Sonochemical Synthesis of AgInS₂ Quantum Dots and Characterisation

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AgInS₂ (Silver Indium Sulphide) quantum dots of size ~ 1.4 nm have been prepared by sonochemical method using precursor complex. Dodecylamine has been used as capping agent. The Precursor complex, containing Silver, Indium metal ions and sulphur used for the synthesis of the quantum dots has been prepared by simple precipitation and filtration. Then the complexes have been irradiated under high intensity ultrasound to get small size AgInS₂ quantum dots within short reaction duration of ~ 5 minutes. The prepared quantum dots then have been characterised by XRD, UV-VIS spectroscopy, fluorescence spectroscopy and DLS analysis. The results show that AgInS₂ can be prepared by sonochemical method in small time period. From the UV-VIS absorbance spectroscopy the band gap of the prepared material calculated is found to be around 2.15 eV. Some physical parameters of the prepared material have also been calculated from XRD and UV-VIS spectroscopy using some empirical relations.

Keywords: Silver Indium Sulphide quantum dots, Sonochemical method, Characterisation, Band gap, Dislocation density.

1. INTRODUCTION

Semiconductor nanocrystals having quantum confinement effects on their electronic structures are called quantum dots (QDs). These show properties in between bulk semiconductors and discrete molecules. This may be due to the fact that small clusters have electronic structures having high density of states but not continuous bands [1]. Since the discovery of these particle by A. Ekimov in 1980, quantum dots have attracted significant research interests due to their application in a number of diverse fields such as biological imaging [2, 3, 4, 5], sensors [6, 7], solar cells [8, 9, 10], photo catalysts [11, 12], optoelectronic devices [13], photographic suspensions, xerography. The wide range of application of quantum dots may be attributed due to bright, stability and high extinction coefficient [14, 15]. Quantum dots makes them attractive target for photonic and electronic devices because of multiple exciton generation properties [16, 17, 18]. The application of multiple exciton generation has the prospective to attain maximum efficiency upto 44 % in 3rd generation Photovoltaic cells [19]. Among the various types of quantum dots the AgInS₂ quantum dots have special importance as solar energy materials because of direct band gap $n-$type Semiconductor, well matching to the solar Spectrum, high absorption coefficients, ecofriendly and stability [20, 21, 22]. So far as synthesis is concerned, the various methods for synthesis of AgInS₂ are (1) thermal decomposition of a single-source precursor or mixture or solution phase reaction [23, 24, 25]. Here the medium is heated above 1000 °C for long time either in N₂ or inert atmosphere. (2) Organometallic synthesis [26, 27]. Here also heating above 300 ⁰C is required. (3) Microwave hydrothermal synthesis [28] (4) sonochemical method [29] etc. So far as Sonochemical method is concerned, it is best and suitable for synthesis of quantum dots [1]. The main attraction of the Sonochemical method for synthesis of quantum dots are its simplicity, operating conditions (ambient conditions) and simple way to control the size of nanoparticles by varying the precursors concentrations in the solution [30]. The reaction time is very short and long time heating is not required. Ultrasound influences the chemical reaction, involving the formation, growth and collapse of bubbles in liquid. In this technique, sound waves of high frequency are passed through the slurry or solution of metal complex precursors. The bubble creation, growth and its collapse takes place in the liquid has been explained by Gedanken [31]. In our present work we have synthesised the Quantum Dots by Sonochemical method taking precursor complex and capping agent.

2. EXPERIMENTAL

2.1 Materials

Sodium diethyl dithio-carbamate, Silver nitrate, Indium nitrate, Ethanol, Dodecylamine, Methanol, Acetone and Chloroform used in the work were purchased from Sigma Aldrich, India (98.5 % purity). All chemicals were used without further purification. Aqueous solutions of the chemicals were prepared with Millipore deionised water purified by a Millipore Milli-Q system.

2.2 Synthesis of Precursor Complex

Ag-In-s precursor complex was prepared by mixing mixture solution (50ml) of silver nitrate (0.0125 M) and indium nitrate (0.0125 M) with 50 ml of 0.05 M sodium diethyldithiocarbamate solution with constant stirring. The precipitate formed (within one minutes) was collected by centrifugation, washed with millipore deionised water, dried and recrystallised then again dried at 60 ⁰C for one night to get powder of the precursor.

2.3 Synthesis of AgInS₂ Quantum Dots

The AgInS₂ Quantum Dots were prepared by sono-

chemical method taking the precursor complex and Dodecylamine. In this process, the complex (53 mg) and capping agent (10 ml) were taken in a 20 ml glass reactor. Then it was sonicated in the glass reactor using a probe sonicator (20 KHz, Sonic Vibro cell, USA) for 5 minutes in air atmosphere. The suspension was then kept at room temperature for 5 minutes. Then 5 ml chloroform and 5 ml methanol was added and centrifuged at 4000 rpm. The supernatant was then mixed with equal volume of methanol and again centrifuged at 7000 rpm to isolate the Quantum Dots. The resulted materials were then divided into two parts. One part is mounted in glass slide (2cm × 2 cm) for *XRD* and the other part was dispersed in chloroform for absorbance, photoluminescence and *DLS* studies.

