

# Strong Quantum Confined Lead Sulphide Quantum Dots using Ionic Reaction and Their Properties

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Lead sulfide quantum dots have been synthesized from a cost- effective and facile chemical method namely ionic reaction using lead nitrate and sodium sulphide as precursors in aqueous solutions. The as prepared nanocrystals are characterized for their optical, structural and electrochemical properties using optical absorption spectroscopy, transmission electron microscopy and cyclic voltammetry respectively. The PbS quantum dots have an average size of 6 nm. The strong size quantization is observed from cyclic voltammetry and absorption spectroscopy.

Keywords: Lead sulphide; Quantum dots; Single crystalline; TEM; SAED

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## Introduction

Nanomaterials with their potential applications in various fields have been the most explored functional materials for the past three decades. In view of this, zero-dimensional (0D) semiconductor nanostructures called quantum dots (QDs) have attracted the attention of scientists due to their unique optical and electronic properties from both the fundamental and application perspective. These are nanocrystals that have acquired their class mostly because of their size regime being comparable to that of Bohr excitonic radius<sup>1</sup> of the material.

QDs possesses a size dependent and discrete electronic energy spectra due to quantum confinement effect<sup>24</sup> which gives rise to a series of properties in them.<sup>5</sup> Innumerable types of quantum dots like CdS,<sup>6</sup> CdSe,<sup>7,8</sup> InP,<sup>9</sup> PbS,<sup>10,11</sup> PbSe<sup>11</sup>etc.<sup>10-12</sup> are synthesized by researchers and have a wide range of applications. Among metal chalcogenides, lead chalcogenides, especially PbS and PbSe QDs have been interesting nanostructures due to their characteristic property for demonstration of multiple exciton generation<sup>13-15</sup> (MEG), where a single photon can yield three excitons, hence are useful in highly efficient photo voltaic conversion.<sup>16</sup> Also, PbS quantum dot sensitized solar cell gave a very high photocurrent.<sup>17</sup> In view of these, the synthesis and application of PbS has assumed to have a great importance. PbS is a IV- VI semiconductor with Bohr excitonic radius of 18 nm. It has a bulk band gap of 0.41  $eV^{18}$  that can be tuned up to 1.5eV at the OD level and hence it shows a strong quantum confinement effect. PbS has its applicability in Sensors,<sup>19</sup> photography,<sup>20</sup> IR detector<sup>21</sup> (due to absorption Near IR region), Solar absorber<sup>22</sup> etc.

Ample techniques have been developed by the researchers to synthesize PbS QDs like hydrothermal,<sup>23-26</sup> sono-chemical,<sup>27</sup> micro emulsion<sup>28</sup> and organometallic methods.<sup>29,30</sup> Out of which organometallic

Advanced Physics Laboratory, Department of Physics, Savitribai Phule Pune University, Pune-07 \**E-mail:* pathan@physics.unipune.ac.in method gives a better size distribution but the formation of PbS nanocrystals involves a hazardous and unstable chemicals like (TMS)<sub>2</sub>S trioctylphosphine, so it is significant to find a simple route to synthesize the narrow size distributed of quantum dots. Besides the previous reports, PbS QDs have resulted in either polycrystalline<sup>5,31</sup> or single crystalline synthesized with the help of a coordinating agent.<sup>32,33</sup>

In the present report, we have synthesized PbS QDs by employing a very simple ionic reaction technique, that doesn't require high vacuum, large power supply or hazardous chemicals. It differs from other technique of decompositions of metal complexes due to its slow generation of chalcogenides and allowing them a slow formation of QDs, which was supported by ultrasonication using lead nitrate and sodium sulphide as precursors in aqueous media, without involving any harmful chemicals or by-products. Sonication is significant stage in the synthesis that produces cavitations effect in the solution, which is equivalent to pressures of few hundreds of atmosphere and that has been provided after the addition of precursors in order to avoid the agglomeration of PbS.<sup>34</sup> This is mainly in order to avoid the hazardous chemicals, capping agents and its effect. The synthesized single crystalline PbS QDs has been characterized using Transmission electron Microscopy (TEM), High Resolution TEM (HRTEM), Optical absorption spectroscopy (UV-Vis) and Cyclic Voltammetry (CV).

