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Optical Properties of DNA Induced PbS Nanoparticles and Application in Bio-Sensors

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Abstract

In this communication, we present synthesis of starch capped PbS nano particles conjugated with Calf-Thymus DNA and their characterization by XRD, HRTEM, UV-Vis absorption and PL spectroscopy. The XRD pattern of PbS showed polycrystalline nanoparticles (NP) having cubic Structure was also confirmed from HRTEM and the average particle size of the PbS nanoparticles was found 15 nm. The UV absorption spectra exhibited distinct blue shift with respect to their respective bulk absorption edges, which is attributed to strong quantum confinement. The band gap of the PbS nanoparticles increases from 2.39 eV to 4.25 eV with decrease the molar concentration from 0.1M to 0.01 M. DNA capped nanoparticles exhibited further increase in band gap, which may be attributed to the change in dielectric constant around the nanoparticles due to capping. The PL spectra of the PbS nanoparticles exhibited slight blue shift and enhancement of intensity after conjugation with DNA. This is due to stabilization of nanocomposites governed by bio-molecules and that of Dexter energy transfer with the effective charge separation. This result shows the applicability of the PbS nanomaterials in development of efficient bio markers and biosensors.

Keywords: *Nanoparticles, Starch, Agglomeration, DNA, Bio-sensors.*

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1.0 Introduction

Application of semiconductor quantum dots (QDs) in biological field has been the subject of intensive research interest during the last decade. The optical properties of QDs largely depend on size of the nanocrystals. PbS is an IV-VI semiconductor with a cubic rock salt structure and a narrow band gap of 0.41 eV with continuous optical absorption at shorter wavelengths. Most of the reported work observed that the band gap of PbS is increase from 0.41 to 5.4 eV with reduction in crystallite size from 20 to 2 nm [1].Compared to II-VI semiconductors, PbS QDs exhibit a strong quantum confinement effect. As a result, PbS QDs with narrow size distribution exhibit a distinct absorption spectrum with large blue-shift [2].Capping agents or stabilizers plays most important role to achieve strong quantum confinement effect. Semiconductor nanoparticles has greater importance because of their size tunable optical and electrical properties for potential applications in nanoelectronic devices, such as light emitting diodes (LED), solar cells, nanoscale lasers, photo detectors, drug delivery, sensors and biological applications [3,4]. The PbS nanoparticles have various limitations for application as they are mostly toxic and bio-incompatible, unstable, uncontrolled crystal growth. Uses of biological materials are gaining importance to overcome these limitations as they are nontoxic and environmental friendly [4].In the present work, PbS NPs below 10 nm have been synthesized through CBD technique using potato starch as a capping agent and those were conjugated with DNA. The structural morphologies and optical properties of the synthesized materials exhibit the possibility of use in development of biological labelling and bio – sensors.

2.0 Experimental details

There are different methods for synthesizing nano-crystalline materials but the Chemical Bath Deposition (CBD) technique is relatively less expensive and suitable for large scale synthesis with widernano crystal size and shape. A clear well dispersed starch solution (3%wt) from potato starch powder was used as stock solution prepared with constant stirring at temperature (60^0C) and maintained for 6 hours. Lead acetate was separately added to an aqueous solution (3%) of starch with constant stirring at room temperature to obtain

respective metal ion solution. The solutions were left for 24 hours to get a transparent liquid indicating complete dissolution of lead acetate. The pH of the solution was maintained at around 11.0 by slowly adding NH_4OH solution drop wise. The equal molar solution of thiourea was added to each of the metallic complex solutions. The amount of the thiourea solutions were maintained 2:1 with lead acetate. Within a few seconds colour of the mixture solution of lead complex and thiourea turned into dark brown.

The reaction mechanism for synthesis of PbS is as follows [5]:

$$Pb(CH_3COO)_2.3H_2O \rightarrow Pb^{2+} + 2CH_3COO^- + H_2O$$

$$Pb^{2+} + 4NH_3 \rightarrow Pb(NH_3)_4^{2+}$$

$$SC(NH_2)_2 + 2OH^- \rightarrow S^{2-} + CH_2N_2 + 2H_2O$$

$$Pb(NH3)_4^{2+} + SC(NH_2)_2 + 2OH^- \rightarrow PbS + 4NH_3 + CH_2N_2 + 2H_2O$$

DNA solutions (5 ml) of Calf- Thymus of 0.5 M molarity was mixed with each solution under constant stirring for several hours to allow the nanoparticles completely. In this way, the prepared samples were conjugated with DNA. The starch was expected to act as cross linker to bind DNA molecule on the surface of the synthesized composites. The samples were characterized by XRD, HRTEM, UV-vis absorption spectroscopy and Photoluminescence spectroscopy.

