Homogeneous precipitation at solid/solution interface as a novel chemical route for synthesis of nanoparticles: application to Cd(II) and Pb(II) sulfides

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ABSTRACT
Nanoparticles of CdS and PbS were prepared by a novel method in which a sparingly soluble salt of the metal is brought into contact with the preparation solution mixture, without mixing, to introduce Cd\(^{2+}\) or Pb\(^{2+}\) ion into the medium at infinitesimal doses. The aqueous solution mixture contained \(n\)-heptane; thioacetamide, as sulphide ion precursor; cetyltrimethylammonium bromide (CTAB), as capping agent; and \(n\)-butanol, as co-surfactant. At the solid/solution interface CTAB-capped nanometal sulphide is formed through a metathesis reaction in extreme dilute medium. UV-visible, FTIR, and X-ray diffraction spectroscopy, as well as transmission electron microscopy were used to characterise the nanoparticles. The results showed that in solution, the diameters of the prepared CdS and PbS are 2.67 and 1.87 nm, respectively. In crystalline form, the corresponding diameters are 3.8–6.6 nm, and 6.88–13.9 nm, respectively. The crystalline structure of CdS is cubic or hexagonal, while that of PbS is face-centred cubic. The FTIR studies proved that CTAB acted as a capping agent of the investigated nanoparticles.

1. Introduction
In recent decades, the synthesis of nanoparticles of cadmium and lead sulfides has gained great interest due to their increasing scientific and technological applications [1–6]. To obtain nanoparticles by metathesis precipitation reaction, almost all the previously reported methods required the use of water soluble toxic salts of Cd(II) and Pb(II) in the presence of a capping, blocker, or dispersing agent to suppress the growth process [7–12]. This contributes to the pollution of the environment, and also increases the probability of metal ions co-precipitation over the large surface of the nanoparticles. Mbese and Ajibade [13] used the dithiocarbamato-Cd complex, as single molecule precursor of both Cd\(^{2+}\), and S\(^{2–}\) in homogeneous solution precipitation of CdS nanoparticles. Nevertheless, the method was not simple since it involved synthesis and analysis of the coordinated compound as preparatory steps to the preparation process. Moreover, the use of such metal precursor introduces organic molecules into the matrix of the precipitation medium. The sparingly soluble salt, PbCl\(_2\), and thioacetamide, have been used [14] to prepare...
nanoparticle of PbS using a solvothermal reaction. The method was energy and time-consuming because it required continuous heating at 100–200 °C for 10–30 h.

This raises the need to establish a simple method which is energy and cost effective, simple, and most importantly does not require to use solutions of the toxic cations, Cd(II) and Pb(II). The present article describes a new method to prepare nanoparticle of CdS and PbS formed within immediate vicinity of solid precursor/solution interface. The sparingly soluble salts, CdCO₃, CdC₂O₄, and CdS, as well as PbCl₂, PbCO₃, and PbS, were employed as precursors to Cd(II) and Pb(II) ions, respectively, via their solubility equilibriums. The metal cation was thus introduced continuously at constant concentration equals to the molar solubility of the sparingly soluble salt, i.e. 1.6 × 10⁻⁷, 1.2 × 10⁻⁴, and 1.0 × 10⁻¹⁴ M in case of using CdCO₃, CdC₂O₄, and CdS, respectively, and 1.6 × 10⁻², 2.7 × 10⁻⁷, and 1.7 × 10⁻¹⁴ M, in the case of using PbCl₂, PbCO₃, and PbS, respectively [15,16].

The disappearance of the equilibrated metal cation, as a result of combination with the sulphide ions, produced from the hydrolysis of the thioacetamide [17], was spontaneously compensated by a forward shifting of the solubility equilibrium. This kept the concentration of metal ions constant at infinitesimal values throughout the whole precipitation process, and therefore avoided the problems of metal ions co-precipitation and the disposal of the toxic free Cd(II) or Pb(II) cations with the filtrate. The method is considered simple, cost effective and can be applied to preparation of a broad range of nanoparticles; further, it makes possible converting insoluble salts like CdS, and PbS, from bulk to nanoparticles. Moreover, the metal precursors are commercially available and easy to obtain in pure state.

2. Experimental

2.1. Chemicals and reagents

All reagents used were of analytical grade. Thioacetamide, cetyltrimethylammonium bromide (CTAB), n-heptane, n-butanol, polyvinyl alcohol (PVA), CdCO₃, CdC₂O₄, CdS, PbCl₂, PbCO₃, and PbS have been obtained from Sigma-Aldrich.

