $hv$ when $\alpha=0$. The direct band gap energy of bulk PbTe is 0.32 eV. The blue shift of 0.42, 0.43 and 0.45 eV of (16-2-16), (14-2-14) and (12-2-12) capped nanoparticles respectively is due to the result of quantum confinement (Figure 4.2.8). As the size NPs or alternatively the quantum dots become smaller and approaches the Bohr radius of the bulk exciton, quantum confinement effects become possible and a blue shift in exciton energy can be observed (Brus, 1984). The blue shift progressively decreases with increases particle diameter.

The optical band gap of semiconductor nanoparticles, a crucial electronic parameter is also studied by cyclic voltametry (CV). 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. Here, the oxidation current can be related to the addition of holes to
the HOMO level, while the reduction is related to the addition of electron to the
LUMO of the NPs, which are directly derivable from the onset of anodic and
cathodic currents in CV traces (Haram et al., 2001; Liu et al., 2011). Cyclic
voltametry 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 (0.05M).
The scan rate was fixed at 100 mV/s. Three anodic peaks at +0.30, +0.29 and +0.27
V and three cathodic peaks at -0.14, -0.12 and -0.08 V were observed for
nanoparticles (1mM) respectively. The electrochemical band gap from the different
anodic and cathodic peaks from Figure 4.2.10 is calculated as 0.44, 0.41 and 0.35
V for (12-2-12), (14-2-14) and (16-2-16) capped lead telluride nanoparticles
respectively, which is close to the values obtained spectroscopically Figure 4.2.9.
Figure 4.2.9: Tauc plots for (a) (12-2-12), (b) (14-2-14) and (c) (16-2-16) capped lead telluride NPs, dotted lines representing extrapolation of band gap.
Figure 4.2.10: CV response of (12-2-12), (14-2-14) and (16-2-16) capped lead telluride NPs in the presence of tetrabutylammonium perchlorate (TBAP). Inset represents CV response of TBAP without NPs.

4.2.7. Photoluminescence

For the optical property, measurements of photoluminescence spectra were performed at room temperature. Figure 4.2.11 (a) shows the PL spectra of as prepared lead telluride nanoparticles. Photoluminescence is a two-step process consisting of absorption of the incoming photon by electron and emission of the outgoing photon by the thermalized electrons. As a result of the thermalization, the outgoing photon is not coherent with the incoming photon. Generally two emissions can be perceived from semiconductor nanomaterials: one is the acute excitonic emission located near the absorption band edge and another is the broad emission due to surface states or defects (Kripal et al., 2010; Zwijnenburg, 2012). It has been shown that lead telluride nanoparticles exhibit a strong peak around 813 nm and broad emission peak around 649 nm. The hydrothermal treatment of lead telluride nanoparticles in the presence of (12-2-12), (14-2-14) and (16-2-16) Gemini surfactants leads to the narrowing of the PL band and the increase in the...
intensity by an order of magnitude respectively. One should note that increase in the tail length of Gemini surfactants also results in the increase of the PL intensity. The broadening of PL emission peaks are observed as the diameter of nanoparticles decreases for \((16-2-16)\), \((14-2-14)\) and \((12-2-12)\), capped NPs respectively. This broadening of PL peak can be attributed to strain in nanoparticles caused by size induced quantization effect. The defects or strain/stress are imported in the NPs due to quantum confinement effects at nanoscale (Gholamrezaei et al., 2014). Both the absorption and photoluminescence properties suggest that these nanoparticles can be possibly used for third generation quantum dot solar cells and other devices.

4.2.8. Raman spectroscopy

The PbTe nanoparticles prepared were further characterized by Raman scattering spectroscopy, the Raman spectra obtained are presented in fig. As shown in Figure 4.2.11 (b) spectra exhibits the bands at 73 and 182 cm\(^{-1}\) for \((12-2-12)\) and at 73 and 103 cm\(^{-1}\) for \((14-2-14)\) and \((16-2-16)\) capped NPs are due to the phonon modes of lead telluride, used in different critical points of Brillouin zone (Zimina et al., 2014; Bencherif et al., 2011). Meanwhile the peak at around 725 cm\(^{-1}\) for \((12-2-12)\) and at 692 cm\(^{-1}\) in case of \((14-2-14)\), \((16-2-16)\) capped NPs have been imputed to the ground state energy of the polaron in PbTe nanoparticles (Trujillo et al., 2012; Huang and Qi, 2009). In the present system, the shift of some of the bands towards lower as well as high wavelength sides may be associated with the shape of dispersion of lattice phonon with a maximum wavelength at the zone centre, which decreases as the phonon vector moves towards the zone edges. Presently it is acclaimed that the confinement of phonons, optical as well as acoustic, influences the phonon spectra evidently when the grain size falls to nanometer size regime. Quantum confinement of optical phonon causes an asymmetry in the line shape and a shift towards the low frequency side compared to that for bulk lead telluride (Prabhu and Khadar, 2009). It is also proposed that the optical phonon line will also get broadened with the decrease in size. This broadening may also arise from the disorder present in lead telluride nanoparticles due to the quantum confinement effects (Fomin et al., 1998).
Figure 4.2.11: (a) Photoluminescence and (b) Raman spectra of (12-2-12), (14-2-14) and (16-2-16) capped lead telluride NPs.
4.2.9. Electrical conductivity

