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Research Article

Synthesis, Structural and Optical Properties of TOPO and HDA Capped Cadmium Sulphide Nanocrystals, and the Effect of Capping Ligand Concentration

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The thermal decomposition of bis(*N,N*-diallyldithiocarbamato)Cd(II) in a "one-pot" synthesis in tri-n-octylphosphine oxide (TOPO) and hexadecylamine (HDA) afforded CdS (TOPO-CdS and HDA-CdS) of varying optical properties and morphologies. The influence of the ratio of the precursor concentration to the capping molecule, as a factor affecting the morphology and size of the nanoparticles, was investigated. The particles varied in shape from spheres to rods and show quantum size effects in their optical spectra with clear differences in the photoluminescence (PL) spectra. The PL spectrum of the HDA capped CdS nanoparticles has an emission maximum centred at 468, 472, and 484 nm for the precursor to HDA concentration ratio of 1 : 10, 1 : 15, and 1 : 20, respectively, while the TOPO capped nanoparticles show emission peaks at 483, 494, and 498 nm at the same concentration ratio. Powdered X-ray diffraction (p-XRD) shows the nanoparticles to be hexagonal. The crystallinity of the nanoparticles was evident from high resolution transmission electron microscopy (HRTEM) which gave well-defined images of particles with clear lattice fringes.

1. Introduction

Cadmium sulphide is an interesting direct semiconductor with high photosensitivity [1], which makes it an excellent n-type window material in heterojunction solar cells [2]. Since the properties and efficiency of materials are enhanced when employed in their nanocrystalline forms, research interest has grown immensely in areas of obtaining CdS in their nanoparticulate sizes. Many attempts have been made to prepare the materials in different morphologies and structures, such as nanospheres, nanorods, and nanowires [3, 4].

One of the recent trends in nanomaterials research is the control of particle shape, by manipulating the precursor concentration, temperature of reaction, and capping environment, which are factors that affect the morphology and size of the nanoparticles. The shapes of semiconductor nanocrystals have significant effect on their electronic, magnetic, catalytic, and electrical properties [5, 6]. For example, rod- or wire-shaped semiconductor nanocrystals possess clearly different optical properties in comparison to their dot-shaped analogues [7]. Cadmium sulphide is one of the materials of considerable interest in shape control due to its wide variation in 1D morphology with changes in reaction conditions during synthesis [8].

Solvothermal route has emerged as a powerful method for the preparation of high quality nanomaterials with special optical and structural properties. The elevated temperature during the reactions enhances the ligand solubility and the reactivity of the reactants. This method offers ideal means for

modulating the physical properties of nanoparticles through the control of the formation and growth of the synthesized nanoparticles [9–12]. The controlled growth of nanocrystals in solution is carried out in the presence of a capping molecule, which passivates the "bare" surface atoms with protecting groups. The capping or passivating of particles protects the particle from its surrounding environment and provides electronic stabilization to the surface [13]. However, the choice of the capping molecules is important in the synthesis of semiconductor nanoparticles. It is important that the bonding between the capping molecules and the precursors is neither too weak nor too strong. Particle growth is fast and bigger crystallites are formed when the bonding between capping molecule and nanocrystal is too weak. On the other hand, if the binding is too strong, the growth of the nanoparticles is hindered. During the nanoparticle formation, the rate at which the capping molecules attach and deattach to the surface influences the growth rate and, therefore, the final size of the particles. Thus, the properties of the capping group could be used to influence size of the nanoparticles through the dynamics of attaching and deattaching. Synthesis conditions such as temperature, the concentration of the reactants, and the capping molecule are also significant [14]. In order to control the growth, it is necessary to change the surface energies indirectly by adjusting the types and ratios of organic surfactants.

Trioctylphosphine oxide (TOPO) and hexadecylamine (HDA) have been utilised as capping molecules in the synthesis of cadmium chalcogenide nanoparticles [15, 16]. As an amine, HDA can act as a ligand and coordinates to the metal ions [17–20]. It, thus, limits the crystal growth and provides the stability of the structure in solution [21]. Similarly, the stability of TOPO capped CdS particles is due to the high affinity of TOPO for the Cd^{2+} ions. The bulky nature of TOPO provides increased steric hindrance. Bulky surfactant coating on the surface of nanocrystals reduces the rate at which atoms are added to the growing crystal. The longer the chain of the capping molecule is, the lower the diffusion coefficient would be for the [Cd-capping ligand] complex [22].

In this work, bis(*N,N*-diallyldithiocarbamato)Cd(II) complex was used as a precursor for the synthesis of CdS nanoparticles. The precursor was thermolysed in HDA and TOPO, using an established procedure for the preparation of nanoparticles. Furthermore, the influence of the ratio of the precursor concentration to capping molecule, as a factor affecting the morphology and properties of the nanoparticles, was investigated.