2.2. Synthesis of the metal sulphide nanoparticles

A preparation cell consisting of two concentric glass tubes fit together at the neck through a ground glass joint was used (Figure 1). The outer tube is closed and has a flat bottom, with an inner diameter of 4.0 cm, and a capacity of about 150 mL, while the inner tube is open at the bottom and has an inner diameter of 1.8 cm. In the outer tube, 1.5 g of thioacetamide and 5.0 g of CTAB have been dissolved in 50 mL of bi-distilled water. With this solution, 30 mL of n-heptane, as organic phase, and 20 mL of n-butanol, as co-surfactants, have been added and the mixture was thoroughly mixed for 5 min. The water-insoluble metal salt, CdCO₃, CdC₂O₄, CdS, PbCl₂, PbCO₃, or PbS was contained in a filter paper and introduced into the lower end of the inner tube, and then the tube was fixed as appropriate (Figure 1). The cell has been heated gently, and the solution was stirred vigorously for 2 h. The yellow, cadmium sulphide (Figure 1(a), inset), or the reddish-black PbS formed in the outer tube (Figure 1(b), inset) was separated by centrifugation, washed with water, followed by ethanol, and then dried at 120 °C for one hour. It is also an advantage
of the method that the formation process can be halted at any time by just removing the internal tube and vice versa.

2.3. **UV-visible spectroscopy**

The prepared nanosulphides were dispersed in a PVA solution and their spectra were run by the VWR UV-1600 PC spectrophotometer.

2.4. **Fourier transform infrared spectroscopy**

Infrared spectra of the prepared compounds were scanned with JASCO FT-IR 6300 Spectrometer using the regular KBr pellets technique.

2.5. **Transmission electron microscopy**

The obtained nanocrystals were investigated by transmission electron microscopy using high resolution JEOL microscope, model JCM 5700 Carry Scope. The software program, *Imagej*, was used to determine the size of the particles from TEM images.

2.6. **X-ray diffraction spectroscopy (XRD)**

The prepared nanoparticles were subjected to mineralogical analyses using SIEMENS D5000 X-ray Diffractometer, equipped with a position sensitive detector. The powder XRD patterns were collected in the angular range between 10° and 80° 2θ, with a 2θ scan step of 0.015° and step time of 0.2 s, using CuKα1 radiation (λ = 1.5406 Å) and Ni filter. The computer program DIFFRAC<sup>plus</sup> (BRUKER AXS, INC., 2004 with ICDD library) has been used to identify the minerals.

*Figure 1.* The preparation cell containing powder CdS (a), and PbCl₂ (b) salts, as precursors, thioacetamide, and CTAB; inset: the cell after 15 min.
3. Results and discussion

3.1. UV-visible spectroscopy

The absorption spectra of the nano metal sulphide species, prepared from the different metal salts exhibited similar patterns in general, as depicted in Figure 2(a) for CdS. Average values of absorption edges at 330.0 and 325.3 nm for CdS and PbS were obtained, respectively (Table 1). These values are far less than the reported ones for bulk CdS (512 nm) [18] and PbS (3020 nm) [19]. This large blue shift at the onset of absorption certainly confirms existence of the quantum confinement effect as a result of formation of nanosized metal sulphides [19].

To calculate the energy gap (Eg) for the synthesized nanoparticles, Tauc relation [20] has been used and \((\alpha h\nu)^2\) was plotted versus \((h\nu)\), where \(\alpha\) is the molar extinction coefficient of the confined particle, \(h\) is Planck’s constant, and \(\nu\) is the frequency. Representative plots for CdS are shown in Figure 2(b), where the intercept obtained from the straight line with the energy axis is the band energy gap (Eg) of the nanoparticle. The average values of

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**Figure 2.** Absorption spectra of the nanoparticles of CdS (a), and application of Tauc's equation to determine the energy gap (b).
the energy gaps obtained were 3.70 eV for the nano CdS particles, and 3.75 eV for the nano PbS particles. These values are larger than the known optical band gap (2.42 EV) of bulk CdS [21], and 0.41 EV of bulk PbS [22] which support the formation of nano CdS and PbS particles characterised with great quantum confinement effect [23].

The particle radii \( (r) \) of the synthesised CdS, and PbS nanoparticles were calculated from modified Brus equation [24–26]:

\[
E_{np} = E_g + \left( \frac{\hbar^2}{8 \pi^2 r^2} \right) \left[ \left( \frac{1}{m_e^*} \right) + \left( \frac{1}{m_h^*} \right) \right]
\]

\( E_{np} \) and \( E_g \) (in joules) are the absorption edges of the nano- and bulk sulphide, respectively, \( r \) is the radius of the nanoparticle, in metres, and \( m_e^* \) and \( m_h^* \) are the effective masses of the electron and its corresponding hole, respectively.

