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Effect of Polymer Concentration on Size and Optical Properties of PbS Quantum Dots Embedded in PVA

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The properties of materials drastically change when matter performs a transition from 1*D*, 2*D*, 3*D* to 0*D*. The quantum dots (QDs) of lead sulphide (PbS) embedded into polyvinyl alcohol (PVA) are synthesized *via* one-pot synthesis chemical method. Different concentrations of organic matrix are taken, and the quantum dot size and optical properties are studied for each case. The specimen has been analysed by UV–Vis absorption spectroscopy, x-ray diffraction study, high-resolution transmission electron microscopy, and fluorescence spectroscopy. The effects of increasing the PVA capping concentration on the structural and optical properties are reported.

Властивості матеріялів різко змінюються, коли речовина виконує перехід від 1*D*-, 2*D*-, 3*D*- до 0*D*-виміру. Квантові точки сульфіду Плюмбуму (PbS), вбудовані в полівініловий спирт (ПВС), синтезуються за допомогою хемічної методи синтези «в одному горщику». Беруться різні концентрації органічної матриці, а для кожного випадку вивчається розмір квантових точок і оптичні властивості. Зразок був проаналізований за допомогою абсорбційної спектроскопії у видимій й ультрафіолетовій областях світла, рентґеноструктурного дослідження, електронної мікроскопії з високою роздільчою здатністю та флюоресцентної спектроскопії. Повідомляється про вплив підвищення обмежувальної концентрації ПВС на структурні й оптичні властивості.

Key words: PbS, quantum dots, polyvinyl alcohol, one-pot synthesis, nanotechnology.

Ключові слова: PbS, квантові точки, полівініловий спирт, синтеза «в одному горщику», нанотехнології.

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1. INTRODUCTION

Synthesis of semiconductor quantum dots and their applications in the field of electronics is the topic of interest among many researchers in recent times [1]. The nanoparticles of lead sulphide, PbS, have shown an increased demand in the last decade due to their unique physical properties. PbS nanoparticles are generally prepared in colloid solutions or embedded in transparent solid media such as glass, zeolite and polymer. Several sophisticated methods like molecular beam epitaxy (MBE), radio-frequency sputtering (RF) and liquid-phase epitaxy (LPE) are generally used to prepare semiconductor quantum dots. However, most of them are expensive and requires sophisticated lab set up [2]. Chemical method is found to be very attractive as they are relatively simpler and less expensive. The size of quantum dot (QD) is controlled by controlling the concentration of capping agent PVA. The quantum dots are fabricated in the interstitial gaps of the PVA, in a controlled manner. The PVA restricts the size growth of QDs, but itself does not take part in the reaction. The physical properties of PVA are shown in Table 1, and the structure of PVA is shown in Fig. 1 [3].

Thus, in this work, we have used simple chemical method of one-pot synthesis on different concentrations of polyvinyl alcohol (PVA), followed by the characterization using UV–Vis spectroscopy, XRD, HRTEM, and fluorescence spectroscopy. In this method, the quantum dots are synthesized directly in the aqueous medium [4], *i.e.*, to obtain the water-soluble nanoparticles. The one-pot synthesis

TABLE 1. Physical properties of polyvinyl alcohol (PVA).

Physical properties	PVA
Melting point, °C	200
Specific gravity	1.30
Specific heat (J/gm·K)	1.66
Thermal conductivity (W/m·K)	2.0
Resistivity (Ohm·cm)	$(3.1–3.38)\cdot10^{7}$
pH	neutral or slightly acidic
Dielectric constant	2.0

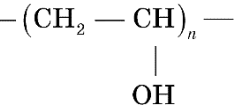

Fig. 1. Structure of polyvinyl alcohol (PVA).

is experimentally simpler and has a higher reproducibility and low cost. Lead acetate and sodium sulphide are used for the synthesis of PbS QDs. As both the $Pb(AcO)_2$ and Na_2S are readily soluble in water, hence, they form strong electrolytes in solution form. When these two solutions are mixed, the main reaction that occurs is

$$Pb^{2+} + S^{2-} = PbS. \quad (1)$$

The lead sulphide formed here is poorly soluble in water and is collected as precipitate. Other by-products of the reactions are soluble in water.