2. Experimental

2.1. Materials. Diallyl amine, trioctylphosphine (TOP), trioctylphosphine oxide (TOPO), and hexadecylamine (HDA) were purchased from Sigma-Aldrich chemical Co. Carbon disulphide and sodium hydroxide pellets were purchased from Merck chemical Co. The solvents, chloroform, toluene, methanol, and ethanol were received from ACE. All chemicals were used as received without further purification.

2.2. Physical Measurements. Infrared spectra were recorded on a Bruker alpha-P FT-IR spectrophotometer directly on small samples of the compounds in the 500–4000 cm^{-1} range. The NMR spectra were recorded on a 600 MHz Bruker Avance III NMR spectrometer. The crystalline phase of the nanoparticles was identified by X-ray diffraction (XRD), employing a scanning rate of 0.0018° min^{-1} from 20° to 80°, using a Röntgen PW3040/60 X'Pert Pro XRD diffractometer equipped with nickel filtered Cu Ka radiation (k = 1.5418 Å) at room temperature. The morphology of the nanoparticles was characterized by a TECNAI G2 (ACI) TEM with an accelerating voltage of 200 kV. A PerkinElmer Lambda 20 UV-Vis spectrophotometer was used to carry out the optical measurements. The samples were placed in silica cuvettes (1 cm path length), using toluene as a reference solvent. A Jobin Yvon-spex-Fluorolog-3 Spectrofluorometer with a xenon lamp (150 W) was used to measure the photoluminescence of the particles.

2.3. Synthesis of the Precursor Compound, Bis(N,N-diallyldithiocarbamato)Cd(II) Complex. A 20 mL ethanol solution of $CdCl_2{\cdot}2H_2O$ (1.10 g, 0.005 mol) was added to a 20 mL ethanol solution of sodium *N,N*-diallyl-dithiocarbamate (1.96 g, 0.010 mol). Solid precipitates formed immediately, and the mixture was stirred for approximately 45 min, filtered, and rinsed several times with distilled water. Crystals suitable for single crystal X-ray analysis were obtained from recrystallisation in chloroform/ethanol. Yield: 1.28 g (56%), M.p. 133–135°C. Selected IR, ν (cm^{-1}): 1461 (C=N), 1173 (C_2–N), 918 (C=S), 2976 (allylic C–H).

Anal. Calc. for $C_{14}H_{20}N_2S_4Cd$ (456.98): C, 36.79; H, 4.41 N, 6.13; S, 28.06.

Found: C, 36.38; H, 4.40; N, 6.50; S, 28.42%.

^{1}H-NMR (δ ppm, J Hz, DMSO-d_6): 4.43 (d, $J_{\alpha\beta}$ = 5.8, 8H, $CH_{2,\gamma}$=CH_β–$C\underline{H}_{2,\alpha}$), 5.22 (bd, $J_{\text{trans},\beta\gamma}$ = 16.2, 4H, $C\underline{H}_{2,\gamma}$=$CH_\beta$–$CH_{2,\alpha}$), H_γ-trans, 5.23 (bd, 4H, $J_{\text{cis},\beta\gamma}$ = 10.7, $C\underline{H}_{2,\gamma}$=$CH_\beta$–$CH_{2,\alpha}$), H_γ-cis, 5.89 (ddt, 4H, $J_{\text{trans},\beta\gamma}$ = 16.2, $J_{\text{cis},\beta\gamma}$ = 10.7, $J_{\alpha\beta}$ = 5.8, $CH_{2,\gamma}$=$C\underline{H}_\beta$–$CH_{2,\alpha}$).

^{13}C-NMR (δ ppm, DMSO-d_6): 56.84 ($CH_{2,\gamma}$=CH_β–$\underline{C}H_{2,\alpha}$), 118.25 ($\underline{C}H_{2,\gamma}$=$CH_\beta$–$CH_{2,\alpha}$), 131.69 ($CH_{2,\gamma}$=$\underline{C}H_\beta$–$CH_{2,\alpha}$), 206.92 (N$\underline{C}$S).

2.4. Synthesis of TOPO Capped CdS Nanoparticles, TOPO-CdS. Synthetic methods are similar to the ones reported previously [23]. The cadmium complex (0.3 g) was dissolved in TOP (6.0 mL) and the resultant solution was injected into TOPO (3.0 g) in a three-neck flask at 250°C. The solution turned to a yellowish colour and a drop in temperature was observed. The yellowish solution was allowed to stabilize at 250°C for 1 h. An excess of methanol was added which led to the formation of flocculants. The precipitate was separated by centrifugation and redispersed in toluene for characterization. The same experiment was repeated using 4.5 g and 6.0 g of TOPO, while maintaining all other conditions and concentration of the precursor complex.