Electrical conductivity is an impressive factor conceding information about the transport phenomena. Recent works on electrical properties of semiconductor nanoparticles have paid considerable attention towards the conduction mechanism. The electrical conductivity of lead telluride NPs was carried out in the temperature range of 293-373 K. The consequence of electrical conductivity can be altered by adjusting the size of electrically conducting material as the particles size plays an imperative role in conductivity. Increased confinement causes a reduction in the overall available density of states leading to a decrease in electrical conductivity (Dirmyer et al., 2009; Dresselhaus et al., 2007). The synthesized lead telluride nanoparticles exhibit a linear current-voltage (I-V) curve that is symmetric about the origin (Figure 4.2.12a, b and c). The current increases linearly with voltage which implies that the conduction is ohmic. The resistance of lead telluride samples at different temperature was calculated from the slope of the I-V curve. Figure 4.2.12d, e and f shows temperature dependence of electrical resistivity for (12-2-12), (14-2-14) and (16-2-16) capped lead telluride nanoparticles, which varies for different lead telluride nanoparticle as (25.89 to 16.34 Ω cm), (22.05 to 14.55 Ω cm) and (12.01 to 8.06 Ω cm) respectively at different temperatures (293-373 K). On account of the resistance and size including length, width and thickness of the samples the electrical conductivities of lead telluride NPs have been measured to be 0.04-0.06 S cm\(^{-1}\), 0.05-0.07 S cm\(^{-1}\) and 0.08-0.12 S cm\(^{-1}\) for (12-2-12), (14-2-14) and (16-2-16) capped NPs respectively. The lead telluride nanoparticles have a good conductivity with the increasing temperature which displays the metal conductance (Kharlamov et al., 2013). The increase in conductivity of NPs with temperature is due to a decrease in grain boundary concentration (Kungumadevi and Sathyamoorthy, 2013). The curve obtained for the electrical conductivity in NPs is in excellent agreement with available experimental data (Wana et al., 2009; Tai et al., 2008). In our experiment, the observed values of conductivity at different temperature for gemini surfactants stabilized lead telluride nanoparticles have been found to be greater as compared to previous reported results (Wang et al., 2009). Strong dependence of electrical conductivity on size and shape parameters of NPs creates an opportunity for re-engineering of optical, electronic and thermal properties of this nanostructure through modification which leads to makes these nanoparticles a topic of ongoing interest.
Figure 4.2.12: I-V characteristics at different temperature (a), (b), (c) and (d), (e), (f) variation of resistivity with temperature for (12-2-12), (14-2-14) and (16-2-16) stabilized lead telluride NPs
4.3 Synthesis of (12-2-12) TTS capped Copper Telluride nanoparticles at 150°C for 8h.

4.3.1. X-ray analysis

Figure 4.3.1 represents the XRD pattern of Cu\(_{\text{2-x}}\)Te nanoparticles. All the reflection peaks of 2 theta at 26.6°, 36.4°, 43.3°, 50.5° and 74.2° can be indexed as (101), (202), (111), (200) and (220) planes of hexagonal copper telluride respectively, which is in good agreement with the reported data (Kumar and Singh, 2009). On the basis of Scherrer formula (Park et al., 2007), average particles size for CuTe nanoparticles has been calculated to be about 21 nm.

![XRD pattern of Cu\(_{\text{2-x}}\)Te nanoparticles](image)

Figure 4.3.1: XRD pattern of Cu\(_{\text{2-x}}\)Te nanoparticles.

The morphology of purified Cu\(_{\text{2-x}}\)Te product has been investigated by SEM as shown in Figure 4.3.2a and the chemical composition of the product was further affirmed by EDX, as revealed in Figure 4.3.2b. Figure 4.3.2c and d represents TEM images of copper telluride divulging particles size and the morphology of copper telluride. TEM images demonstrate that the product comprise of particles with an average size in the range of 15 ±6 nm, which is close to the particles size calculated from XRD. Copper telluride nanoparticles exhibited pearl necklace like arrangement in irregular fashion.
4.3.2. Possible reaction mechanism

The mechanism for formation of copper telluride nanoparticles, on the basis of above observations, can be proposed in same way as shown in reaction steps 4.12 and 4.17. Hydrazine combines with copper ions to form the metal amides, which effectively repress the formation of copper oxide. The copper amide reacts with active Te\(^2\) in solution to form the copper telluride nucleus (Dong et al., 2012).

Figure 4.3.2: (a) SEM image displaying network of spherical nanoparticles; (b) EDX spectrum of Cu\(_{(2-x)}\)Te nanoparticles; (c) and (d) TEM images at different magnifications of Cu\(_{(2-x)}\)Te nanospheres.
During the course of present work, we encountered lead telluride and copper telluride nanomaterials with smaller size distribution i.e. 20±5 nm and 15±6 nm respectively. The smaller sized chalcogenide nanoparticles may provide a guiding platform to brand semiconductor nanomaterials suitable for electronic, optical properties and countless innovative applications in the contemporary semiconductor industry.

4.3.3. Williamson-Hall Methods

Williamson-Hall analysis of copper telluride NPs data have also been carried out by assuming three main models i.e. Uniform deformation model (UDM), Uniform stress deformation model (USDM), and Uniform deformation energy density model (UDEDM). Williamson-Hall method varies with tan $\theta$ and does not follow $1/cos \theta$ dependency in the Scherrer equation. This major difference allows for separation of reflection broadening when both the microstructural causing small crystalline size and micro-strain transpire together (Zak et al., 2011). The strain induced in the powders due to crystal imperfection and distortion was calculated using the formula shown in equation 4.5.

The particle size & strain contribution to the line broadening are independent of each other and the observed line breadth is simply the sum of the two terms shown in equation 4.6.

Uniform Deformation Model (UDM), where it has been assumed that strain is uniform in all crystallographic directions, thus recognizing the isotropic nature of crystal, where all the material properties are independent of the direction along which they are measured (Prabhu et al., 2013). $\beta cos \theta$ was plotted with respect to $4sin\theta$, while strain and particles size have been calculated from the slope and y-
intercept of the fitted line respectively. The plots exhibited a negative strain for the nanoparticles which may be due to the lattice shrinkage that was observed in the calculation of the lattice parameters. The uniform deformation model analysis results for copper telluride are shown in Figure 4.3.3 (a). The different plot of Hall equation for copper telluride indicate positive and negative slope. Positive slope indicates the presence of tensile strain in lattice, negative slope attributed to the presence of compressive strain. The strain is manifestation of dislocation network, and the decrease of strain indicates a decrease in concentration of lattice imperfections.