2. EXPERIMENTAL

To prepare 0.2 M PVA solution, 0.215g of PVA was added to 25 ml distilled water, and then, the solution was stirred above 60°C until the solution become clear, and then, kept overnight to obtain a viscous transparent solution. 1.89 g of lead acetate ($PbC_2H_3O_2$) is added to 25 ml of distilled water to make 0.2 M lead acetate solution. The lead acetate solution was then added to the polymeric solution with stirring at 60°C for 3 hours by applying magnetic stirrer. The pH value of solution was of 6. Solution was given one day standing time to obtain a viscous transparent solution. In a similar way, 0.1 M, 0.15 M, 0.25 M, and 0.3 M PVA solutions are also prepared. After one day, 0.2 M sodium sulphide was prepared by dissolving 0.39 g sodium sulphide (Na_2S) in distilled water, then, added to each Pb/PVA matrix solution and stirred at 60°C for 3 h. Lead sulphide nanocrystals' formation is indicated by appearance of black colour precipitate (Fig. 2). Lead sulphide nanocrystals' precipitate was then separated and washed three times by distilled water and air dried [4, 6].

Fig. 2. Prepared PbS QDs.

The synthesized samples have been tested by UV–Vis spectrophotometer, x-ray diffraction spectrometer, energy dispersive x-ray (EDX) study and high-resolution transmission microscope (HRTEM). Energy dispersive x-ray (EDX) study and PL study are also done to understand the doping characteristics in quantum dots. UV–Vis light absorption spectra were obtained using Perkin Elmer Lambda 35 ultraviolet visible (UV–Vis) spectrophotometer. X-ray diffraction (XRD) patterns (Bruker AXS, x-ray source—CuK_α) and high-resolution transmission electron microscopy (HRTEM) ones (JEM 1000 C XII) were obtained. Perkin-Elmer LS 45 fluorescence spectroscope at 350 nm wavelength excitation within the range of

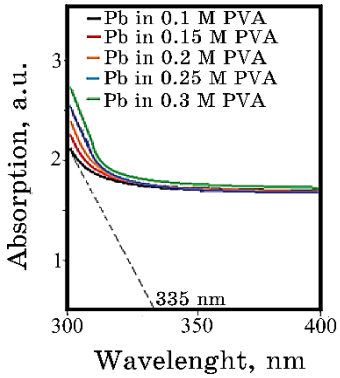

Fig. 3. UV–Vis absorption spectra of PbS quantum dots at different PVA concentrations.

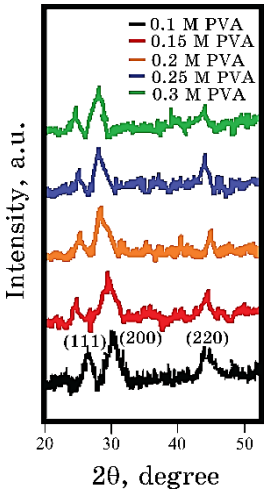

Fig. 4. XRD of PbS quantum dots at different PVA concentrations.

800–1200 nm is used for PL study.

3. RESULTS AND DISCUSSIONS

Figure 3 shows the optical absorption spectra of fabricated PbS quantum dots. The blue shift in the absorbance edge is a proof of QD formation. Particle size is estimated using hyperbolic band model [7]:

$$R = \sqrt{\frac{2\pi^2 h^2 E_{gb}}{m^* \left(E_{gn}^2 - E_{gb}^2\right)}}, \tag{2}$$

where R is the quantum dot radius, E_{gb} is the bulk band gap, E_{gn} is the quantum-dot band gap, h is Planck's constant, m^* is the effective mass of electron of the specimen. Here, the bulk band gap (E_{gb}) for PbS is of 0.41 eV, and electron effective mass at room temperature is of $0.175m_0$ [8], where m_0 is the electron rest mass.