2.5. Synthesis of HDA Capped CdS Nanoparticles, HDA-CdS. In a method similar to the above, the cadmium complex (0.3 g) was dissolved in TOP (6 mL) and injected into hot HDA (3.0 g) at 250°C. The temperature of the reaction mixture was found to drop by 25–30°C. The temperature of the solution was slowly increased and allowed to stabilize at 250°C for 1 h. The yellowish solution was cooled to approximately 70°C, and excess methanol was added which led to the formation of flocculants. The solution was centrifuged and the separated precipitate was redispersed in toluene for characterisation. The same experiment was repeated using 4.5 g and 6.0 g of HDA, while maintaining all other conditions and concentration of the precursor complex.

3. Results and Discussion

3.1. Spectroscopic Characterization of the Precursor (FTIR and NMR). The complex is diamagnetic and white in colour. The infrared spectra of the complex were assigned based on standards already established for dithiocarbamate-metal complexes [24–26]. The compounds showed peaks in the region 1445–1460 cm^{-1}. Bands in this region are characteristic of dithiocarbamate compounds and are ascribed to the vibrational frequency due to the thioureide, ν(CN). The positions of these peaks suggest a considerable double bond character in the C···N bond vibration. An increase in vibrational frequency of about 15 cm^{-1} was observed upon complexation which could be due to the movement of the electron cloud of the –NCSS group after coordination to the metal center [27]. The result is a stronger metal-sulphur (M–S) bond and more stable chelates [28]. The band present in the 930 cm^{-1} range is attributed to the prevailing contribution of C···S. Vibrations in these ranges have been used effectively in differentiating between the bonding formats of the dithiocarbamate ligand to the metal ion. The presence of only one strong band indicates symmetrical bidentate coordination of the dithio ligand, whereas a doublet is expected in the case of unsymmetrical monodentate coordination [28]. Medium to low bands at 2962–2973 cm^{-1} are attributed to the asymmetric ν(allylic)C–H cm^{-1} stretching vibration, while bands at 3054–3075 cm^{-1} are due to ν(allylic)=C–H. The single medium peak which appears around 1636 cm^{-1} is attributed to the ν(C=C) band.

The ^{1}H-NMR spectra of the complex show correct proton peaks and multiplicities for the allyl ligand. The peaks were assigned based on similar ligands [29, 30], and the coordination of the ligand to the metal can be assumed by the general chemical shift differences of the allylic protons as compared to the free ligands [31]. The peaks in the range 4.43–5.25 ppm are ascribed to the allylic protons, while the peaks in the range 5.82–5.95 ppm are characteristic of the vinylic protons. These peaks indicate the presence of the coordinated allyldithiocarbamate ligand. The ^{13}C-NMR spectrum shows three different peaks for the allyldithiocarbamate at 57.10, 131.55, and 118.32. These signals are due to the carbons of the α-CH_2, β-CH_2, and γ-CH_2 allyl group. The fourth signal at 206.95 is assigned to the CS_2 carbon. The observed peaks are in good agreement with the given structure.

3.2. Synthesis of TOPO or HDA Capped CdS Nanoparticles. The sudden introduction of the precursor complex into a hot solvent (TOPO or HDA) and the subsequent immediate supersaturation resulted in the formation of CdS nuclei. The drop in temperature upon the injection of room temperature complex-TOP solution prevented further nucleation, and further increase in temperature resulted in growth of particles by Ostwald ripening [32]. The use of long-chain compounds containing a donor atom (P or N) was found to be ideal. They coordinate to the surface of the CdS nanoparticles, providing physical and electronic passivation. The labile nature of the surfactants allows desorption from the particle surface, to allow growth, yet coordinating strongly enough to allow particle isolation and provide the required protection for the nanoparticle.

3.3. Morphology of the TOPO and HDA Capped CdS Nanoparticles. Figure 1 shows the TEM images of HDA capped CdS nanoparticles synthesized from the precursor complex at different concentrations of HDA (a) 3.0, (b) 4.5, and (c) 6.0 g at 250°C. The images showed some irregular polygons at all concentrations. However, as the concentration of the capping molecule increased, a slight increase in the average diameter of the CdS nanoparticles occurred. The average size of the HDA capped CdS nanoparticles was 3.8 ± 0.90, 4.2 ± 1.12, and 5.5 ± 1.32 nm, at the concentration ratio of 0.1, 0.07, and 0.05, respectively. It has been reported that, at lower capping molecule concentrations, the cation-capping molecule complex favours faster particle growth. At higher capping molecule concentration the reaction is slower yielding well passivated and more dispersed particles [14]. However, in this case, the increase in particle size with increase in the concentration of HDA may be related to the steric properties of the ligand which affects the surface ligand coverage on the of CdS nanoparticles. Increase in the concentration of the ligand results in the enhancement of the steric effect. Thus, the lower precursor to capping group ratio tends to promote growth of the nanoparticles. When the capping molecule was changed to TOPO, at the highest concentration, particles with an average diameter of 4.0 were observed (Figure 2(a)). A reduction of the precursor concentration results in an evolution of shape; particles were slightly elongated forming rod-shaped nanoparticles with an average length and diameter of 4.8 ± 0.5 and 2.8 ± 0.4 nm, respectively (Figure 2(c)). Shape transformation of particles is controlled by various factors such as the nature of precursor molecule, reaction temperature, and concentration. In this case, increase in the TOPO concentration facilitates wurtzite growth of CdS along the c-axis, thus generating the nanorods, and the anisotropic particle growth could be due to oriented attachment [33].