For Uniform Stress Deformation Model (USDM) strain have been calculated from Hook’s law, retaining only the linear proportionality between stress and strain as given by $\sigma = \varepsilon E_{hkl}$, where $\sigma$ is the stress of the crystal and $E_{hkl}$ is the modulus of elasticity or young’s modulus. This equation is an approximation that is valid for a significantly small strain. Presuming the existence of a small strain in copper telluride nanoparticles, the Williamson-Hall equation has the form shown in equation 4.8.

Young’s Modulus, $E_{hkl}$ for copper telluride has been reported 115 GPa respectively (Vasilevskiy et al., 2012). Designated as USDM plots and drawn between $4\sin\theta/E_{hkl}$ and $\beta \cos\theta$ for copper telluride has been revealed in Figure 4.3.3 (b). The energy density of crystals was calculated from a model called Uniform Deformation Energy Density Model (UDEDM). The crystals have been assumed to retain homogenous and isotropic nature. The energy density $u$ (energy per unit volume) for elastic system that follows Hook’s law, the energy density can be calculated from $u = \varepsilon^2 E_{hkl}/2$. The plots of $\beta_{hkl} \cos\theta$ versus $4\sin\theta \ (2u/E_{hkl})^{1/2}$ have been constructed and the data fitted to lines. From the slope the anisotropic energy density $u$ was calculated and the average crystalline size $D$ from the y-intercept from the deformation stress and deformation energy density are related as $u = \sigma^2/2E_{hkl}$.

It may be noteworthy that both the above equation takes into account the anisotropic nature of elastic constant, so they are essentially different. The observation of the three interpretations for copper telluride nanoparticles is possible from the analysis of Figure 4.3.3.
Figure 4.3.3: W-H analysis of copper telluride NPs capped with (12-2-12) surfactant assuming UDM (a), USDM (b) and UDEDM (c). Fit to the data, the strain is extracted from the slope and the crystalline size is extracted from the y-intercept of the fit. For SSP (d) the particle size is obtained from the slope of the linear fitted data, and the root of the y-intercept gives the strain.

The scattering of the points away from the linear expression is much less in Figure 4.3.3c in contrast to Figure 4.3.3a and Figure 4.3.3b. The crystalline size estimated from the y-intercept of the graphs from Figure 4.3.3a, b and c is for copper telluride, crystalline size was found to be 11.8 nm (UDM and USDM) and it was 44 nm (UDEDM).

**Size-strain plot method**

Williamsons-Hall plot exhibited that line broadening was imperatively isotropic whereas owing to micro-strain contribution the diffracting domains were isotropic. Size–strain parameter may be attained from the “size-strain plot” (SSP). The data from the reflections at high level have less importance and data precision is usually
lower for the same. Under the preview of this estimation, it has been assumed that profile is illustrated by strain-contour via a Gaussian function and the crystalline size by Lorentzian function from equation 4.10 (Goncalves et al., 2012). Figure 4.3.3d demonstrates the construction of plots of \( d^2_{hkl} \beta_{hkl} \cos \theta \) versus \((d_{hkl} \beta_{hkl} \cos \theta)^2\) and the data fitted to lines. The particle size is calculated from the slope and the root of the y-intercept gives the strain.

The results obtained from Williamson-Hall method has been summarised in Table 4.3.1. It is important to note here that for Cu\(_{(2-x)}\)Te tensile strain appears to be dominated as calculated by UDM method. UD EDM procedure show occurrence of tensile strain only in both type of aforementioned nanoparticles.

<table>
<thead>
<tr>
<th>NP</th>
<th>Scherrer Method</th>
<th>Williamson-Hall Method</th>
<th>Size-Strain Plot</th>
<th>TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>UDM</td>
<td>USDM</td>
<td>UDEM</td>
</tr>
<tr>
<td>(12-2-12)</td>
<td>Cu(_{(2-x)})Te</td>
<td>21</td>
<td>9.5</td>
<td>-4.4</td>
</tr>
</tbody>
</table>

Where \(T=\) Tensile Strain and \(C=\) Compressive Strain

**4.3.4. Optical characterization**

The optical properties of copper telluride quantum dots were examined by UV-Vis absorption spectroscopy as shown in Figure 4.3.4a. Strong absorption peaks at 400 nm have been encountered for copper telluride nanoparticles. The optical band gap energy of nanoparticles was calculated using Tauc relation.
The optical band gap have been determined by extrapolating the straight portion of curve between \((\alpha hv)^2\) and \(hv\). The optical band gap of as-prepared copper telluride samples have been appraised as 3.4 eV from the UV-visible absorption spectrum, which is larger than the direct band gap (between 1.1 to 1.7 eV) of bulk (Li et al., 2013; Tai et al., 2008) clearly indicating quantum confinement. The quantum confinement may have been arising when size of particles was comparable to Bohr exciton radius. The higher band gap can be attributed to size effect of the present nanostructure. Consequently, the increase of band gap as compared to bulk can be understood on the basis of quantum size effect which may have been arising due to very small size of NPs (Figure 4.3.4b). The calculated band gap was plotted as a
function of the NP size and the band gap increases cogently with decreasing NPs size.

