Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Der Chemica Sinica, 2014, 5(4):17-24

ISSN: 0976-8505
CODEN (USA) CSHIA5

Synthesis and analysis of ternary alloyed $Zn_XCd_{1-X}S$ nanocrystals

George N. Ndifor-Angwafor[1*], Solomon G. Anagho[1,2] and Donald Raoul T. Tchuifon[1]

[1]Laboratory of Noxious Chemistry and Environmental Engineering, Department of Chemistry,
Faculty of Science, University of Dschang, Dschang, Cameroon
[2]Department of Chemistry, Faculty of Science, University of Bamenda, Bambili, Cameroon

---

ABSTRACT

Cadmium acetate salt was exploited in the synthesis of $Zn_xCd_{1-x}S$ alloyed nanocrystals by reacting it with zinc salts and elemental sulphur in dodecylamine at high temperatures. Interestingly the obtained $Zn_xCd_{1-x}S$ nanocrystals possess quantum confinement. The prepared $Zn_xCd_{1-x}S$ nanocrystals were digested in acid and the metal ions present in solution were determined. It was found that Cd to Zn ratio in the particles after preparation is the same as in the reaction vessel during preparation.

Keywords: *Cadmium acetate, cadmium zinc sulfide, Atomic absorption spectroscopy, Stripping voltammetry.*

INTRODUCTION

Semiconductor nanocrystals are of great interest for both fundamental research and technical applications as a consequence of the large ratio of surface atoms and the three dimensional quantum confinement of excitons [1-5]. $Zn_xCd_{1-x}S$ nanocrystals are promising materials for high density optical recording devices, blue or even ultraviolet laser diodes, and photovoltaic cells [6-7]. Recent advances have let to the exploration of tunable optical properties from the $Zn_xCd_{1-x}S$ nanocrystals [8-14]. The lack of adequate synthetic methods for producing the desired high quality nanocrystals is currently a bottleneck in this field.

In this paper, we report a chemical route to the synthesis of ternary alloyed $Zn_xCd_{1-x}S$ nanocrystals using cadmium acetate salt as the widely used cadmium stearate is no longer commercially available. It is a one-pot method involving the reaction of cadmium acetate as the cation source and elemental sulfur as the sulfide source in the commonly available high boiling-point long chain amines at high temperatures. Next the analytical procedures employed to analyse the zinc and cadmium ion concentrations in the nanocrystals is introduced. It is shown that the ratio of Zn: Cd in the particles after preparation is the same as that present in the reaction vessel during preparation. The results of the different $Zn_xCd_{1-x}S$ are detailed and discussed in terms of the solubility products of the cadmium and zinc precursors that were used in the preparation of the $Zn_xCd_{1-x}S$ nanocrystals.

MATERIALS AND METHODS

2.1 Chemicals

Hexadecylamine (HDA, tech, 90%), dodecylamine (98%), Zinc stearate ($Zn(ST)_2$), tech, sulfur powder (99.98%), Zinc acetate (99.99%) were purchased from Aldrich. Cadmium acetate (anhydrous) 99.99+ % was obtained from Chem Pur.

2.2 Preparation of Ternary Alloyed $Zn_xCd_{1-x}S$ nanocrystals

Cadmium acetate and zinc acetate, with different molar ratios, were mixed with HDA and heated to 270°C under an argon flow. The injected amount of sulfur (dissolved in dodecylamine) was equal to the total molar amount of zinc and cadmium precursors. For example, 23 mg (0.1 mmol) of cadmium acetate, 5.8 mg (0.03 mmol) of zinc acetate, and 3.5 g of HDA was heated to 270 °C under an argon flow. A 1.0 ml solution of sulphur (4.2 mg, 0.13 mmol) in dodecylamine was swiftly injected into this solution. The reaction mixture was then kept at 260 °C for 30 minutes for the growth of the nanocrystals. The growth of the nanocrystals was stopped by immersing it in chloroform solution. The resulting nanocrystals in chloroform solution were precipitated with acetone and allowed to settle by gravity. The separation with a mixture of acetone and resuspension in chloroform process was repeated 3 times. The purified nanocrystals were then digested using standard acid digestion [15].The digested solution was then diluted for cadmium and zinc ion analysis.