2.4 Characterisation

The powder *X*-ray diffraction measurements (PXRD) were performed on a Siemens (Cheshire, UK) D5000 X-ray diffractometer using CuKα (λ = 1.5406 A) radiation at 40 kV and 30 mA with a standard monochromator using a Ni filter. Dynamic light scattering (DLS) characterizations were done by a Malvern Zetasizer Nano series (Nano ZS). UV-VIS datas were recorded on a UV-VIS-DRS Spectrophotometer Carry-5000. Time-resolved fluorescence measurements were carried out using HORIBA Jobin Yvon spectrofluorometer.

3. RESULTS AND DISCUSSION

Compositional studies of the prepared precursor complex have been performed using EDAX. The datas obtained in weight percentage show that the complexes have been formed around the nominal composition. EDAX data shown in Table 1 gives the compositions of prepared precursor sample in weight percentage.

Table 1 – EDAX data of precursor Complex

Complex name	Element	Weight percentage	
		Element (%)	Atomic (%)
Silver indium diethyldithio-carbamate	CK	33.5	55.91
	NK	16.79	24.4
	SK	24.87	15.55
	AgL	14.95	2.79
	InL	9.88	1.73
	Total	100	100

The Crystal structure of the AgInS$_2$ quantum dots was analyzed using powder *X*-Ray diffraction (XRD), with a the Siemens (Cheshire, UK) D5000 *X*-ray diffractometer (Fig 1). The results shows peaks at $2\theta = 27.5°$ and $44.9°$ which were assignable to diffractions corresponding to (112) and (204) plane of tetragonal structure [32]. In both the peaks, broadening was observed. The broadening of XRD peaks can arise in principle due to different reasons such as the presence of mircrostrain, small size of the crystallites, and instrumental effects. However, the broadening observed here is much higher than the instrumental broadening

(< 0.1°). Thus the major contribution to the line broadening may be arising from small size effect or due to strain. In case of an ideal crystal of infinite size the diffracted intensity in all directions other than those satisfying the Bragg condition will be zero as a result of destructive interference. However, for crystals of small size, this destructive interference will not be complete, leading to a broadening width of the diffraction peaks
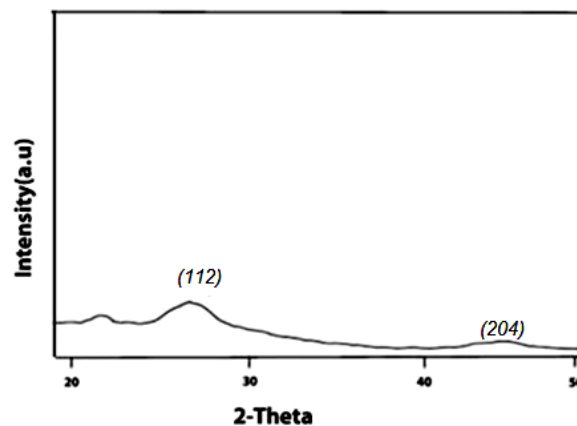

Fig. 1 – XDR pattern of AgInS$_2$ quantum dots

The crystallite size of the quantum dots has also been calculated by Scherrer formula equation 1:

$$D = \frac{k\lambda}{\beta\cos\theta} - 1 \qquad (1)$$

Where k = shape factor, λ = *X*-ray wavelength, β = full width at half the maximum intensity (FWHM), θ = Braggs angle and D = mean size (diameter) of particle and the size was found to be ≈ 1.4 nm

The absorbance spectra were taken using the UV-VIS-DRS Spectrophotometer Carry-5000 at a range of wavelength (200 nm-900 nm) of the AgInS$_2$ quantum dots (Figure 2A).
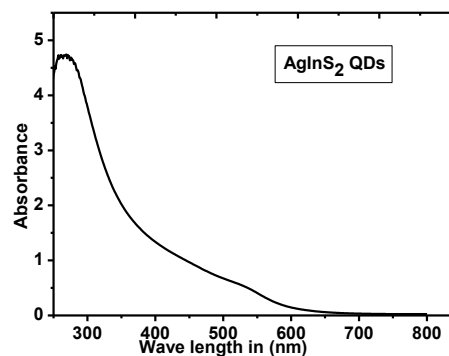