Figure 4 shows the x-ray diffraction (XRD) pattern of PbS quantum dots. XRD investigation shows that pure PbS shows peaks at 28° (111), 30° (200) and 45° (220). The change in PVA concentration does not result in any significant change in the XRD pattern of PbS. All detectable peaks corresponding to (111), (200) and (220) planes belong to the pure cubic phase of PbS (JCPDS no. 78–1901) [9]. From x-ray diffraction study, average particle size (crystallite size) is calculated by using Scherrer formula [10]:

$$D = \frac{0.9\lambda}{W \cos\theta}, \tag{22}$$

where λ is the wavelength of x-rays (0.1541 nm), W is FWHM (full width at half maxima), θ (theta) is the glancing angle, and D is particle diameter (crystallite size). Considering all the peaks (2θ in degree) in the x-ray diffraction pattern, the average crystallite (quantum dot) size has been assessed, and average size is determined. The results of absorption and XRD are shown in Table 2.

Figure 5 shows the photoluminescence spectrum of different concentrations of PVA-capped PbS nanoparticles. The emission wavelength peaks are at around wavelength of 690 nm. This emission wavelength has been shifted towards to the red, when compared to the absorption spectra of the PbS quantum dots. This emission is due to the recombination of electron and hole pairs (EHPs) [11]. As absorption is a direct transition phenomenon whereas fluorescence involves trap state (or states) as a result, the value of absorbed wavelength is different from emitted wavelength. As the emission band gap is less than absorption band gap, hence, the emitted wave-

TABLE 2. Data from UV–Vis and XRD spectra of PbS quantum dots at different PVA concentrations.

PVA concentration, M	Absorption edge, nm	Band gap E_{gn}, eV	QD radius, nm	XRD peaks	Avg. QD radius, nm
0.10	335	3.70	3.2	111, 200, 220	3.42
0.15	329	3.77	3.15	111, 200, 220	3.31
0.20	321	3.86	3.07	111, 200, 220	3.19
0.25	315	3.90	3.02	111, 200, 220	3.11
0.30	305	4.06	2.9	111, 200, 220	3.03

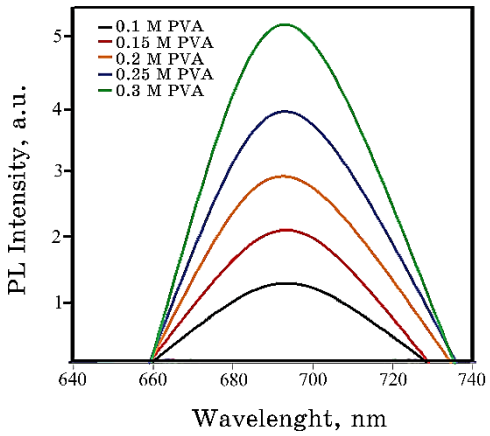

Fig. 5. Photoluminescence spectra of PbS quantum dots at different PVA concentrations.

length is always greater than that of absorbed one (the red shift) [3, 12].

The high-resolution transmission electron microscopy (HRTEM) images of the synthesized PbS quantum dots are shown in Fig. 6. The size of all quantum dots lies within 10 nm.

4. CONCLUSIONS

PbS quantum dots have been synthesized for different PVA capping matrix concentrations using simple chemical method of 'one-pot synthesis'. The optoelectronic and crystalline properties of the synthesized PbS quantum dots have been studied in details by using various characterization techniques. The absorption spectra, x-ray diffraction spectra, HRTEM images, and the photoluminescence emission spectra are studied for each concentration of PVA capping

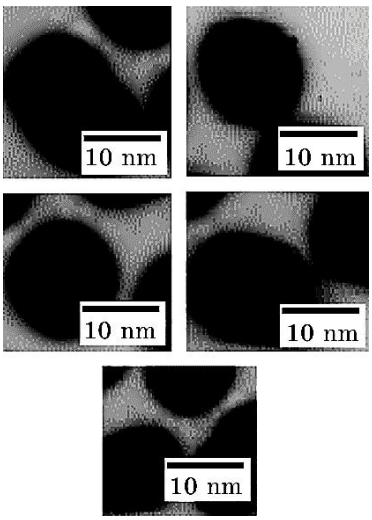

Fig. 6. HRTEM images of PbS quantum dots at different PVA concentrations.

on PbS quantum dots.

It can be observed from the study that size of the quantum dots can be varied by changing the doping concentration of capping matrix. With increasing concentration of PVA, the QD size decreases, absorption edge shifts towards lower wavelength and photoluminescence intensity increases. Thus, by changing the PVA concentration, we can easily control the QD size, as well as the absorption and photoluminescence emission spectra. Manipulating these properties, the quantum dots can be used for various other applications.

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