2.3 Analytical Protocol to Determine the Composition of $Zn_xCd_{1-x}S$ Nanocrystals

2.3.1 Concentration of Zn^{2+} in $Zn_xCd_{1-x}S$ Nanocrystals

The concentrations of zinc ions in aliquots of the digested solutions of $Zn_xCd_{1-x}S$ nanocrystals were determined using electroanalysis (ECA) and atomic absorption spectroscopy (AAS). Anodic stripping voltammograms were recorded at a scan rate of 20 mVs^{-1} and deposition time of 80 s at different applied potentials relative to a saturated calomel reference. Different volumes of standard zinc nitrate solution (0.05 mol dm^{-3}) were added to the cell to give a range of concentrations of zinc ions. The voltammograms obtained were analysed to give the peak area (charge) associated with stripping the zinc deposited. The charges required to strip the zinc was then plotted against the Zn^{2+} concentrations. This gave a linear relationship relating charge, or area under each voltammogram, to the Zn^{2+} concentration, see figure 2-1**.** Aliquots of samples taken from the digested solutions were analysed for Zn^{2+}. The charge under the stripping peak was determined and the calibration graph used to calculate the Zn^{2+} concentration as shown in equation 2-1

$$X = \frac{Y}{20199} \qquad \text{2-1}$$

Where
Y = Charge below the stripping peak in the voltammogram
X = Zinc concentration in the solution.

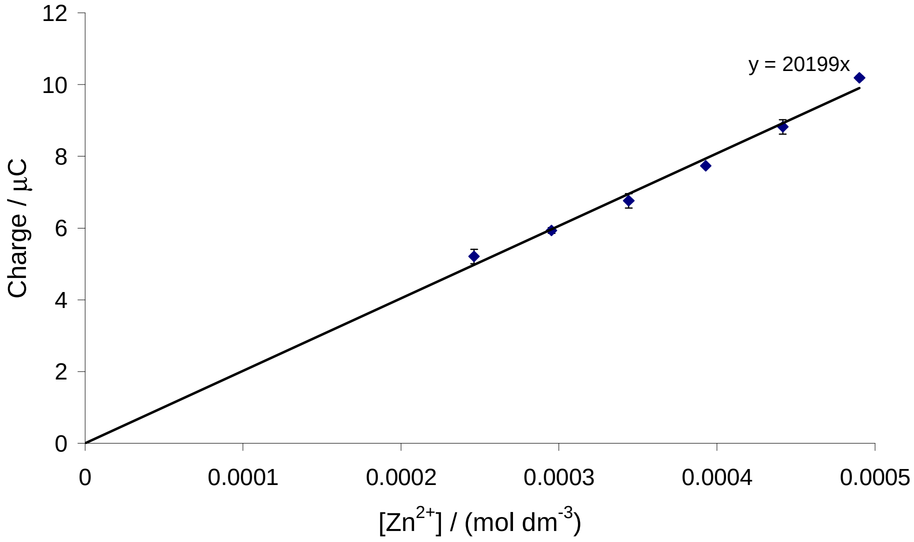


Figure 2-1: Standard zinc calibration curve by the electro analytical method using different zinc ion concentration and fixed mercury ion concentration. The curve gives a linear relationship in which zinc ion concentration in the analysis cell can be calculated by dividing the charge obtained by 20199

The zinc ion concentrations were those of Zn^{2+} present in the cell used for the analysis. To get the actual concentration of zinc in the aliquots (and hence in the samples), the concentration of Zn^{2+} in the cell was multiplied by a dilution factor calculated as in equation 2-2 below:

$$\text{Dilution factor} = \frac{V_{NaCl}+V_{HgCl_2}+V_{Zn(NO_3)_2}}{V_{Zn(NO_3)_2}} \qquad 2\text{-}2$$

In the AAS method a zinc calibration was obtained, figure 2-2, using solutions of known concentration, prepared by dilution of a 1000 ppm standard zinc solution.