For CdS, the known values of \( m_e^* \) and \( m_h^* \), are 0.19 and 0.80 me, respectively [27], where me is the electron mass in kg; while for PbS, the corresponding values are 0.08 and 0.075 me, respectively [28]. The average diameters of the solvated CdS and PbS nanoparticles are 2.67 and 1.87 nm, respectively (Table 1).

### 3.2. Infrared spectroscopy

The FTIR spectral data on pure CTAB and CTAB-bound CdS and PbS nanoparticles are given in Table 2. The \( (\text{CH}_3\text{-N})^+ \) symmetric stretching of pure CTAB at 1479 cm\(^{-1}\) was shifted to 1600 cm\(^{-1}\) in all spectra of the CTAB-capped nanoparticles except for PbS prepared from PbCO\(_3\) where the band was so weak that it could not be detected (Table 2). This large shift revealed that \( (\text{CH}_3\text{-N})^+ \) plays an important role in the capping process [29]. The \( (\text{CH}_3\text{-N})^+ \) asymmetric stretching of pure CTAB at 1401 cm\(^{-1}\) appeared in the

| Mode of vibration | CTAB (cm\(^{-1}\)) | CdS nanoparticles (cm\(^{-1}\)) | PbS nanoparticles (cm\(^{-1}\)) | Ref. |
|-------------------|------------------|-----------------------------|-----------------------------|-----|
| \((\text{CH}_3\text{-N})^+\) Symmetric stretching | 1479 (s)* | 1619 (s) 1619 (m)* 1616 (m) | 1624 (w)* – 1597 (w) | [29] |
| \((\text{CH}_3\text{-N})^+\) Asymmetric stretching | 1401 (w) | 1414 (m) 1417 (s) 1426 (w) | 1375 (w-b)* 1382 (w-b) 1330 (w-b) | [29] |
| \((-\text{CH}_2\text{-})\) Asymmetric stretching | 2919 (s) | 2845 (w) 2850 (m) 2852 (w) | 2950 (w) – – | [30–32] |
| \((-\text{CH}_2\text{-})\) Symmetric stretching | 2849 (s) | 2913 (w) 2919 (w) 2920 (w) | 2919 (w) – – | [30–32] |
| \(-\text{O-H}\) stretching of adsorbed water | – | 3420 (s-b) 3402 (s-b) 3424 (s-b) | 3426 (m-b) 3426 (w-b) 3426 (w-b) | [33,34] |

Note: (‘’) s = strong; m = medium; w = weak; b = broad.
nanoparticles spectra slightly shifted from that of pure CTAB. The \( \text{–CH}_2 \text{–} \) asymmetric and symmetric stretching frequencies of pure CTAB appeared at 2919 and 2849 cm\(^{-1}\), respectively [30–32]. The same bands appeared in the spectra of the nanoparticles with a slight shift in location and change of intensity. In case of PbS nanoparticles prepared from PbCO\(_3\) and PbS the two bands were so weak that they were not detected, indicating that the prepared nanoparticles have interacted with the CTAB molecules, and this interaction substantially suppresses the development of the particles.

It is worthy to observe that a broad hump around 3300 cm\(^{-1}\) appeared in the spectra of all the prepared sulphides, which is most probably due to stretching vibrations of O–H bonds of adsorbed water. In fact, adsorption of water is common for all powdered samples exposed to the atmosphere, and is still so in case of nanosized particles due to high surface area [33,34].

3.3. Transmission electron spectroscopy

TEM images of the prepared CdS and PbS nanoparticles are shown in Figure 3 with insets exhibiting histograms of the particle size distribution. It is clear that the nano sulphide particles formed from bulk CdS and PbS, Figure 3(c, f), respectively; are less agglomerated than those obtained from the other salts. This may be attributed to the great difference between the molar solubility of bulk CdS (1.0 \( \times \) 10\(^{-14} \) M) and bulk PbS (1.7 \( \times \) 10\(^{-14} \) M) in comparison to those of CdCO\(_3\) (1.6 \( \times \) 10\(^{-7} \) M) and CdC\(_2\)O\(_4\) (1.2 \( \times \) 10\(^{-4} \) M) in case of CdS; and of PbCl\(_2\) (1.6 \( \times \) 10\(^{-2} \) M), and PbCO\(_3\) (2.7 \( \times \) 10\(^{-7} \) M) in case of PbS. The extremely small molar solubility of bulk CdS and PbS allow only a little agglomeration of the formed nanoparticles in crystal during synthesis.