3.4. Optical Properties of the TOPO and HDA Capped CdS Nanoparticles. The optical absorption spectra of the CdS nanoparticles are shown in Figures 3(a) and 3(b), respectively. The absorption spectra of the HDA capped particles, at all concentrations, show a sharp band edge which is blue-shifted from the bulk band edge of 515 nm. The absorption

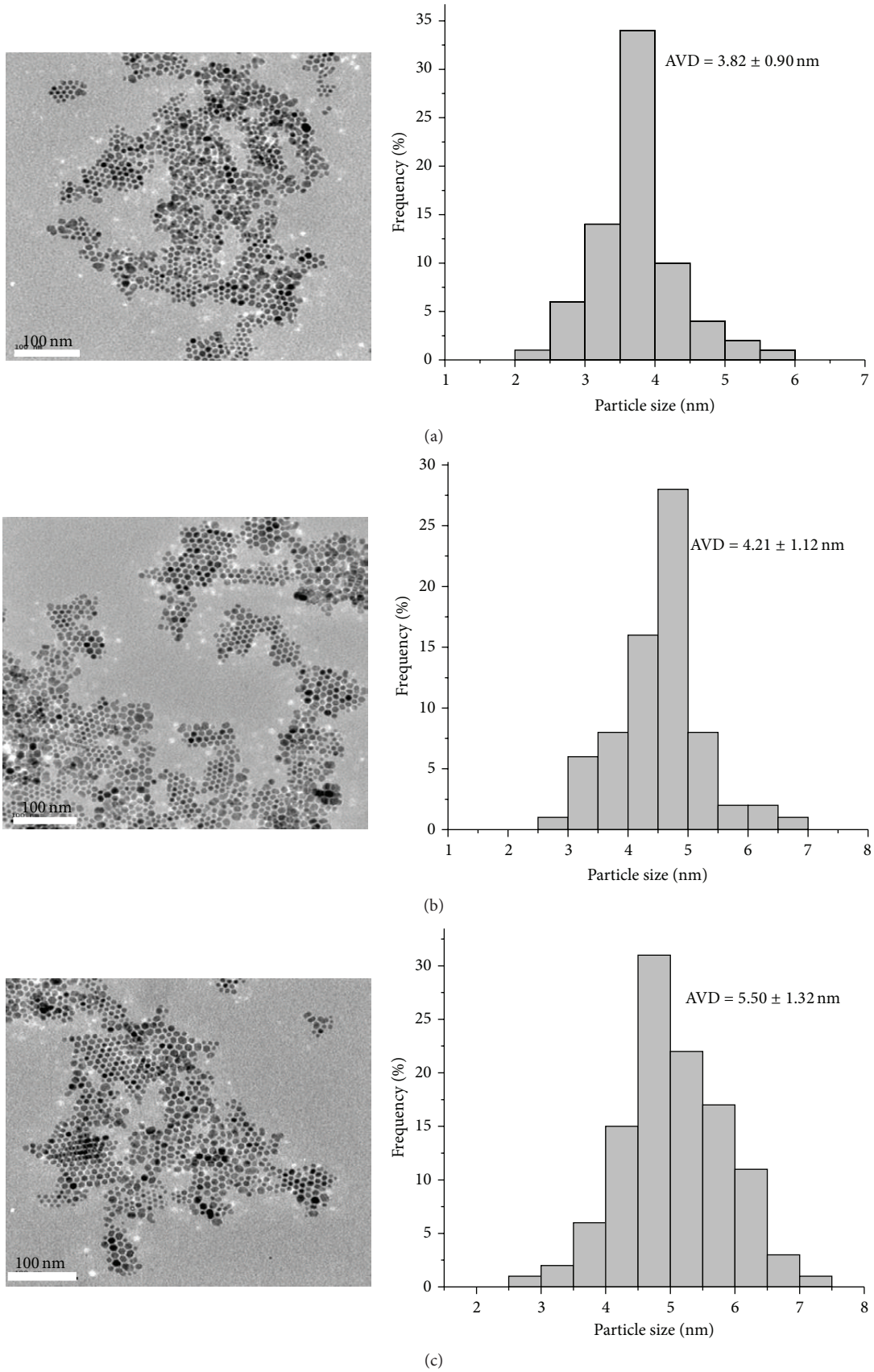


Figure 1: TEM images of CdS nanoparticles prepared with 0.3 g of the complex with (a) 3.0 g, (b) 4.5 g, and (c) 6.0 g of HDA at 250°C for 1 h.