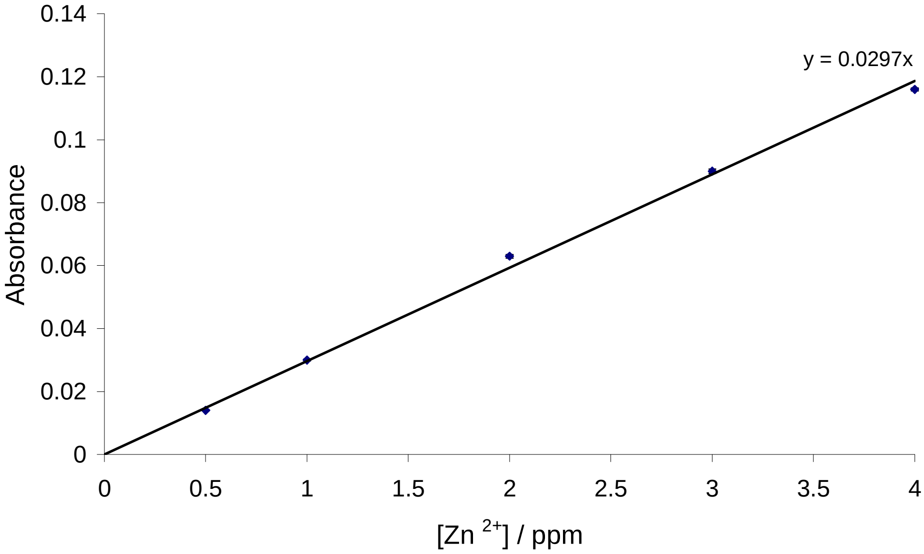


Figure 2-2: Standard zinc calibration curve by the AAS method using known zinc concentrations. The curve gives a linear relationship in which the concentration of zinc in the analysis solution can be calculated by dividing the absorbance obtained by 0.0297

2.3.2 Concentration of Cd^{2+} ion in $Zn_xCd_{1-x}S$ Nanocrystals

The same procedure as in the determination of Zn^{2+} ion in 2.3.1 was used to determine the concentration of Cd^{2+} ion concentration in the nanocrystals. The linear relationship relating charge or area under each voltammogram to the Cd^{2+} ion concentration is given in figure 2-3

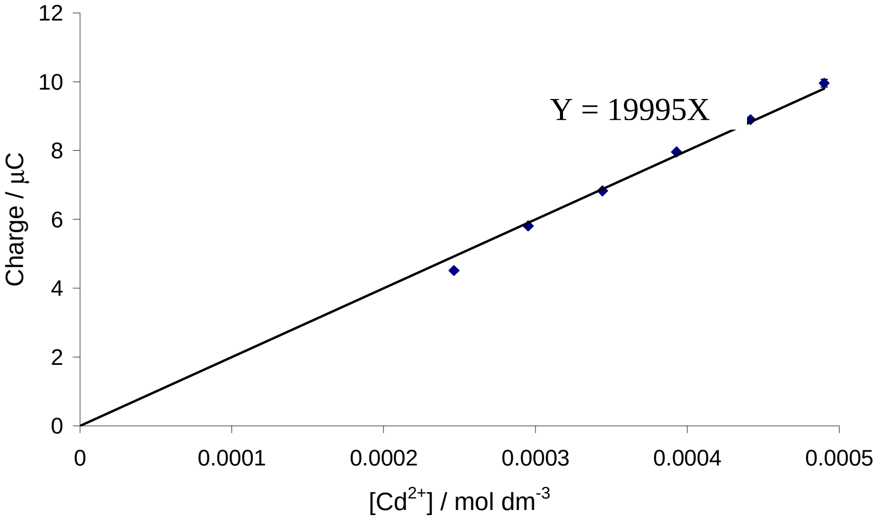


Figure 2-3: Standard cadmium calibration curve by the electro analytical method using different cadmium ion concentration and fixed mercury ion concentration. The curve gives a linear relationship in which cadmium ion concentration in the analysis cell can be calculated by dividing the charge obtained by 19995

The charge under the stripping peak was determined and the calibration graph used to calculate Cd^{2+} concentration as shown in equation 2-3.

$$X = \frac{Y}{19995} \qquad 2\text{-}3$$

Where
Y = Charge or area below each voltammogram
X = Cadmium concentration that caused the voltammogram.

The cadmium ion concentrations were those of Cd^{2+} present in the cell used for the analysis. To get the actual concentration of cadmium in the samples, the concentration of the Cd^{2+} in the cell was multiplied by a dilution factor calculated as shown in equation 2-4.

$$\text{Dilution factor} = \frac{V_{NaCl} + V_{HgCl_2} + V_{Cd(NO_3)_2}}{V_{Cd(NO_3)_2}} \qquad \text{2-4}$$

A similar procedure as for the Zn^{2+} concentration was also used to determine the cadmium ion concentration by the A.A.S technique using the linear relationship from figure 2-4