The histograms of the nanoparticles size distribution as obtained from the TEM images of the CTAB-capped nanoparticles are shown in the insets of Figure 3, and the obtained diameters are given in Table 3. The results exhibit that the sizes of all the prepared particles are within the nanoscale. It is noticeable that all obtained diameters are larger than the values obtained from the uv-visible spectroscopic measurements. This is because the particles in solution are solvated moieties, while in solid state they exist in crystalline form.

3.4. X-ray diffraction spectroscopy

Structural identification of the synthesized nano sulphide particles was carried out with X-ray diffraction in the range of 2\( \theta \) between 10\(^{\circ}\) and 80\(^{\circ}\).

3.4.1. Nanoparticles of CdS

Figure 4 displays the X-ray diffraction patterns of the CdS nanoparticles. It is clear that the particles prepared from CdCO\(_3\) (Figure 4(a)) and CdS (Figure 4(c)) showed reflections from (111), (220) and (311) planes, which match well with the standard reflection lines of cubic crystals (JCPDS file no. 42-1411) [35]. Furthermore, comparing the intensity of the peaks reveals that the crystals are preferentially oriented along (111) direction. The characteristic lines for particles prepared from CdC\(_2\)O\(_4\) indicate reflection from the planes (100), (002), (101), (102), (110), (103), (112), (203) and (105) (Figure 5(b)) which corresponds to a hexagonal lattice structure [36]. All patterns were free of the peaks from
Table 3. The crystallite size and lattice structure of the nano CdS and PbS as obtained by TEM and XRD techniques.

| Nano crystallite | Metal precursor | Diameter TEM (nm) | Diameter XRD (nm) | Crystalline form       |
|------------------|-----------------|-------------------|-------------------|------------------------|
| CdS              | CdCO$_3$        | 3.80              | 6.60              | Cubic                  |
|                  | CdC$_2$O$_4$    | 6.50              | 5.29              | Hexagonal              |
|                  | CdS             | 4.00              | 5.55              | Cubic                  |
| PbS              | PbCl$_2$        | 6.88              | 9.93              | Face centred cubic     |
|                  | PbCO$_3$        | 11.0              | 11.6              | Face centred cubic     |
|                  | PbS             | 11.4              | 13.9              | Face centred cubic     |

Figure 3. Transmission electron micrographs of the CTAB-capped nanoparticles of CdS (a–c) and PbS (d–f) and histograms of the size distribution of the prepared particles (insets).
impurities, such as CdO or S, revealing that all samples were highly pure CdS nanoparticles.

Debye–Scherrer equation was used to calculate the particle sizes of the samples as previously described [37]:

$$D = \alpha \lambda / \beta \cos \theta$$

where $\alpha$ is the shape factor and equals to 0.89, $D$ (nm) is the mean diameter of the crystal, $\lambda$ (nm) is the X-ray wavelength, $\theta$ (radian) is the diffraction angle, and $\beta$ (radian) is the
maximum peak width in half-height. The obtained diameters (Table 3) showed an average value of 6.08 nm for the CdS cubic lattice and 5.29 nm for the CdS hexagonal lattice. These values are fairly within the nanoparticles scale; yet, these are larger than the exciton Bohr radius of CdS which is 3.0 nm [37].

3.4.2. Nano particles of PbS

Figure 5 shows the X-ray diffraction patterns of the synthesised PbS nanoparticles as obtained from PbCl₂, PbCO₃, and PbS. It is clear that the general patterns of the three diffractions are similar and each exhibits nine sharp peaks due to reflections from the planes (111), (200), (220), (311), (222), (400), (331), (420), and (422), which are characteristics of a face centred cubic lattice structure (JCPDS file no. 5-592) [38,39].

The average lattice diameter of the crystal as obtained by applying Debye–Scherrer equation was 11.8 nm (Table 3). This value is much smaller than the exciton Bohr radius of 18 nm [38], the prepared nanoparticles, therefore, may find numerous applications in the field of quantum dot semiconductors.

4. Conclusion

The solubility equilibria of sparingly soluble metal salts can be successfully used to provide the metal ion through a suitable permeable membrane to a solution containing thioacetamide as sulphide precursor. In the presence of a capping agent like CTAB, nano metal sulphide particles can be obtained through a metathesis reaction at the interface separating the solid salt from the thioacetamide solution. Such technique will enable the introduction of the metal cation into the reaction medium at constant infinitesimal doses throughout the whole precipitation process. The method is environmentally friendly because it does not require solutions of the toxic Cd(II) and Pb(II) cations. Moreover, it has the advantage of eliminating the possibility of co-precipitation of the metal ions on the surface of the formed nanoparticles.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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