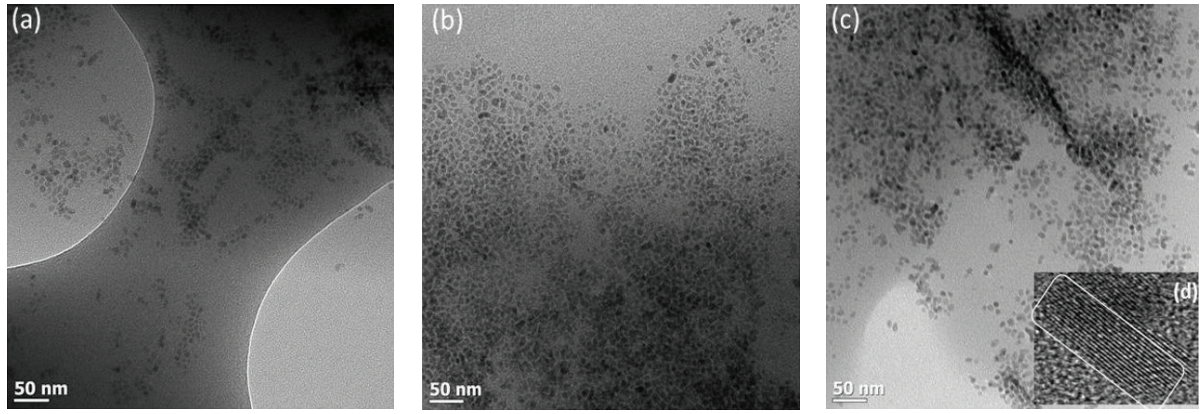


Figure 2: TEM images of CdS nanoparticles prepared with 0.3 g of the complex with (a) 3.0 g, (b) 4.5 g, and (c) 6.0 g of TOPO at 250°C for 1 h. Inset (d) shows a single rod-shaped particle with distinct lattice fringes.

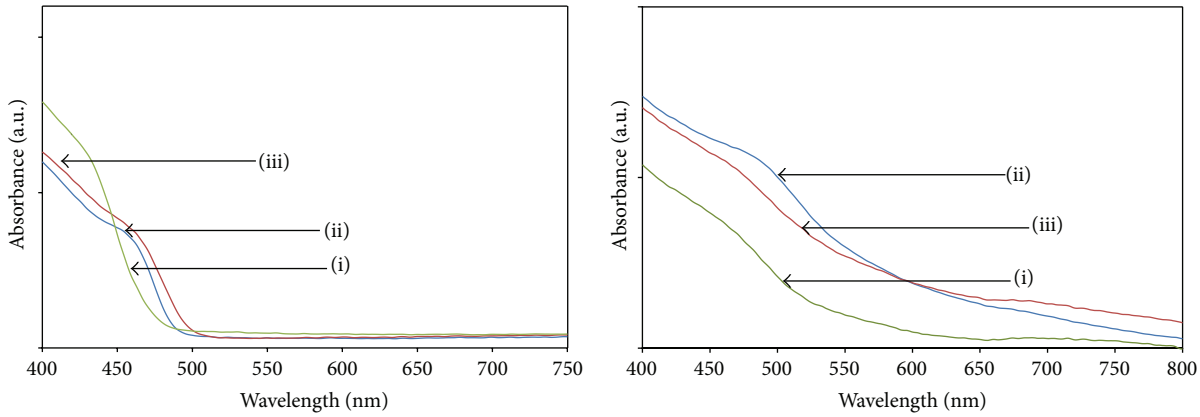


Figure 3: (a) Absorption spectra of CdS NPs prepared using 0.3 g of the complex and (i) 3.0 g, (ii) 4.5 g, and (iii) 6.0 g of HDA at 250°C for 1 h; and (b) absorption spectra of CdS NPs prepared using 0.3 g of the complex and (i) 3.0 g, (ii) 4.5 g, and (iii) 6.0 g of TOPO at 250°C for 1 h.

spectra of the TOPO capped particles exhibit a broad band edge which are only slightly blue-shifted in relation to the bulk. Nanoparticles usually show a characteristic blue shift in their optical spectra due to quantum confinement. However, it has been reported that size is not the only property which influences the band gap because shape also plays an important role. The band gap of elongated particles depends on both their width and length although it is more sensitive to their width [34]. In the case of the TOPO capped particles, due to the anisotropic morphology, both the length and the width of the particles contribute to the resultant band edge. It is also noticed that the sharp excitonic feature that is visible in the spectra of the HDA capped CdS nanoparticles is less evident in the TOPO capped nanoparticles.