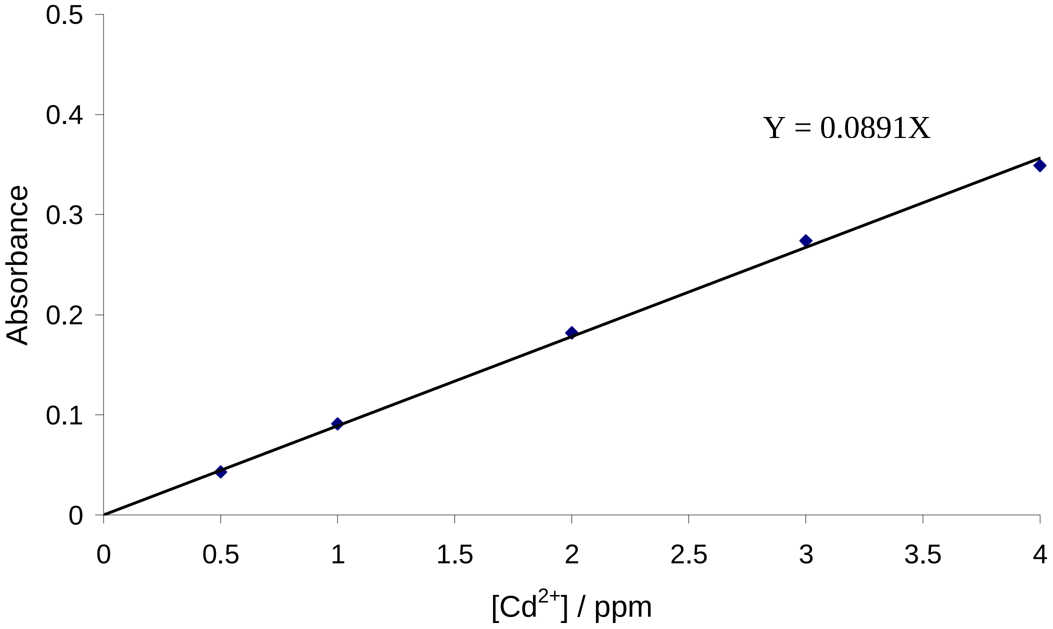


Figure 2-4: Standard cadmium calibration curve by the AAS method using known cadmium concentrations. The curve gives a linear relationship in which the concentration of cadmium in the analysis solution can be calculated by dividing the absorbance obtained by 0.0891

RESULTS AND DISCUSSION

3.1 UV-vis Spectroscopy

Figures 3.1 show the UV- Visible absorption spectra of $Zn_xCd_{1-x}S$ nanocrystals prepared by using varying ratio of zinc acetate.

3.2 Transmission Electron Microscopy

The HR-TEM of the ternary alloyed nanocrystals prepared using different zinc salts are shown in figure 3-2. Their particle sizes as revealed by TEM is 6.6 ± 0.1nm, 6.9 ± 0.3 nm and 7.2 ± 0.2 nm. They have nearly equal particle sizes. Figure 3-3 displays their energy dispersive X-ray analysis spectra showing the presence of cadmium, zinc and sulfur. The samples for the TEM analysis were prepared on a copper grid hence the appearance of copper on the energy dispersive X-ray analysis spectra.

3.3 Zinc and Cadmium ions Concentration in $Zn_xCd_{1-x}S$ Nanocrystals

The zinc content and cadmium content of $Zn_xCd_{1-x}S$ nanocrystals was determined using AAS and electroanalytical techniques. The concentrations of zinc and cadmium obtained from the analysis of the nanocrystals are shown in tables 3-1 and 3-2. The experimentally determined Zn:Cd ratio of the particles is shown in table 3-3.

Table 3-1: Quantities of zinc and cadmium present in the preparation of $Zn_xCd_{1-x}S$ mnanocrystals

Nanocrystals	$[Zn^{2+}]$ (M)	$[Cd^{2+}]$ (M)
$Zn_{0.24}Cd_{0.76}S$	3.2×10^{-5}	1.0×10^{-4}
$Zn_{0.48}Cd_{0.52}S$	9.2×10^{-5}	1.0×10^{-4}
$Zn_{0.72}Cd_{0.28}S$	2.6×10^{-4}	1.0×10^{-4}