# **Experimental**

Lead Nitrate  $Pb(NO_3)_2$  and Sodium Sulphide  $Na_2S$  were purchased from SRL Chemicals Ltd, India and used without further purification. 0.02 M of  $Pb(NO_3)_2$  and  $Na_2S$  (very well dispersed) solutions were prepared in double distilled water (DDW) at room temperature separately. These solutions were then added drop by drop (0.5 ml lead-  $Pb^{2+}$  followed by Sulphur-  $S^2$ ) to large aqueous flask containing 400 ml DDW, till colour variations were observed under probe sonication. As the concentration of precursor's increases, the deviation in colour of the solutions varies from pale yellow, yellow, brown and shady brown in the aqueous bath. The samples were named as A, B, C and D respectively.

The UV-Vis spectra of liquid samples (A-D) are acquired with

JASCO V-670 in the wavelength range of 400 nm to 1400 nm, whereas TEM and HRTEM images are captured with TECNAI 200 G2, operated at 200 kV for which sample was loaded on copper grid by drop casting at room temperature.

The electrochemical nature of species that diffuses to electrode surface can be studied by cyclic voltametric measurement at room temperature by using Potentiostat/Galvanostat (IVIUM: Vertex). The CV measurement of as synthesized aqueous PbS QDs was carried out with platinum as a counter electrode, glossy carbon as a working electrode and Ag/AgCl as a reference electrode. The desired scan rate is of 100 mV/sec, to the switching potential which then reverses the direction and return to initial potential, ranges from -2 V to +2 V with a step of 10 mV/sec.

#### **Result and Discussion**

Due to drop wise addition of the precursors in the large aqueous bath, the concentration of both precursor increases and results in colour variation probably hinting at the particle size enhancement. The steps shown in Fig. 1 are repeated till the colour variation was observed in aqueous bath with a continuous stirring under probe sonication. The rate of reaction increases the rate of agglomeration; more the addition of the precursors, greater is rate of reaction. Most of the researchers have synthesized PbS quantum dots with irregular shapes<sup>35</sup>, Ludmila Bakueva et al<sup>36</sup> formed in aqueous pot, with thiols as a capping agent, Dawei Deng et al used dihydrolipoic acid (DHLA) as a stabilizer<sup>37</sup> Dong et al<sup>5</sup> have used sodium sulphide as a precursors for synthesis of PbS QDs, but they have also used an Oleic acid as coordinating agent for controlling growth, stabilizing the resulting colloidal dispersion and electronically passivating the semiconductor surface. Low toxicity and simple inexpensive way is the advantage of aqueous synthesis of QDs over organic medium.38 The large size shows increase in the relative absorptivity in the blue region of the spectrum due to higher effective density of states. Lee etal reported that highly monodisperse gold metal nanoparticles were synthesized by conventional ultrasonic bath and that has significant effect on particle size and morphology.<sup>39</sup>

In the present report, the capping agent is strictly avoided, as an effect the stability of QDs reduces up to 100 hrs. But unlike in other methods, we have controlled the growth of PbS QDs by large aqueous bath and probe sonication. Thus, growth is not hasty to form bulk and hence it finally results in well-defined PbS QDs.

Initially with the dropwise addition of  $Pb^{2+}$  and  $S^{2-}$  precursors, the colour of the solution varies with time from colourless to pale yellow as in Fig. 1 and further addition of precursors changes the colour of the solution from pale yellow-yellow- brown to shady brown. A prompt nucleation occurs when there is rapid injection of lead nitrate and sodium sulphide into aqueous bath shown in Fig. 1(After), which is marked by an immediate black colour observed in the reaction vessel. In a hasty addition it was critical to attain a narrower size distribution.



Fig. 1 Colour variation in synthesis process for sample A-D.

The reaction involved in the bath can be given in a simple way,  $Pb(NO_3)_2$  and  $Na_2S$  were primarily dissolved (0.02 M) in aqueous, it will form a  $Pb^{2+}$ ,  $(NO_3)^2$ ,  $Na^+$  and  $S^2$  free ions respectively and equally both the precursors were dissolved in a large aqueous bath drop wise, it yields a pure form of PbS QDs as follows,

$$Pb_{(aq)}^{2+} + 2(NO3)_{(aq)}^{-} + 2Na_{(aq)}^{+} + S_{(aq)}^{2-} \rightarrow PbS_{(aq)}^{+} + 2NaNO_{3(aq)}^{-}$$

It is interesting to note that absorption of Photons is followed by electron-hole pair generation in PbS QDs. The optical absorption spectra in Fig. 2a reveals that, the first excitonic peak is observed at 1155 nm and it is sharp with absorption in near infrared region indicating the formation of PbS QDs and have a narrow size distribution, which is as evidenced from TEM.