Figures 4(a) and 4(b) show the room temperature luminescence spectra of the HDA and TOPO capped CdS nanoparticles, respectively. The CdS nanoparticles show only band edge emission and the emission maximum appears at about 468, 472, and 484 nm for the precursor to HDA concentration ratio of 1 : 10, 1 : 15, and 1 : 20, respectively. Similarly, the TOPO capped nanoparticles show emission peaks at 483, 494, and 498 nm at the same concentration ratio. The origin of these emissions might be from the recombination of electrons trapped in the sulphur vacancy with the holes in the valence band of CdS, as previously reported [35]. In all cases, the emission peaks of the samples have identical narrow shape, which indicates monodispersed particles that are well passivated. The increase in the emission peak as the concentration of the capping molecule decreases indicates size increment.

3.5. XRD of the TOPO and HDA Capped CdS Nanoparticles. CdS shows dimorphism of cubic form (zinc-blend type) and hexagonal form (wurtzite type) [36]. In the bulk form, CdS usually exist in the hexagonal phase. In the nanoparticle form, it can exist as either cubic or hexagonal phase [37]. While only the wurtzite type is found at relatively high temperatures, the cubic and the hexagonal form can occur at relatively low temperatures. The existence of a mixture of cubic and hexagonal phase with the predominance of one over the other is also a possibility [38]. Figure 5 shows the X-ray diffraction (XRD) patterns of the synthesised CdS nanoparticles. The

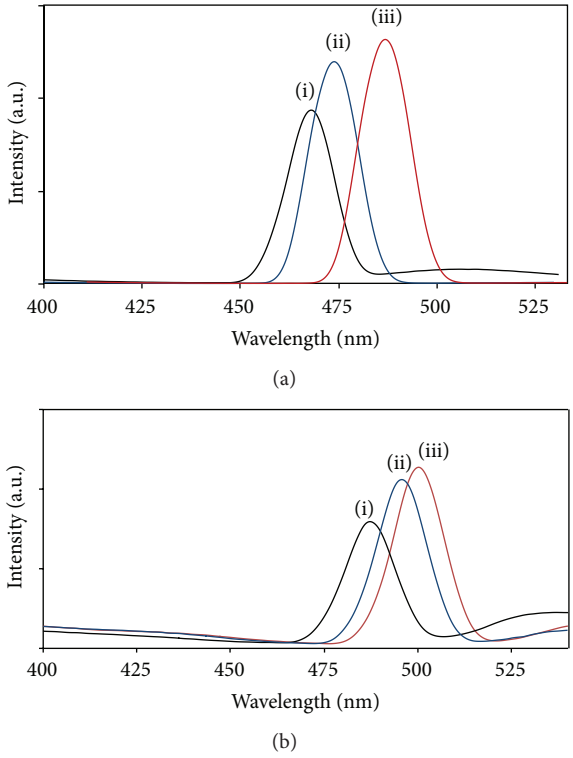


Figure 4: (a) Photoluminescence spectra of CdS NPs prepared using 0.3 g of the complex and (i) 3.0 g, (ii) 4.5 g, and (iii) 6.0 g of HDA at 250°C for 1 h; and (b) photoluminescence spectra of CdS NPs prepared using 0.3 g of the complex and (i) 3.0 g, (ii) 4.5 g, and (iii) 6.0 g of TOPO at 250°C for 1 h.

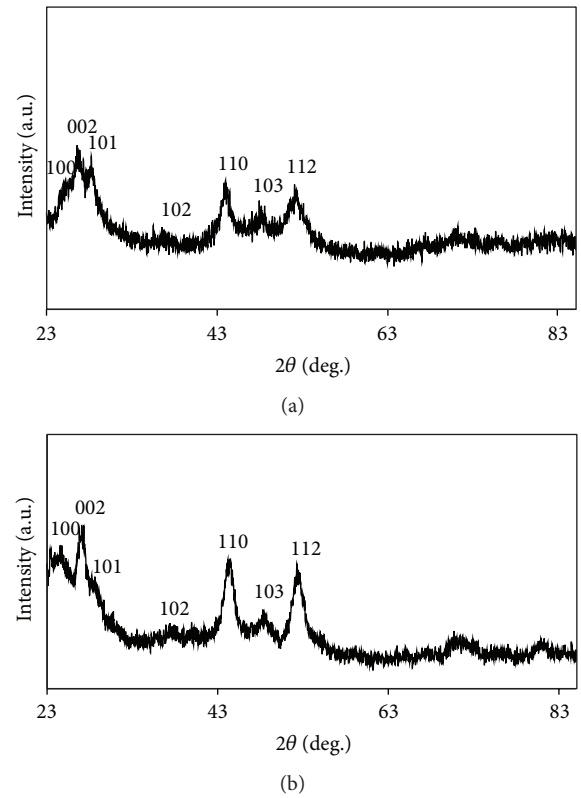


Figure 5: Powder X-ray diffraction patterns of CdS nanoparticles obtained by the thermolysis of the cadmium complex using (a) hexadecylamine and (b) trioctylphosphine oxide as capping molecule.

reflection patterns of the HDA-CdS matched with JCPDS card number (04-006-4886) for Greenockite, syn, while the reflection patterns of TOPO-CdS matched with JCPDS card number (04-004-8895) corresponding to hexagonal structure. The high intensity and narrower (002) peak in p-XRD pattern of TOPO-CdS nanoparticles indicate that the nanoparticles were elongated along the c-axis [39]. It can be concluded that the nature of the capping group influences the preferable growth direction of CdS nanoparticles. Furthermore, it could be observed that the diffraction peaks of TOPO-CdS are sharper than that of HDA-CdS, indicating that the crystallinity of the CdS nanostructure synthesized in the presence of trioctylphosphine oxide might be higher than that prepared using hexadecylamine.