3.0 Results and discussion

The X-Ray Diffraction (XRD) pattern of starch capped PbS NPs prepared at 0.1 M and 0.01 M are shown in Fig.1. The synthesized film is polycrystalline in nature having cubic rock salt type structure, which is confirmed from standard data (JCPDS-PDF No: 78-1901). Broadening of diffraction peak confirms the formation of nano rang sized particles. The prominent peaks are found at (2θ) 25.9^0, 29.9^0, 43.0^0, 51.0^0 and 53.4^0 corresponding to (111), (200), (220), (311) and (222) planes. Rock salt type structure is quite common in chemically synthesized lead sulphide [6].We assume overall line broadening is due to size only and the average crystalline sizes *(D)* are calculated by Debye – Scherer formula-

$$\mathbf{D = k\lambda/\beta\cos\theta} \qquad \mathbf{(1)}$$

where β is the full width half maximum (FWHM) of the most preferred prominent peak along (111) and k is a constant. The crystalline sizes are found13.6nm and 15.9 nm for molarities 0.1 and 0.01 respectively (Table 1).

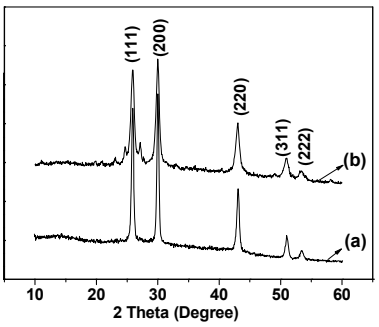

Fig 1: XRD pattern of PbS film synthesized at (a) 0.01 M and (b) 0.1M

Table 1: Structural parameters of Potato starch capped PbS nanoparticles prepared at 0.1M and 0.01 M

Sample Molarities (M)	2θ/degree	d/A^0	(hkl)	D/nm
0.1	25.9	0.176	(111)	13.6
	29.9	0.154	(200)	
	43.0	0.113	(220)	
	51.0	0.099	(311)	
	53.3	0.096	(222)	
0.01	25.9	0.176	(111)	15.9
	29.9	0.154	(200)	
	43.0	0.113	(220)	
	51.0	0.099	(311)	
	53.3	0.096	(222)	

The HRTEM images and SAED pattern of PbS nanoparticles synthesized at 0.1 M and 0.01M are shown in fig 2. The average particle sizes of synthesized PbS NPs are15 nm.

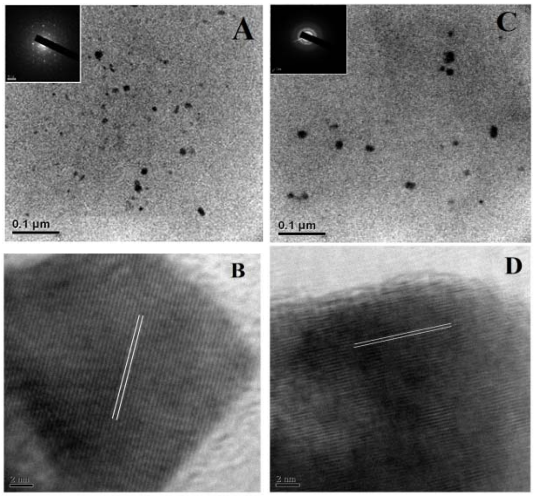

Fig 2: (A) & (C) HRTEM images of PbS nanoparticles at 100 nm scale with SAED pattern synthesized at 0.1 M and 0.01 M respectively, (b) & (d) HRTEM images of PbS nanoparticles at 2 nm synthesized at 0.1 M and 0.01 M respectively.

The fundamental absorption which corresponds to the electron excitation from the valence band to the conduction band can be used to determine the nature and value of the optical band gap. The relation between the absorption coefficient (α) and the independent photon energy ($h\upsilon$) can be written as [7]

$$(\alpha h\upsilon)^{1/n}=A(h\upsilon-E_g) \quad (2)$$

where A is a constant, E_g is the band gap of the material and the exponent n depends on the types of transition. The values of n depends for direct allowed, indirect allowed and direct forbidden transmissions are n = ½, 2 and 3/2 respectively. The absorption spectra and Tauc plots for (a) PbS at 0.1M, (b) PbS at 0.01M, (c) PbS+DNA at 0.1M , (d) PbS+DNA at 0.01M are shown in figs 3 and 4. The direct band gaps are obtained from the linear portion of Tauc's plot $(\alpha h\upsilon)^2$ vs $h\upsilon$, which is lie in the range 2.39 – 4.25 eV (Table2).

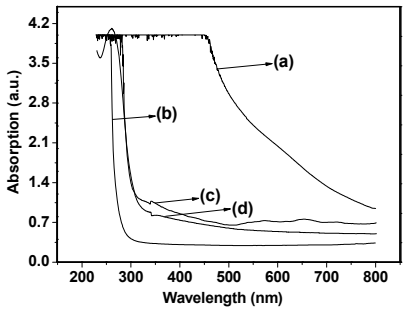

Figure 3: UV absorption for (a) PbS at 0.1M, (b) PbS at 0.01M, (c) PbS+DNA at 0.1M , (d) PbS+DNA at 0.01M.