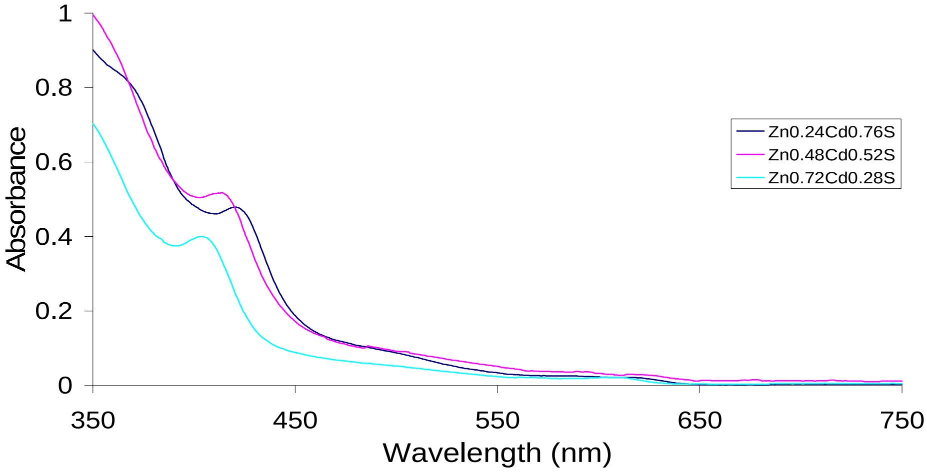
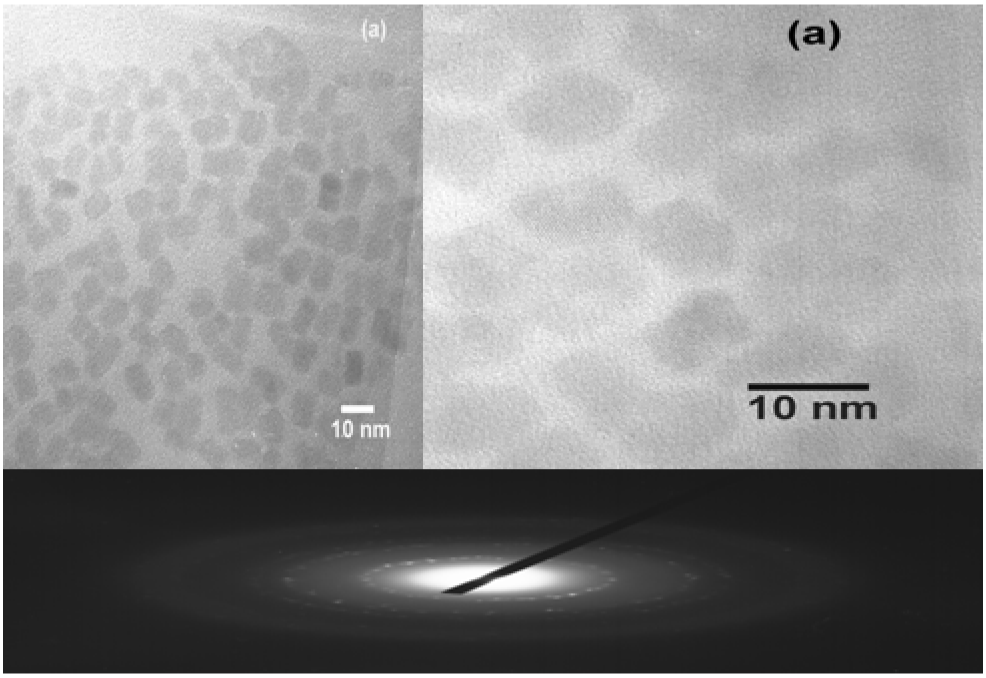


Figure 3-1: UV-Vis absorption of $Zn_xCd_{1-x}S$ nanocrystals samples with different molar ratios of zinc acetate and cadmium acetate in the reaction vessel. Samples were removed from the reaction vessel after 30 minutes

Table 3-2: Experimental quantities of zinc and cadmium present in $Zn_xCd_{1-x}S$ nanocrystals alloyed with zinc acetate salt

Alloyed Nanocrystal	$[Zn^{2+}]$ (M) by AAS method	$[Zn^{2+}]$ (M) by ECA method	$[Cd^{2+}]$ (M) by AAS method	$[Cd^{2+}]$ (M) by ECA method
$Zn_{0.24}Cd_{0.76}S$	$2.7953 \times 10^{-5} \pm 2.5158 \times 10^{-7}$	$2.7741 \times 10^{-5} \pm 1.2194 \times 10^{-6}$	$9.1147 \times 10^{-5} \pm 1.0938 \times 10^{-6}$	$9.2683 \times 10^{-5} \pm 1.2976 \times 10^{-6}$
$Zn_{0.48}Cd_{0.52}S$	$8.2127 \times 10^{-5} \pm 1.0335 \times 10^{-6}$	$8.3213 \times 10^{-5} \pm 2.7346 \times 10^{-6}$	$9.1859 \times 10^{-5} \pm 8.2673 \times 10^{-7}$	$9.2186 \times 10^{-5} \pm 2.8578 \times 10^{-6}$
$Zn_{0.72}Cd_{0.28}S$	$2.1948 \times 10^{-4} \pm 2.4143 \times 10^{-6}$	$2.2461 \times 10^{-4} \pm 3.2845 \times 10^{-6}$	$9.2426 \times 10^{-5} \pm 6.4698 \times 10^{-7}$	$9.3106 \times 10^{-5} \pm 3.8173 \times 10^{-6}$