Fig. 2A – UV-Visible Absorbance spectra of AgInS2 QDs

The nature of spectrum shows that The Quantum Dots absorb light in the entire visible region. The onset of absorption peak was observed at 650 nm with a maximum at 270 nm which is blue shifted from the bulk AgInS$_2$ [23]. This may be attributed due to quantum confinement effects.
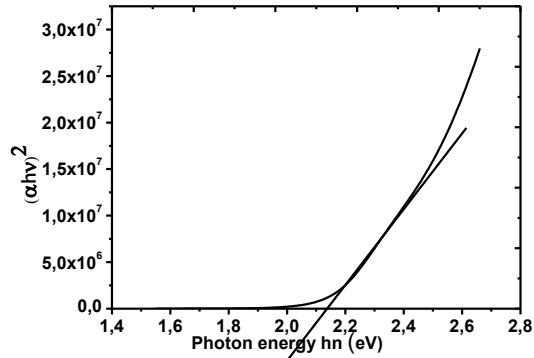
Fig. 2B – For calculation of band gap

The band gap energy of the quantum dots has been calculated by extrapolating the linear portions of the $(\alpha h\nu)^2$ against $h\nu$ graph on the $h\nu$ axis to $\alpha = 0$. The obtained band gap energy value has been found to be 2.15 eV (figure 2B). As compared to bulk band gap of 1.98 eV, the band gap obtained for $AgInS_2$ quantum dots was widened approximately 0.17 eV due to quantum size effect [33]. The quantum size effect might be more in small quantum dots [34].

The hydrodynamic diameter was measured by dispersing the quantum dots in chloroform and the diameter of the $AgInS_2$ quantum dots was found to be 2.5 nm (Figure 3) which indicate that the smaller sized crystallites as estimated from XRD are slightly aggregated in the suspension.
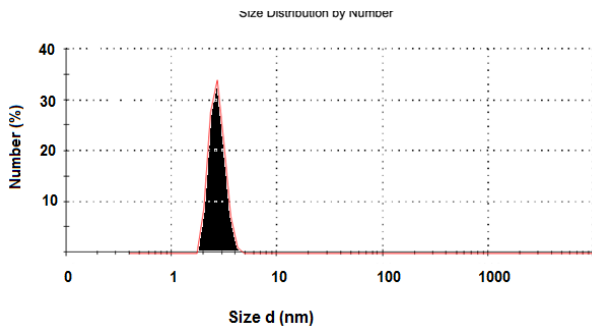

Fig. 3 – Hydrodynamic Sixe Distribution by DSL for $AgInS_2$ QDS

The PL spectrum of the sample was taken at 350 nm excitation wavelength (Figure 4). The Quantum Dots show a broad peak at 750 nm. From the peak, the band gap of the $AgInS_2$ Quantum Dots has been calculated and found to be 1.66 eV [35]. The broad peak of Photoluminescence spectra may be attributed by intragap levels created by structural defects [22] and the smaller band gap value might be due to electron hole pair recombination.

Some physical parameters have also been calculated form XRD UV-VIS spectroscopy using equation (2-5) [36, 37, 38]. The calculated values are given in Table 2.
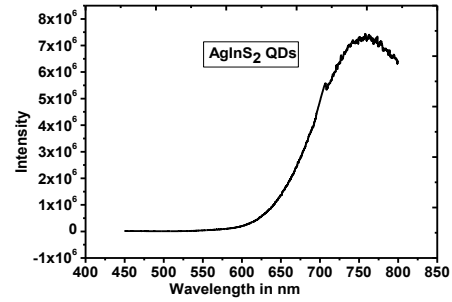

Fig. 4 – Fluorescence spectra of AgInS2 QDs

$$\varepsilon_{str} = \frac{\beta \cot \theta}{4} - 2$$

$$\delta = \frac{1}{D^2} - 3$$

$$n = n^0(1 + ae^{\beta E_g}) - 4 \qquad (2)$$

$$\varepsilon_r = n^2 - 5$$

Where ε_{str} = average strain, δ = dislocation density, n = refractive index, ε_r = dielectric constant, β = FWHM, θ = Bragg angle, D = average size and $n^0 = 1.73$, $a = 1.9017$, $\beta = 539$

Table 2 – Physical Parameters of *AgInS2* quantum dots.

Parameter	Value
Average Strain	51.5×10^{-3}
Dislocation Density	$51 \times 10^{16} cm^{-1}$
Refractive Index	2.763
Dielectric Constant	7.745

4. CONCLUSION

A facile synthesis of non-toxic $AgInS_2$ Quantum Dots containing non-toxic elements was investigated by use of the sonochemical method taking diethyldithiocarbamate complex of metal ions as precursor. The prepared sample was characterized by DLS, XRD and UV-Vis and fluorescence spectroscopy to confirm the formation of quantum dots. Importantly this synthetic approach eliminates the requirement of heating at high temperature for the decomposition of the complex to form quantum dots and hence should be useful in synthesizing other compositions as well.

5. ACKNOWLEDGEMENTS

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