4.3.5. Electrical conductivity measurements
Copper telluride quantum dots also exhibit a linear Current- Voltage (I-V) curve (Figure 4.3.5a) that is almost symmetric about the origin, indicating that the contacts are ohmic. The resistance of the samples, as calculated from the slope of the I-V curve have been found about 1-4 Ω. Figure 4.3.5b displays the temperature dependence of electrical resistivity for Cu_{(2-x)}Te quantum dots, which varies from 0.09 to 0.45 ohm cm at different temperature (383 K- 473 K). Based on the resistance and size including length, width and thickness of the sample, the electrical conductivities of copper telluride have been measured to be 2.18-10.10 S cm⁻¹. The observed values of resistivity agree well with the reported values (Dong et al., 2012; Zhang et al., 2010). It may be interpreted that the particle size plays a crucial role in the conductivity and the semiconductor quantum dots possess better conductivity in comparison to their bulk equivalents. The quantum confinement effect arise when the size of the quantum dots fall below the Bohr exciton radius of the material and dominates over the grain boundary defects phenomena, hence resulting better conductivity (Wang and Herron, 1991; Saravanan et al., 2011).
Figure 4.3.5: (a) I-V characteristics and (b) variation of resistivity with temperature for copper telluride nanoparticles.

4.3.6. FTIR measurements

Figure 4.3.6 shows FTIR spectral studies of pure (12-2-12) surfactant as well as interactions of capping surfactant molecule with Cu_{(2-x)}Te nanoparticles at surfactant concentration of 1 mM. In the higher frequency region IR spectrum of pure (12-2-12) and copper telluride NPs show symmetric and asymmetric stretching vibrations of methylene in the alkyl chains at 2959 and 2858 cm\(^{-1}\), 2921 and 2854 cm\(^{-1}\), respectively. Scissoring mode of vibration at (\(\delta_{s}(C-H)\)) at 1469 cm\(^{-1}\), which shifts to 1454 cm\(^{-1}\) for Cu_{(2-x)}Te NPs and v(C-N\(^{+}\)) mode at 1056 cm\(^{-1}\) shift to 1020 cm\(^{-1}\) which can be used as an indicator of the higher energies of stretching vibrations corresponding to more gauche defects. Small vibrational frequency shifts have also been detected for TTS engineered nanoparticles, indicating a high
Results and discussion

2.5.2 Distribution of TTS on the nanoparticles (Bakshi et al., 2007; Naselli et al., 1985; Zhang et al., 2006).

Figure 4.3.6: FTIR spectra of (a) pure surfactants and (b) Cu$_{(2-x)}$Te NPs synthesized with (12-2-12) surfactants

4.4 Synthesis of (12-2-12), (14-2-14) and (16-2-16) TTS capped Copper Telluride nanoparticles at 150$^\circ$C for 32h.

4.4.1 X-ray analysis

The powder XRD pattern of as prepared copper telluride NPs prepared has been shown in Figure 4.4.1 with characteristic feature corresponding to (101), (202), (111), (200), (104) and (220) planes. All the peaks are very much prominent and refer to the hexagonal structure of a crystalline copper telluride. Powder XRD data are consistent with the published XRD data (Kumar and Singh, 2009). As expected, the peaks of copper telluride were considerably broadened with the decreased size of the nanoparticles, confirmed by TEM observations. The size of the nanoparticles were estimated using the Scherrer’s formula (Borah et al., 2008) based on full width at half-maximum (FWHM) of different diffraction peaks, with different values (Table 4.1.1).
Where $A$ is crystallite size, $\beta$ is the full width at half maximum of the diffraction peak, $\lambda$ (1.5418 Å) is the wavelength of X-ray radiation and $\theta$ is the angle of diffraction.

As shown in Figure 4.4.1 XRD peaks of different samples become progressively broader when the particle size decreases from (16-2-16) to (12-2-12) capped NPs. That is the full width at half-maximum (FWHM) of (12-2-12) stabilized copper telluride nanoparticles were much broader than those of (14-2-14) and (16-2-16) stabilized nanoparticles. From different theta values, the average particle size for copper telluride nanoparticles with (12-2-12), (14-2-14) and (16-2-16) surfactants has been calculated to be about 15.24 nm, 28.76 nm and 34.69 nm respectively. The XRD pattern illustrate that the pure copper telluride nanoparticles were obtained under present synthetic conditions.

![XRD pattern of Cu$_{(2-x)}$Te spherical nanoparticles capped with different Twin-tail surfactants.](image)

Figure 4.4.1: The XRD pattern of Cu$_{(2-x)}$Te spherical nanoparticles capped with different Twin-tail surfactants.
4.4.2. Transmission Electron Microscopy (TEM) analysis

In order to explore the influence of hydrocarbon chain length of gemini surfactants on shape and size of copper telluride NPs, the microstructure of copper telluride NPs was investigated by TEM. The spherical copper telluride NPs with (12-2-12), (14-2-14) and (16-2-16) at concentration 1mM, 0.5mM and 0.25mM respectively have been shown in Figure 4.4.2 with successive increase in hydrocarbon chain length from top to bottom. We do not observe any appreciable change in the morphology, but the size of copper telluride NPs dramatically increased with the increase in chain length (m=12 to 16). For (12-2-12), spherical particles of 25 ±10.8 nm in size have been encountered. As the hydrocarbon chain length approaches m=14 and 16 for (14-2-14) and (16-2-16), there is formation of large sized particles 45 ±18.7 nm and 130 ±31.6 nm respectively. This is suggestive of an increment in the average particle diameter with increasing tail length. Formation of some nanorods with (16-2-16) might be attributed to the long tails of surfactants and short spacers which paves the way to high solution viscosity at cautious surfactant concentration. This demeanour has been ascribed to the formation cross linked threadlike micelles out of the surfactants. The general trend is that, possibility for the formation of nanorods increases with the increase in TTS alkyl...
chain length and these long tails would have a preference to interact with each other via van der Waal interactions to form nanorod structures (shown by block arrows in Figure 4.4.2e) (Jain et al., 2014).