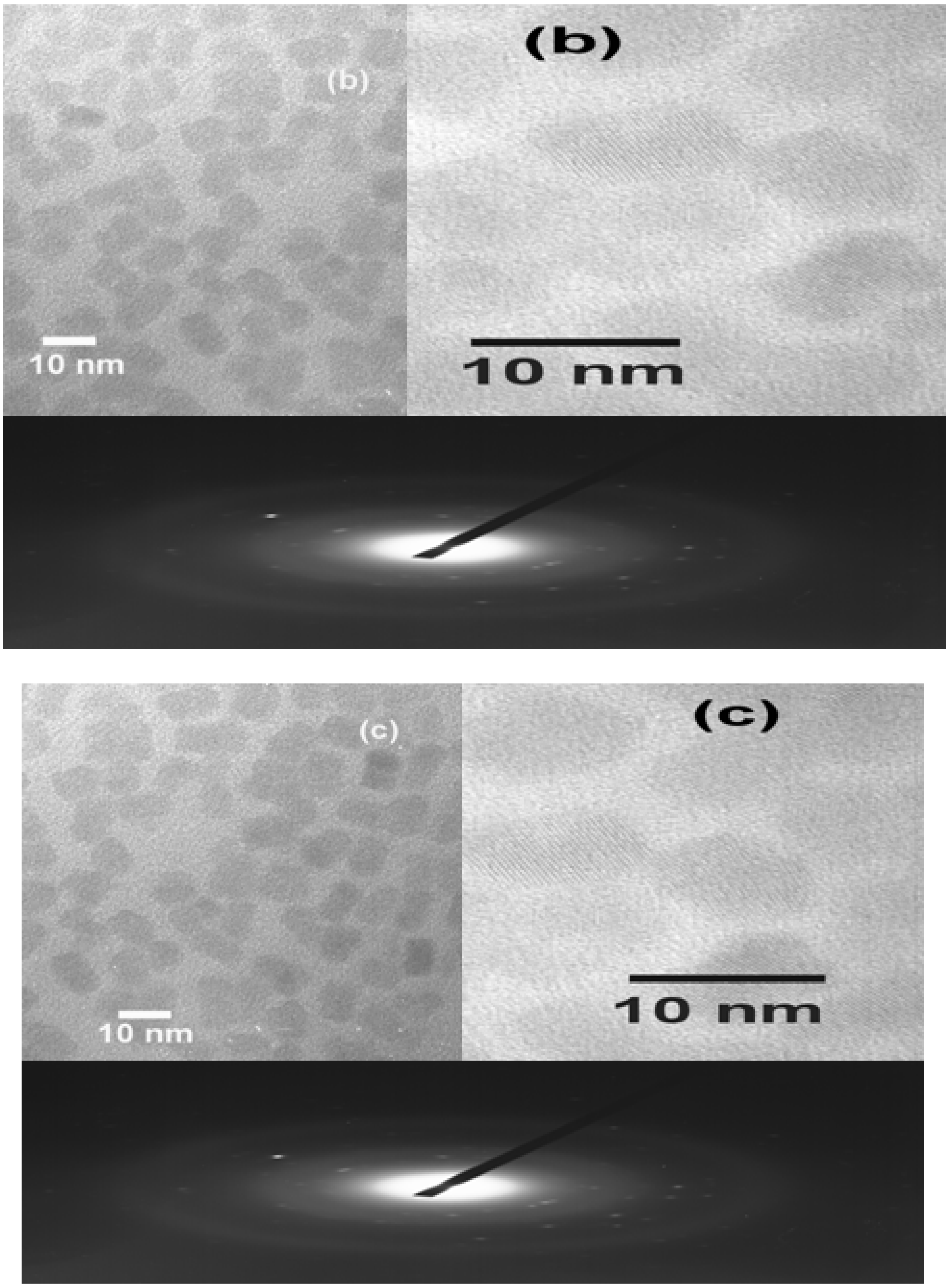


Figure 3-2: HR-TEM of $Zn_xCd_{1-x}S$ nanocrystals after 30 minutes growth prepared, using cadmium acetate and zinc acetate salts with mole fractions of (a) 0.24, (b) 0.48 and (c) 0.72 and particle sizes of 6.6 ± 0.1 nm, 6.9 ± 0.3 nm and 7.2 ± 0.2 nm respectively. All the alloyed nanocrystals are crystalline in nature

Table 3-3: Molar ratios of zinc and cadmium in $Zn_xCd_{1-x}S$ nanocrystals alloyed with zinc acetate salt