The large blue shift in absorption spectra (Sample A-D) shown in the inset, that may be attributed to the quantum confinement effect. The second and third excitonic peaks are detected at 961 nm and 812 nm respectively.



Fig. 2 a) UV-Vis absorption spectra, b) Optical band gap for PbS QDs.

The average radius<sup>19,40</sup> of PbS QDs obtained from the absorption spectra are 2.55 nm. The excitonic peak positions for all samples are same. From sample A to D, as capping agent is avoided, the large agglomeration of PbS particles observed in aqueous bath with increase in the precursor concentration, the absorption spectra intensity for the second and third excitonic peaks reduces. This specifies, as the particle

size increase, the sharpness of absorption spectra intensity decreases for all excitonic peaks from sample A onwards, that affects the nature of excitonic peaks, which increases with the colour deviation. The optical band gaps for samples A, B, C, D are calculated as 2.36 eV, 2.19 eV, 2.09 eV and 1.86 eV respectively, from Absorbance square vs. Energy plot, as shown in Fig. 2 b and the comparison with electrochemical band gap is given in Table 1. The optical band gap shows a strong quantum confinement effect.

The monodisperse QDS with varying size can be prepared by system optimization of synthesis condition such as reaction time and ratio of  $Pb^{2+}$ :  $S^{2-}$ .

TEM image Fig. 3, gives the spherical shape for PbS QDs with the size of the particle in the range of 4 - 9 nm, the average particle size of PbS QDs was found to be 6 nm; the inset shows a particle size distribution (histogram).

Formation of QDs is confirmed from HRTEM image and selected area electron diffraction (SAED) pattern as shown in Fig. 4(a), since the interplanar spacing (0.347nm) observed here is in agreement with the standard PbS data. SAED pattern of the sample shown in Fig. 4(b) for the as-synthesized QDs clearly confirms the formation of predominantly

single nanocrystalline structures. The SAED pattern of PbS QDs display the diffraction fringes for those that match with the PbS cubic phase and labelled rings have been identified as corresponding to the planes (220), (222), (400), (440), (511) [JCPDS no.: 05-0592].

The output of cyclic voltammetry is a plot of current versus potential, through the 0.02M concentration solution of PbS. The semiconductor QDs have discrete energy levels and are expected to undergo electron transfer, facilitated through the valence band and conduction band edges. Haram etal first time shows the correlation between optical band gap and electrochemical band gap.<sup>41</sup>

According to Haram *et al*<sup>42</sup>, the gap between cathodic and anodic peak increases with decrease in size as a consequence of the quantum confinement effect. Hence it is being revealed that quantum confinement effect can be observed in the as synthesized PbS QDs. The colour variation was observed in the samples from A to D as the agglomeration of the particles were formed in an aqueous bath, band gap decreases that confirm change in particle size with addition of precursors. The oxidation and reduction potentials are calculated from the CV curve as shown in Fig. 5, the electrochemical band gap is calculated as the difference in cathodic and anodic peak has values which are very well



Fig. 3 TEM image of PbS QDs. (Inset: Particle size Distribution)





Fig. 4 (a) HRTEM and (b) SAED pattern for PbS QDs (Sample A).

Sample	E <sub>ox</sub>	E <sub>red</sub>	$\Delta E = E_{ox} - E_{red}$ (eV)	Optical Band gap E <sub>g</sub> (eV)
Α	1.474	-1.289	2.763	2.36
В	1.16	-1.15	2.31	2.19
С	1.11	-0.99	2.10	2.09
D	1.04	-0.91	1.95	1.86

Table 1 Details of the band gap for PbS quantum dots from CV and Absorption spectroscopy.

in agreement with optical band gap which is given in Table 1.

The band gap of PbS varies over a large range i.e. from 0.41 eV for bulk to 2.76 eV for quantum dots, this clearly reflects a strong quantum confinement in a large aqueous bath, with a controlled size without capping agent. So PbS QDs have ability to extend their absorption region in near IR region, with a wide application in Schottkey solar cell, depleted heterojunction cell, quantum dot sensitized solar cell etc.

## Conclusion

A facile, hassle free route was developed to synthesize a single crystalline PbS QDs with an average diameter of 6 nm without a capping agent. The QDs showed superior absorption properties, the colour variation in the reaction vessel indicates formation of different sized QDs. The size and single crystalline nature of PbS QD's was confirmed from TEM and SAED analysis. The strong confinement effect fulfils the requirement for fabrication of sensors, photovoltaic device etc.

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