Figure 4.4.2: TEM images of Cu\textsubscript{(2-x)}Te NPs synthesized with (a) (12-2-12) (c) (14-2-14) and (e) (16-2-16) surfactants with insets showing image of single particle capped with bright surfactant layer. Histograms showing particle size distribution in (b), (d) and (f) for different surfactants respectively.
A comprehensive elaboration of the present work is underway by increasing the tail length further to get desired features. Figure 4.4.2b, d and f shows histograms of the nanoparticles that correspond to the TEM images. Three different insets in Figure 4.4.2a, c and e evidently are expressive of the presence of a bright monolayer indicating clear surfactant capping around each particle.

4.4.3. FTIR measurements

For substantiating the surface adsorption of the surfactants on copper telluride NPs surface, FTIR spectral studies of NPs samples and pure surfactants have been carried out. Figure 4.4.3a spectacles representative FTIR spectra of pure surfactants, that is, (12-2-12), (14-2-14) and (16-2-16) and with the copper telluride nanoparticles (Figure 4.4.3b). The peaks at higher frequency region of pure gemini surfactants, that is (12-2-12) show symmetric and asymmetric stretching vibrations of methylene in the alkyl chains at 2858, 2925 and 2959 cm\(^{-1}\), which shifts to 2851, 2921 and 2953 cm\(^{-1}\) in case of (12-2-12) capped copper telluride NPs. Symmetric and asymmetric stretching vibrations at 2854, 2922 and 2959 cm\(^{-1}\) shifts to 2919 and 2848 cm\(^{-1}\) in case of (14-2-14) and (16-2-16) capped NPs. Scissoring mode of vibrations (\(\delta(C-H)\)) at 1469 cm\(^{-1}\) for pure surfactants shifts to 1454, 1463 and 1463 cm\(^{-1}\) for (12-2-12) and (14-2-14) capped copper telluride NPs respectively. The peaks at 1160, 1056, 1042, 984, 974 and 972 cm\(^{-1}\) in case of pure surfactants can be assigned to the \(\nu(C-N^+)\) stretching modes. These peaks shifts to 1015, 840 cm\(^{-1}\) for (12-2-12), 1046, 833 cm\(^{-1}\) for (14-2-14) and 844 cm\(^{-1}\) for (16-2-16) capped copper telluride nanoparticles and may be an indicator of higher energies of stretching vibrations corresponding to more gauche defects. Small vibrational frequency shifts have also been detected for Gemini surfactant stabilized nanoparticles (Naselli, et al., 1985; Zhang et al., 2006). Peak assignment of different surfactants in the absence and presence of Cu\(_2(2-x)\)Te nanoparticles have been shown in table 4.4.2.

4.4.4. Possible reaction mechanism

The formation mechanism of Cu\(_2(2-x)\)Te nanoparticles, on the basis of above observations, can be proposed in the same way as shown in reaction equations 4.12-4.17 (section 4.3).
Figure 4.4.3: FTIR spectra of (a) pure surfactants and (b) Cu_{(2-x)}Te NPs synthesized with (12-2-12), (14-2-14) and (16-2-16) surfactants.
Table 4.4.2: Peak assignment of different gemini surfactants in the absence and presence of Cu(2$x$)Te nanoparticles.

<table>
<thead>
<tr>
<th>Peak assignment</th>
<th>(12-2-12)</th>
<th>(12-2-12)-Cu$_{2x}$Te</th>
<th>(14-2-14)</th>
<th>(14-2-14)-Cu$_{2x}$Te</th>
<th>(16-2-16)</th>
<th>(16-2-16)-Cu$_{2x}$Te</th>
</tr>
</thead>
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<tr>
<td>$\nu_{\text{asym}}$ (C-H)</td>
<td>2959</td>
<td>2953</td>
<td>2959</td>
<td>2919</td>
<td>2959</td>
<td>2919</td>
</tr>
<tr>
<td>$\nu_{\text{sym}}$ (C-H)</td>
<td>2925</td>
<td>2921</td>
<td>2922</td>
<td>---</td>
<td>2922</td>
<td>---</td>
</tr>
<tr>
<td>$\delta$ (C-H)</td>
<td>2858</td>
<td>2851</td>
<td>2854</td>
<td>2848</td>
<td>2854</td>
<td>2848</td>
</tr>
<tr>
<td>$\nu$ (C-N$^+$)</td>
<td>1469</td>
<td>1454</td>
<td>1469</td>
<td>1463</td>
<td>1469</td>
<td>1463</td>
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<td>1160</td>
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<tr>
<td></td>
<td>1042</td>
<td>---</td>
<td>1042</td>
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<td>1042</td>
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</tr>
</tbody>
</table>

### 4.4.5. Williamson-Hall Method

Williamson-Hall analysis of (12-2-12), (14-2-14) and (16-2-16) capped copper telluride nanoparticles have been carried out by assuming three main models i.e. Uniform deformation model (UDM), Uniform stress deformation model (USDM), and Uniform deformation energy density model (UDEDM). Williamson-Hall method varies with $\tan \theta$ and does not follow $1/\cos \theta$ dependency in the Scherrer equation. This basic difference was that both microstructural cause small crystallite size and microstrain occur together from the reflection broadening (Khorsand et al., 2011). Depending on different $\theta$ positions the separation of size and strain broadening analysis is done using Williamson and Hall. The strain induced in the powders due to crystal imperfection and distortion was calculated by using the formula shown in equation 4.5. The particle size & strain contribution to the line broadening are independent of each other and the observed line breadth is simply the sum of the two terms shown by equation 4.6.