3.6. FTIR of the TOPO and HDA Capped CdS Nanoparticles. FTIR red spectroscopy was used as a probe for the presence of TOPO or hexadecylamine on the nanocrystal surface. Figure 6(a) shows the IR spectrum of the TOPO capped nanoparticles. The spectral peaks were compared with the peaks observed in the spectrum of neat TOPO [40]. In both spectra (neat TOPO and TOPO-CdS), the band at 2954 cm^{-1} is the dissymmetric stretching vibration of CH_3, and the bands at 2921 and 2852 cm^{-1} are the dissymmetric and symmetric stretching vibrations of CH_2, respectively. The spectrum of the nanoparticles showed peaks matching all of the TOPO peaks in frequency and relative intensity, except for the P=O stretch. The stretching vibration band of P=O in neat TOPO appears around 1149 cm^{-1} [40]. However, in the nanoparticles this peak is observed to have shifted from 1149 cm^{-1} to 1046 cm^{-1}. The lowering of the peak is ascribed to the complexation of TOPO molecules to the CdS nanoparticles through the O atom of the P=O group. The shift of the P=O frequency to lower energy upon complexation indicates a transfer of electron density from P to O, which could significantly decrease the frequency of the P=O stretching mode, resulting in lower absorption frequency and red shift [41]. In the IR spectrum of the HDA capped CdS nanoparticles, Figure 6(b), the positions of the peak frequencies also provide insight into the local molecular environment in the hexadecylamine capped CdS nanoparticles. In the spectra of the free hexadecylamine [42], the $\nu_{as}(CH_3, ip)$ and $\nu_{as}(CH_2)$ peaks were observed at 2954 and 2916 cm^{-1}, respectively. In the hexadecylamine capped CdS, however, the $\nu_{as}(CH_2)$ peak shifted by 3 cm^{-1}; and the shift is attributed to the constraint of the capping molecular motions, which presumably resulted from the formation of a relatively close-packed hexadecylamine layer on the CdS nanocrystal surface [43]. The shift in the vibrational frequencies of the peaks associated with the N–H stretching (3330 cm^{-1}) and bending vibrations (1608 cm^{-1}) to 3329 and