Zn:Cd ratio	Zn:Cd ratio in the reaction vessel	Zn:Cd molar ratio in $Zn_xCd_{1-x}S$ particles by AAS	Zn:Cd molar ratio in $Zn_xCd_{1-x}S$ particles by ECA
$Zn_{0.24}Cd_{0.76}S$	0.32	0.3067	0.2993
$Zn_{0.48}Cd_{0.52}S$	0.92	0.8941	0.9026
$Zn_{0.72}Cd_{0.28}S$	2.6	2.3747	2.4124

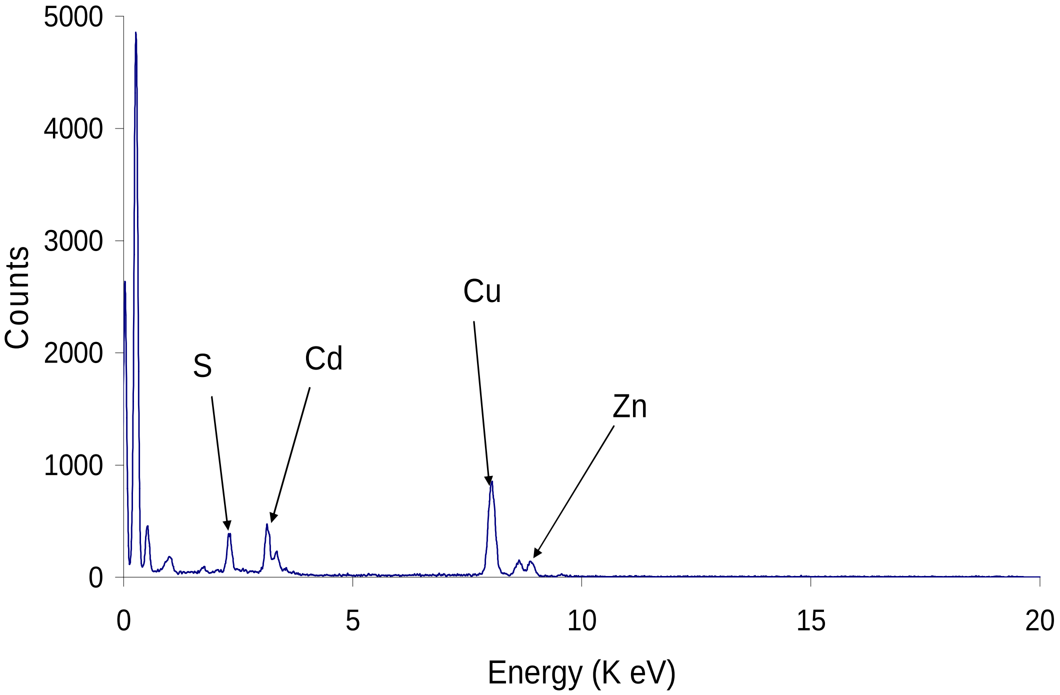


Figure 3-3: EDX of $Zn_xCd_{1-x}S$ nanocrystals confirming the elemental composition of zinc, cadmium and sulfur in the nanocrystal

Cadmium stearate has been widely used as a cadmium salt in the preparation of alloyed $Zn_xCd_{1-x}S$ nanocrystals by reacting with zinc salt and elemental sulfur. The results indicate that cadmium acetate can also act as a cadmium source in the synthesis of ternary alloyed $Zn_xCd_{1-x}S$ nanocrystals. Cadmium acetate was used in this synthesis because the widely used cadmium stearate is no longer produced by chemical companies. High-boiling alkylamines with different lengths of alkyl chains, such as tetradecylamine and octadecylamine or unsaturated amines such as Oleyamine, can act as the coordinating solvent to obtain high quality nanocrystals. Liquid dodecylamine was chosen as the solvent to prepare the sulfur stock solution on the basis of operational convenience. TEM image reveals that the alloyed $Zn_xCd_{1-x}S$ nanocrystals have nearly equal particle sizes of 6.6 ± 0.1nm, 6.9 ± 0.3 nm and 7.2 ± 0.2 nm. The continuous peak-shifting of the monodispersed nanocrystals rules out the possibility of phase separation or separated nucleation. There is an absorption onset in the UV spectra shift to shorter wavelength with the increase of zinc molar ratio in the materials. This observed blue shift (or increase in band-gap energy, Eg) is a strong evidence for the formation of alloyed nanocrystals via the intermixing of the wider band-gap ZnS (Eg = 3.7eV) with the narrow band-gap CdS (Eg = 2.5 eV) [13, 14]. The instant termination of the growth progress may come from the strong reducing effect of the hexadecylamine on the metal salts and the sulfur. The results of the elemental analysis show that the ratio of Zn:Cd in the particles after preparation (table 3-3) tend to match the Zn:Cd ratio present in the reaction vessel during preparation. The solubility product of CdS is 1×10^{-27} while that of ZnS is 2×10^{-25}. However, an organic solvent and not water is used in preparing the nanocrystals. The solvent coordinates the ions making the materials more soluble. For a normal co- precipitation reaction the precipitate should be richer in cadmium than zinc. Both ZnS and CdS are very sparingly soluble and there was an excess of sulphur in the reaction vessel during the preparation than either cadmium or zinc, therefore effectively all the zinc and all the cadmium will be present in the particulate form. The results of the elemental analysis obtained from both the electrochemical and the atomic absorption spectroscopy techniques are in agreement.