The UDM, where the strain was assumed to be uniform in all crystallographic directions, thus considering the isotropic nature of the crystal, where all the material properties are independent of the direction along which they are measured. $\beta_{\cos \theta}$ was plotted with respect to $4\sin \theta$ for the peaks of copper telluride NPs with different twin-tail surfactants. Strain and particles size have been calculated from the slope and y-intercept of the fitted line respectively. The plots exhibited a negative strain for the nanoparticles which may be due to the lattice shrinkage that was observed in the calculation of the lattice parameters. The
uniform deformation model analysis results for copper telluride NPs with various surfactants are shown in Figure 4.4.4a, b and c.

![Image](85x796)

**Figure 4.4.4:** W-H analysis of copper telluride NPs capped with (a) (12-2-12), (b) (14-2-14) and (c) (16-2-16) surfactants assuming UDM. Fit to the data, the strain is extracted from the slope and the crystalline size is extracted from the y-intercept of the fit.

The different plot of Hall equation for copper telluride NPs indicate positive and negative slope. Positive slope indicates the presence of tensile strain in lattice, negative slope attributed to the presence of compressive strain. The strain is manifestation of dislocation network, and the decrease of strain indicates a decrease in concentration of lattice imperfections (Chrastina et al., 2012).

In Uniform Stress Deformation Model (USDM), a generalized Hook’s law refers to the strain, keeping only the linear proportionality between stress and strain as given by

\[ \sigma = \varepsilon E_{hkl} \]

where \( \sigma \) is the stress of the crystal and \( E_{hkl} \) is the modulus of elasticity or young’s modulus. This equation is an approximation that is valid for a significantly small strain. Presuming the existence of a small strain in copper telluride NPs by using Hook’s law (equation 4.8). Young’s Modulus, \( E_{hkl} \) for copper telluride has been reported 115 GPa (Fulari et al., 2010). The USDM plots were drawn with \( 4 \sin \theta / E_{hkl} \) corresponding to x-axis and \( \beta \cos \theta \) to y-axis for copper telluride NPs with different surfactants in Figure 4.4.5a, b and c. There is another
model that can be used to determine the energy density of a crystal called the uniform deformation energy density model (UDEDM). The crystals have been assumed to have a homogeneous and isotropic nature. The energy density \( u \) (energy per unit volume) for elastic system that follows Hook’s law, the energy density can be calculated from \( u = \varepsilon^2 E_{hkl}/2 \).

The uniform deformation energy density model (UDEDM) can be calculated from the slope of the line plotted between \( \beta_{hkl} \cos \theta \) versus \( 4\sin \theta \left( 2u/E_{hkl} \right)^{1/2} \). The anisotropic energy density ‘\( u' \) was calculated from the slope of these lines and crystalline size \( D \) from the y-intercept. The reflection of the three elucidations for copper telluride nanoparticles is possible from the analysis of Figure 4.4.6 because the scattering of the points away from the linear expression is much less in Figure 4.4.5 in contrast to Figure 4.4.4. The crystalline size estimated from the y-intercept of the graphs from Figure 4.4.4 and Figure 4.4.5 are 9.2 nm (UDM), 13 nm (USDM) and 51 nm (UDEDM) for (12-2-12) capped copper telluride NPs. For (14-2-14) capped NPs crystalline size is 11.9 nm (UDM), 12.8 nm (USDM) and 81 nm (UDEDM) While for (16-2-16) capped copper telluride NPs, crystalline size was found to be 90.5 nm (UDM), 85.5 nm (USDM) and 50.6 nm (UDEDM).

![Figure 4.4.5: W-H analysis of copper telluride NPs capped with (a) (12-2-12), (b) (14-2-14) and (c) (16-2-16) surfactants assuming USDM. Fit to the data, the strain is extracted from the slope and the crystalline size is extracted from the y-intercept of the fit.](image-url)
Figure 4.4.6: W-H analysis of copper telluride NPs capped with (a) (12-2-12), (b) (14-2-14) and (c) (16-2-16) surfactants assuming UDEDM. Fit to the data, the strain is extracted from the slope and the crystalline size is extracted from the y-intercept of the fit.

Size-Strain Plot Method

Imperatively isotropic character of the line broadening has been illustrated via Williamson-Hall plot, which indicates that the diffracting domains were isotropic and there was also a microstrain contribution. Size-strain parameter may be attained from the “size-strain plot” (SSP). The data from the reflections at high level have less importance and data precision is usually lower for the same. Under the preview of this estimation, it has been assumed that profile is illustrated by strain-contour via a Gaussian function and the crystalline size by Lorentzian function (equation 4.10) (Chrastina et al., 2012).

Figure 4.4.7 demonstrates the construction of plots of $d_{hkl}^2 \beta_{hkl} \cos \theta$ versus $(d_{hkl} \beta_{hkl} \cos \theta)^2$ and the data fitted to lines. The particle size is calculated from the slope and the root of the y-intercept gives the strain. The results obtained from Uniform deformation model (UDM), Uniform stress deformation model (USDM), Uniform deformation energy density model (UDEDM) and Size-strain plot method have been summarized in Table 4.1.2.
Figure 4.4.7: Size-strain plots of (a) (12-2-12), (b) (14-2-14) and (c) (16-2-16) capped copper telluride NPs. The particle size is obtained from the slope of the linear fitted data, and the root of the y-intercept gives the strain.