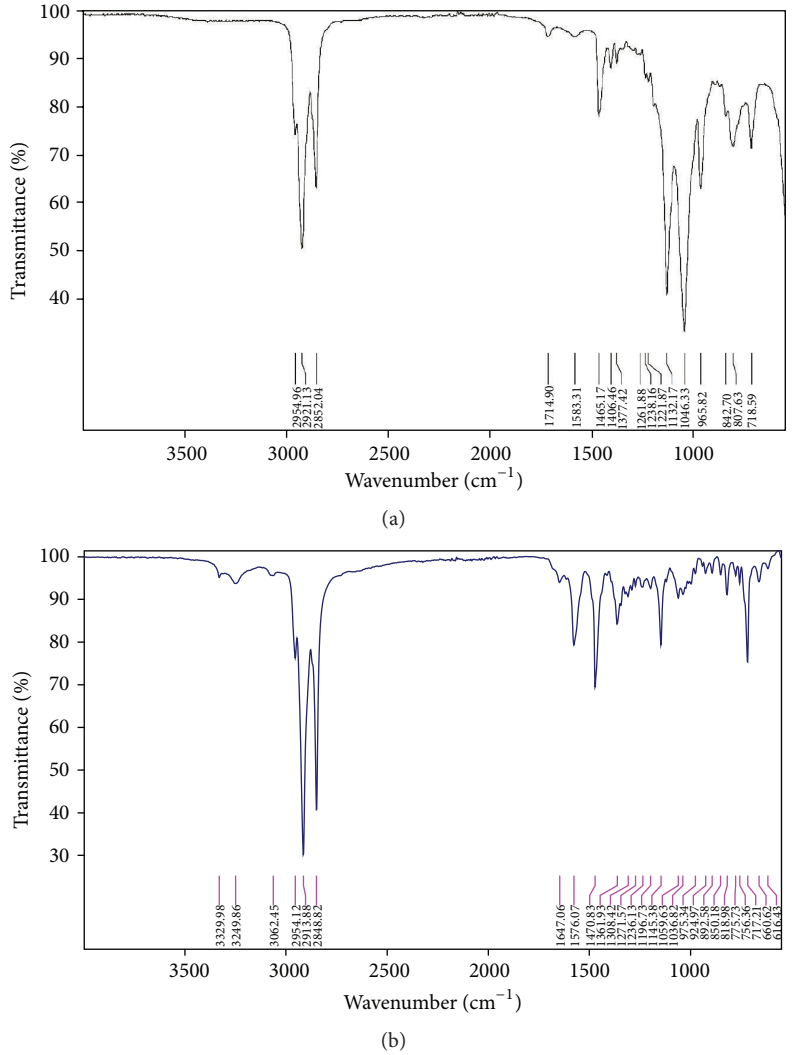


FIGURE 6: FT-IR of (a) TOPO capped CdS and (b) HDA capped CdS prepared from the thermolysis of bis(*N,N*-diallyldithiocarbamato)Cd(II) complex at 180 in TOPO and HDA, respectively.

1647 cm^{-1}, respectively, indicates the binding of the amine group of HDA to the nanoparticles via the nitrogen lone pairs. In both the TOPO and HDA capped nanoparticles, it is assumed that the coordination occurred via the Cd ions. Because both hexadecylamine and TOPO are Lewis bases, neither of them would likely bind to the basic S^{2-} on the surface.

4. Conclusion

Cadmium dithiocarbamate complex, synthesized from sodium *N,N*-diallyl-dithiocarbamate and hydrated cadmium chloride, was successfully used as single-source precursors in the synthesis of CdS nanoparticles capped with trioctylphosphine oxide (TOPO) and hexadecylamine (HDA). By varying the concentration of the capping molecules to the precursor compound, the resultant change in the morphology and optical properties of the as-prepared nanoparticles were investigated. The results of the analyses by TEM, UV-Vis absorption and photoluminescence (PL) spectroscopy, XRD, and FT-IR were presented and discussed. Spherical-shaped morphology was observed for particles synthesized at all concentrations using HDA as capping agent, whereas a change in morphology towards rod-shaped particles was observed as the concentration of TOPO as capping agent increased. X-ray diffraction studies showed that the CdS nanocrystallites exist as the hexagonal phase. Optical spectroscopy measurements indicated quantum confinement of the particles.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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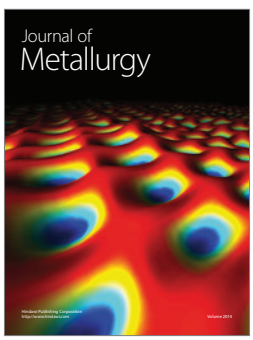




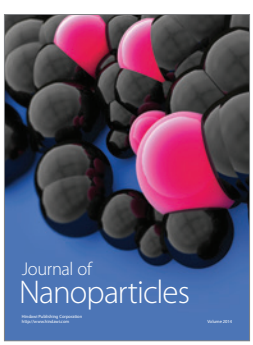


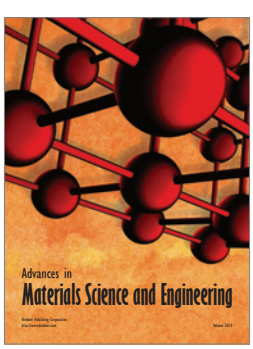


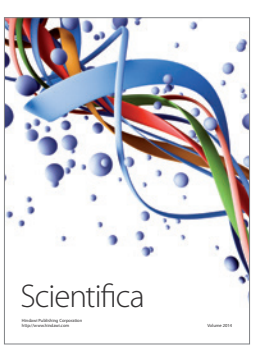


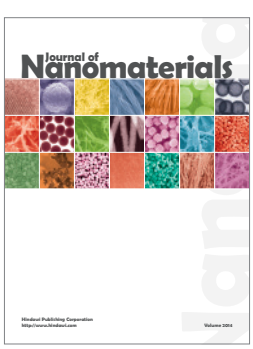






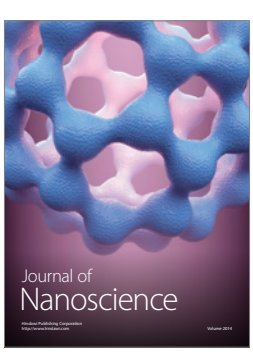




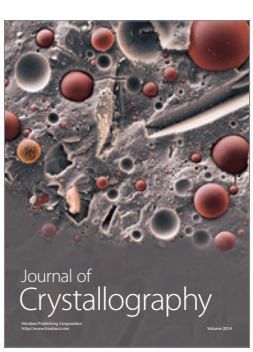




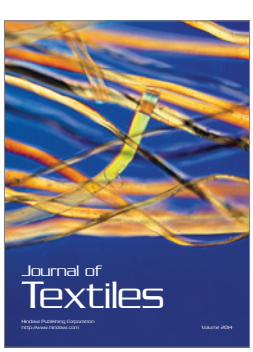












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