CONCLUSION

High quality $Zn_xCd_{1-x}S$ have been synthesized through the reaction of cadmium acetate, zinc acetate metal salts with elemental sulfur in dodecylamine at high temperatures. The absorption onset in the UV spectra of the $Zn_xCd_{1-x}S$ nanocrystals shifts to shorter wavelength with an increase in zinc molar ratio in the materials. This observed blue shift is a strong evidence for the formation of $Zn_xCd_{1-x}S$ nanocrystals through the intermixing of the wider band-gap ZnS (3.7 eV) [16] with narrow band-gap CdS (2.5 eV) [17]. HRTEM and SAED analysis confirms that these nanocrystals are crystalline in nature with particle sizes as determined by TEM of 6.6 ± 0.1 nm, 6.9 ± 0.3 nm and 7.2 ± 0.2 nm respectively. The results of the elemental analysis obtained from both the atomic absorption spectroscopy and the anodic stripping voltammetry techniques show that the quantities of Zn and Cd ions present in the nanocrystals after preparation tend to match the Zn and Cd ions present in the reaction vessel during preparation.

Acknowledgements
Financial support from the School of Chemistry and the University of Bristol is acknowledged. The authors thank Dr Roy Hughes of the Bristol Colloid Centre in the University of Bristol and Dr. D. Jason Riley of the Department of Materials at Imperial College London for their interest in and contributions to this work.

REFERENCES

[1] Alivisatos A.P., *Science*, **1996**, 271.
[2] Colvin V.L., Schlamp M.C., Alivisatos A.P, *Nature*, **1994**, 370, 354.
[3] Tessler N., Medvedev V., Kazes M., Kan S.H., Banin U., *Science*, **2002**, 295, 1506.
[4] Bruchez M.P., Moronne M., Gin P., Weiss S., Alivisatos A.P., *Science*, **1998**, 281, 2013.
[5] Chan W.C.W., Nie S., *Science*, **1998**, **281**, 2016.
[6] Wu B.J., Cheng H., Guha S., Haase M.A., Depuydt J. M., Meishaugen G., Qiu J., *Appl. Phys. Lett.*, **1993**, 63, 2935.
[7] Guha S., Wu B.J., Cheng H., Depuydt J.M, *Appl. Phys. Lett.*, **1993**, **63,** 2129.
[8] Harrison M.T., Kershaw S.V., Burt M.G., Eychmuller A., Weller H., Rogach A.L., *Mater. Sci. Eng.*, **2000**, 69, 355.
[9] Korgel B. A., Monbouquette H.G., *Langmuir*, **2000**, 16, 3588.
[10] Wang W., Germanenko I., El-Shall M.S., *Chem. Mater*., **2002**, 14 **(7)**, 3028.
[11] Kulkarni S.K., Winkler U., Deshmukh N., Borse P.H, Fink R., Umbach E., *Appl. Surf. Sci*, **2001**, 169, 438.
[12] Petrov D.V., Santos B.S., Pereira G.A.L., Donega C.D.M.. *J. Phys. Chem. B*, **2002**, 106, 5325.
[13] Zhong X., Feng Y.Y., Knoll W., Han M.Y., *J. Am. Chem. Soc*., **2003,** 125, 13559.
[14] Zhong X., Han M.Y., Dong Z.L., White T.J., Knoll W., *J. Am. Chem. Soc*., **2003**, **125**, 8589.
[15] Yu W.W., Qu L., Guo W., Peng X., *Chem. Mater*. **2003**, **15**, 2854.
[16] Cao Y.C., Wang J.H., *J. Am. Chem. Soc*. **2004**, **126**, 14336.
[17] Coran A.Y., *J. Appl. Polym. Sci*, **2003**, **87**, 24.