Table 4.4.3: Geometric parameters of (12-2-12), (14-2-14) and (16-2-16) capped copper telluride NPs

<table>
<thead>
<tr>
<th>NPs</th>
<th>Scherrer Method</th>
<th>Williamson-Hall Method</th>
<th>Size-Strain Plot</th>
<th>TEM</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Size, D (nm)</td>
<td>Size, D (nm)</td>
<td>UDM</td>
<td>UDM</td>
</tr>
<tr>
<td>(12-2-12)</td>
<td>15.24</td>
<td>9.2</td>
<td>13</td>
<td>1.76 \times 10^2</td>
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<tr>
<td>-Cu_{2-x}Te</td>
<td>-4.0 \times 10^{-3}</td>
<td>-2.318</td>
<td>209.80</td>
<td>51</td>
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<td></td>
<td></td>
<td></td>
<td>Stress, \sigma (MPa)</td>
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<tr>
<td>(14-2-14)</td>
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<td>11.9</td>
<td>12.8</td>
<td>1.66 \times 10^2</td>
</tr>
<tr>
<td>-Cu_{2-x}Te</td>
<td>9.5 \times 10^{-3}</td>
<td>1.2</td>
<td>-4.6896</td>
<td>50.38</td>
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<td></td>
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<td></td>
<td>Stress, \sigma (MPa)</td>
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<tr>
<td>(16-2-16)</td>
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<td>90.5</td>
<td>85.5</td>
<td>1.55 \times 10^2</td>
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<tr>
<td>-Cu_{2-x}Te</td>
<td>3.8x10^{-3}</td>
<td>4.450 -0.0017</td>
<td>511.7</td>
<td>9.69</td>
</tr>
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<td></td>
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<td>Strain, \varepsilon (Tensile Only)</td>
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<td>Stress, \sigma (MPa)</td>
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<td>Energy Density, u (KJm^{-3})</td>
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<td>Size, D (nm)</td>
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<td>Strain, \varepsilon (Tensile Only)</td>
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<td></td>
<td>Stress, \sigma (MPa)</td>
<td>130</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Energy Density, u (KJm^{-3})</td>
<td>±17.02</td>
</tr>
</tbody>
</table>

Where T=Tensile Strain and C=Compressive Strain
4.4.6. Raman spectroscopy

Raman spectroscopy embroils the study of vibrational-rotational energy changes in molecules by means of scattering of light. Energy from the laser is exchanged with the molecules in such a way that the scattered light photons have a higher or lower energy than the incident photon. The distinction in energy is due to a shift in the rotational and vibrational energy of the molecules and gives information about the molecular energy levels. Raman spectra have been an important method for the determination of molecular structure, for locating functional groups in molecules or various chemical bonds and for the quantitative analysis of complex mixtures. In Raman scattering (Figure 4.4.8) each line has a characteristic polarization, which contribute the additional information about molecular structure (Clark and Dines, 1986). The crests at 142.85 and 217.19 cm\(^{-1}\) are due to the translational and torsional motions of the molecules in lattice vibrations. The lattice vibrational modes of copper telluride nanoparticles have been obtained at room temperature by Raman spectra. (Dhasade et al., 2012; Park et al., 2011) Peaks at 413 and 521 cm\(^{-1}\) in copper telluride nanoparticles are due to metal-surfactant vibrations and presumably due to first overtone of the strongest band in the spectrum respectively. (Minceva-Sukarovaa et al., 1997; Khare et al., 2011) Due to the quantum confinement effects in nanoparticles the peaks at 142.85, 217.19, 413 and 521 cm\(^{-1}\) broadens with decreasing particle size for (16-2-16), (14-2-14) and (12-2-12) stabilized copper telluride nanoparticles respectively. The overall change in Raman spectra with particle size due to all of these effects is shown in Figure 4.4.8 there is also a decent level of agreement with the peak width when strain is considered. Agreement is good, but less perfect, when the effects of confinement and defects are included. Overall, it is grasped that strain also plays the most significant role. Together, strain and confinement can account for much of the broad and asymmetric character of the observed peaks. (Tanaka et al., 1992; Weber et al., 1993) Comparison of Raman spectra suggest that the band intensities relatively decrease as the particle size decreases. The results well agrees with the available literature.
4.4.7. Optical Characterization

The absorption spectra of copper telluride nanoparticles capped with different TTS (12-2-12, 14-2-14 and 16-2-16) have been shown in Figure 4.4.9a, absorption peak will be comparatively bluer shifted and it will be strong for reduced particle size (Figure 4.4.10). To examine the quantum confined effect of the synthesized nanoparticles, UV-Vis absorption spectra were employed. The crests in the UV absorption are indicative of the band gap of the copper telluride nanoparticles. The optical band gap energy of nanoparticles was calculated using the Tauc relation (Tauc et al., 1996).

The optical band gap have been determined by extrapolating the straight portion of curve between \((ahv)^2\) and \(hv\). The optical band gap values of as prepared (12-2-12), (14-2-14) and (16-2-16) capped copper telluride NPs have been evaluated as 3.42 eV, 3.40 eV and 3.37 eV respectively (Figure 4.4.9b). It has been found that evaluated band gap values are larger than the direct band gap of bulk copper telluride (1.1 to 1.7 eV) precisely illustrating quantum confinement. Quantum confinement can be observed once the diameter of a material is of the same
magnitude as the de Broglie wavelength of the electron wave function. When materials are such small, their electronic and optical properties deviate substantially from those of bulk materials. As the confining dimension decreases and reaches a certain limit, typically at nanoscale, the energy spectrum becomes discrete. As a result, the bandgap becomes size-dependent. This ultimately results in a blue shift as the size of the particles decreases as observed in our present studies. Both, absorption and PL spectra shown in Figure 4.4.10 and 4.4.11 exhibit a “quantum size effect”. The excitonic peak position in absorption, shifts little towards higher wavelength when the particle size increases for (12-2-12), (14-2-14) and (16-2-16) stabilized nanoparticles. In the meantime, PL peak also shifts positions at 335.10, 337.12 and 338.22 nm for (12-2-12), (14-2-14) and (16-2-16) stabilized nanoparticles which shows characteristics property of quantum confinement.
Figure 4.4.9: (a) UV-vis spectrum of (12-2-12), (14-2-14) and (16-2-16) capped copper telluride NPs. (b) Tauc plots for copper telluride NPs, dotted lines representing extrapolation for band gap.
Figure 4.4.10: Plots of the wavelength and intensity versus \((12-2-12), (14-2-14)\) and \((16-2-16)\) surfactants capped copper telluride NPs.