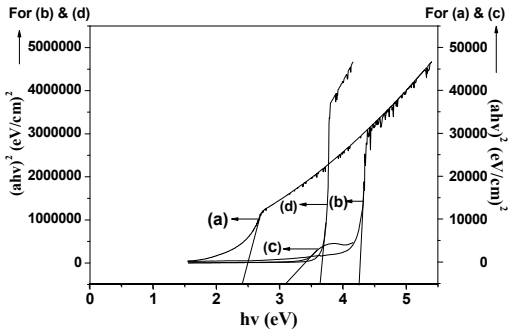

Figure 4: The tauc plots for (a) PbS at 0.1M, (b) PbS at 0.01M, (c) PbS+DNA at 0.1M, (d) PbS+DNA at 0.01M.

These direct band gaps are much higher than that of the respective bulk values of PbS (0.41 eV). This is because of the strong quantum confinement effect of PbS nanocrystals. . It is clear from fig. 3 that the band gap slightly increases with decrease of its molarities as well as when conjugated with DNA. This is due to the fact that particle size is expected to decrease with the reduction of molarities, which implies that better quantum confinement takes place at lower molarities. DNA induced PbS nanocomposites exhibit further contribution in bringing the quantum confinement in this work. Hence the conjugate of nanocomposites with the bio-molecules play a role in determination of surface passivation as well as stabilization of nanoparticles [8].

The photoluminescence spectrum of starch capped PbS and PbS+DNA nanocomposites prepared at 0.1M and 0.01M are depicted in fig. 5.

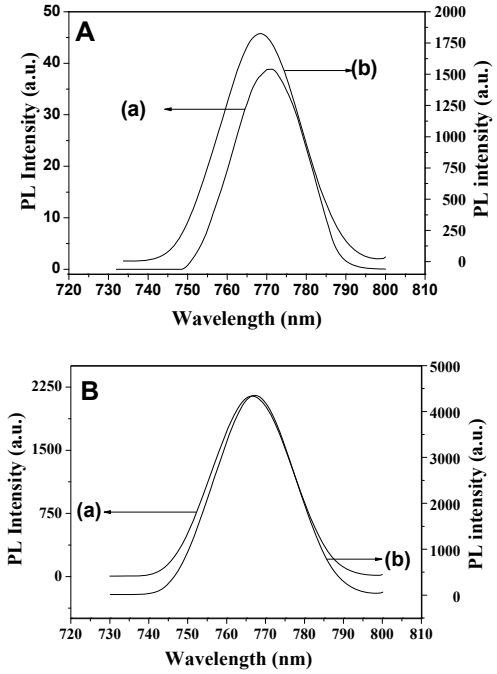

Fig 5: PL spectra for (a) PbS and (b) PbS+DNA synthesized at (A) 0.1M and (B) 0.01M

PbS shows infrared emission in the range 766 – 770 nm with enhance PL intensity. Most of the workers reported the PL emission of PbS in the range 700 – 1600 nm that yielded a high quantum PL efficiencies dissolved in DNA and OVA (ovalbumin) protein solutions [9]. All the PL peaks of PbS have been blue shifted as in case of absorption spectra and the intensity of the photoluminescence peak are enhanced on lowering the molar concentration from 0.1 M to 0.01 M as well as conjugation with DNA. Hence it may be inferred from the above optical studies that PbS – DNA is more favorable for application as biological labels because of their infrared emission. Besides PbS – DNA be an effective donor in the development of biosensor using Fluorescence resonance energy transfer technique (FRET). In FRET, the energy is transferred from donors to acceptors provided the distance between them is 1 – 10 nm [10]. DNA conjugated quantum dots (QDs) makes a probe, when linking with an acceptor. To make an efficient probe, a high luminescent donor is required. However, further studies are required for a detailed characterization of optical properties of PbS NPs conjugated with DNA

Table 2: UV - vis absorption and PL emission characteristics of DNA induced and uninduced starch capped PbS NPs. Here, M: Molarity E_g: Band gap measured from Tauc's plot, λ_{nbg}(nm) : near band gap emission of PL spectra, I(a.u.): Intensity of PL spectra.

Sample	Molarity	Eg (eV)	λ_{nbg}(nm)	I(a.u.)
PbS	0.1	2.39	770	39
PbS	0.01	3.11	769	1832
PbS+DNA	0.1	4.25	768	2154
PbS+DNA	0.01	3.63	766	4363

4.0 Conclusion

The PbS nanostructures have been successfully synthesized by the CBD technique using different molar concentration. XRD showed that the structure of the material obtained was cubic phase and the material possesses polycrystalline in nature. HRTEM and corresponding SAED studies reveal the single crystalline cubic PbS particle with average diameter 15 nm. UV – Vis absorption studies show that the direct band gaps are lying in the range 2.39 – 4.25 eV for PbS. PL spectra showed emission in the range 766 – 770 nm and enhancement in emission intensity of the nanostructures depended on the molar concentration of PbS. Here a slight blue-shift in the emission spectra was also observed. We have a high luminescent donor, which is applicable for biosensors and biological application. This approach could be used to generate various bio – function of nanoparticles with high sensitivity and tailorable optical properties in straight forward and combinational fashion.

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