### 4.4.8. Photoluminescence

The room temperature photoluminescence (PL) spectra of copper telluride nanoparticles were measured at an excitation wavelength of 290 nm. Usually for semiconductor nanoparticles, two emission peaks can be observed—the exciton luminescence and trapped luminescence (Fasoli et al., 2011). Figure 4.4.11 shows broad PL emission spectra of \((12-2-12), (14-2-14)\) and \((16-2-16)\) stabilized copper telluride NPs have emission peaks at around 335.10, 337.12 and 338.22 nm respectively which attributed to the blue emission and is the evidence of quantum confinement effect, with the decreasing nanoparticle size. Another emission peak at around 652.54 nm observed in all copper telluride samples may be attributed to the green emission in the visible region. The green emission peak at around 652.54 nm is defect related emission peak and is generated from deep-level or trap state emission (Kumar et al., 2013). The broadening of PL emission peaks are observed as the diameter of nanoparticles decreases for \((16-2-16), (14-2-14)\) and \((12-2-12)\), capped NPs respectively. The PL emission in nanoparticles is strongly affected by strain, which results shifting and broadening of the PL peaks. This broadening of PL peak can be accredited to strain in the nanoparticles caused by size induced quantization effect. The broadening of PL band may also be caused by the
broadening of the band edges due to variations generated by the high concentration of defects or impurities. The defects or strain/stress are introduced due to confinement effects at nanoscale regime. (Martijn, 2012) It has been shown that the copper telluride NPs grown by hydrothermal method exhibit broad emission PL spectrum at 335.10, 337.12 and 338.22 nm for different nanoparticles.

![Photoluminescence spectra copper telluride nanoparticles capped with (12-2-12), (14-2-14) and (16-2-16) surfactants.](image)

**Figure 4.4.11: Photoluminescence spectra copper telluride nanoparticles capped with (12-2-12), (14-2-14) and (16-2-16) surfactants.**

### 4.4.9. Electrical Conductivity

To probe gemini surfactant capped copper telluride nanoparticles further, the samples were subjected to electrical conductivity measurements. Electrical conductivity is emphatic factor unveiling information about the transport phenomena. Recent works on electrical properties of semiconductor nanoparticles have paid considerable attention towards the conduction mechanism. The electrical conductivity of copper telluride NPs was carried out in the temperature range of 293-373 K. The consequence of electrical conductivity can be altered by adjusting the size of electrically conducting material as the particles size plays an imperative role in conductivity. Increased confinement causes a reduction in the overall available density of states leading to a decrease in electrical conductivity (Dirmyer
The synthesized copper telluride nanoparticles exhibit a linear current-voltage (I-V) curve that is symmetric about the origin (Figure 4.4.11a, b, c). The current increases linearly with voltage which implies that the conduction is ohmic. The resistance of copper telluride samples at different temperature was calculated from the slope of the I-V curve. Figure 4.4.11d, e and f. shows temperature dependence of electrical resistivity for (12-2-12), (14-2-14) and (16-2-16) capped copper telluride nanoparticles, which varies for different copper telluride nanoparticle as (78.31 to 11.49 Ω cm), (105.18 to 21.34 Ω cm) and (44.04 to 21.43 Ω cm) respectively at different temperatures (293-373 K). On account of the resistance and size including length, width and thickness of the samples the electrical conductivities of copper telluride NPs have been measured to be 0.012-0.170 S cm⁻¹, 0.018-0.055 S cm⁻¹ and 0.023-0.053 S cm⁻¹ for (12-2-12), (14-2-14) and (16-2-16) capped NPs respectively. The copper telluride nanoparticles have a good conductivity with the increasing temperature which displays the metal conductance. The increase in conductivity of NPs with temperature is due to a decrease in grain boundary concentration. The curve obtained for the electrical conductivity in NPs is in excellent agreement with available experimental data (Yi, 2008; Mansour et al., 1994). The impact of grain boundaries in the nanoparticles to the electrical conductivities has also been reported by Zhao et al. (2009). Unfortunately, since there are no standard values available about the electrical conductivity of Cu_{(2-x)}Te nanoparticles in literature, we can only compare with present experimental results after repeated experiments. Wang et al. (2012) reported increase in electrical conductivity with rise in temperature for different structures (nanoparticles, nanosheets and nanobelts). The electrical conductivity of nanosheets was less than the nanobelts and nanoparticles were reported as least conductive. The observations can also be compared with the studies carried out by Dong et al. (2012), calculated electrical conductivity of the Cu_{(2-x)}Te nanowires at room temperature were 5.99 x 10³Ω⁻¹m⁻¹. The resistivity values by Yang et al. (2013) for Cu_{(2-x)}Te films prepared by oxidation and reduction methods, have been reported as 1.78 and 11.78 Ω cm, before and after complete reduction. In our experiment, the observed values of conductivity at room temperature for different gemini surfactants stabilized copper telluride nanoparticles have been found to be greater as compared to previous reported results (Pathan et al., 2003). In addition,
the rich behaviour introduced by conductivity in copper telluride nanoparticles makes these materials a topic of ongoing interest.

Figure 4.4.12: I-V characteristics at different temperature (a), (b), (c) and (d), (e), (f) variation of resistivity with temperature for (12-2-12), (14-2-14) and (16-2-16) stabilized copper telluride NPs.