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OPTICAL, STRUCTURAL AND SURFACE MORPHOLOGICAL STUDIES OF N-METHYLANILINE CAPPED LEAD SULPHIDE NANOPARTICLES

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Abstract. N-Methylaniline (N-MA) capped lead sulphide (PbS) nanoparticles have been synthesized by wet chemical route. N-Methylaniline serves as a good capping agent for synthesizing nanoparticles in the quantum confinement regime and it acts as a passivated layer of the PbS particles. Synthesized N-Methylaniline capped PbS nanoparticles has been characterized by X-Ray powder diffraction (XRD), UV-Visible spectrophotometry, FTIR spectroscopy, transmission electron microscopy (TEM), Energy dispersive X-Ray absorption spectroscopy (EDAX) and photoluminescence spectral studies. Size of the PbS nanoparticles observed from TEM is 5 nm which are in uniform distribution. The synthesized PbS nanoparticles exhibit strong blue shift in the optical spectrum.

1. INTRODUCTION

Semiconductor nanoparticle synthesis below 10 nm is of great importance because of their size tunable optical properties for potential applications [1-5] in nanoelectronic devices, such as light emitting diodes (LED), solar cells, nanoscale lasers, photodetectors, *etc.* Optical properties of the semiconductor nanoparticles enhances when compared to that of its bulk size [6-8]. In the semiconductor nanoparticles, optical properties enhancement have been attributed to the modification of surface morphology [6]. When the size of the nanoparticles are below Bohr radius, its lead to the quantum confinement effect [9]. In order to reduce the size of the particles below Bohr radius, passivation of the surface of the particles at the time of formation is essential. The optical properties of the semiconducting materials are tunable while achieving the quantum confinement region [10]. To achieve the quantum confinement regime, introduction of capping agents, stabilizers and dopants are important. Amines [11] and thiols [12] serve as a very good capping agent to synthesis the semiconductor nanoparticles below Bohr radius. The introduction of the capping agent plays a vital role in the nanoparticle synthesis [13,14].

PbS is an important IV-VI semiconductor. It has narrow bandgap (E_g = 0.41 eV) and its excitonic bohr radius is 18 nm. It can be used in various of fields, such as fabrication of solar cells, IR detectors, light emitting diodes, optical communications, *etc.* PbS nanoparticles have been synthesized by different techniques such as solvothermal, electrodeposition, chemical methods, microwave irradiation, *etc.*

In the present work, PbS nanoparticles below the size of the Bohr radius have been synthesized by simple wet chemical route by using

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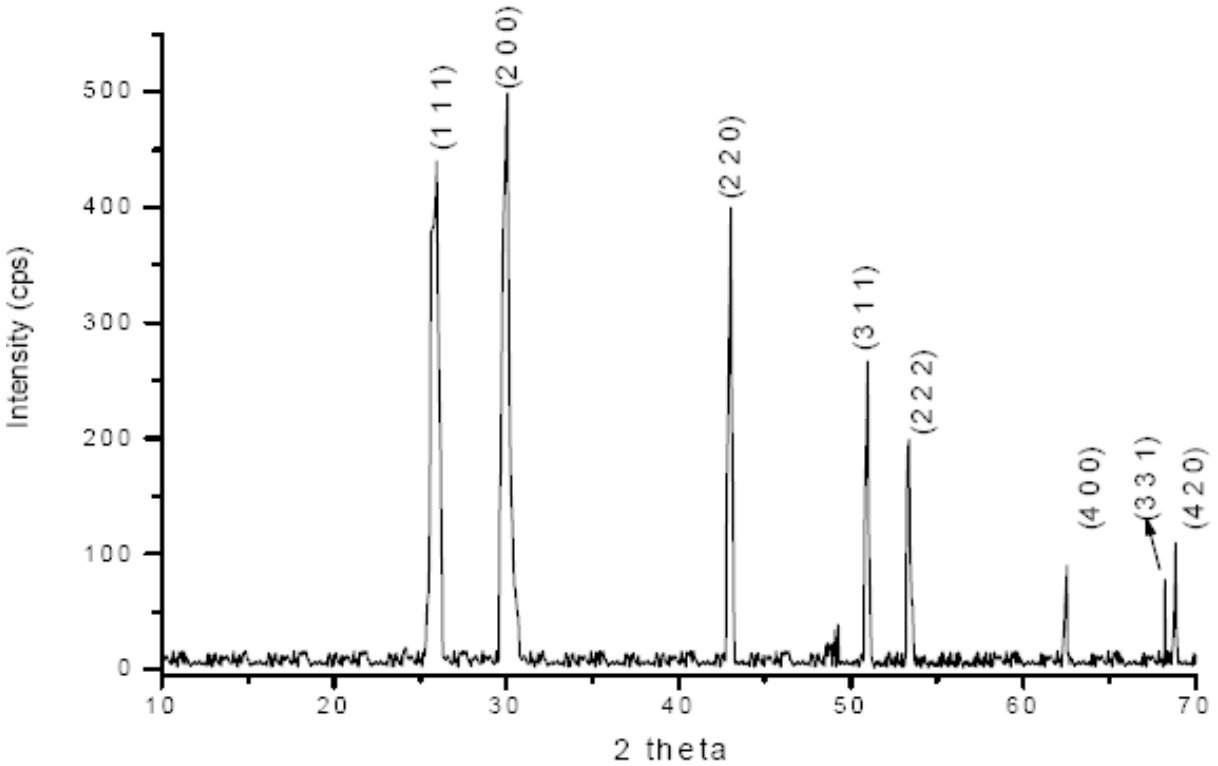


Fig.1. XRD pattern of N-Methylaniline capped PbS nanoparticles.

N-Methylaniline as a capping agent. Morphology and size of the synthesized PbS nanoparticles were obtained by transmission electron microscope. Optical properties have been investigated by UV visible and photoluminescence spectral studies.

2. EXPERIMENTAL

2.1. Sample preparation

All reagents used in the synthesis were analytical grade and used without further purification. In a typical experiment to synthesis PbS nanoparticles, 0.2 mol of lead acetate was dissolved in 50 ml of ethanol. This solution was stirred vigorously by using magnetic stirrer. After 10 minutes, 0.2 mol of thioacetamide was added to the above solution. Further, 0.2 mol of N-Methylaniline was added drop by drop to the above mixture to avoid agglomeration of the particles. The role of the N-Methylaniline is to passivate the surface of the PbS nanoparticles during the reaction. After 2 hours, colour of the solution turns into black. This indicates that the formation PbS nanoparticles. This reaction was continued upto 8 hours to form homogeneous solution. The resultant solution was centrifugalized and the resultant product washed with distilled water for several times. Finally, the product has been dried at 80 °C for 12 hours. The synthesized PbS nanoparticles have been characterized by powder XRD, TEM, FTIR, UV-Visible, and photoluminescence spectral studies.

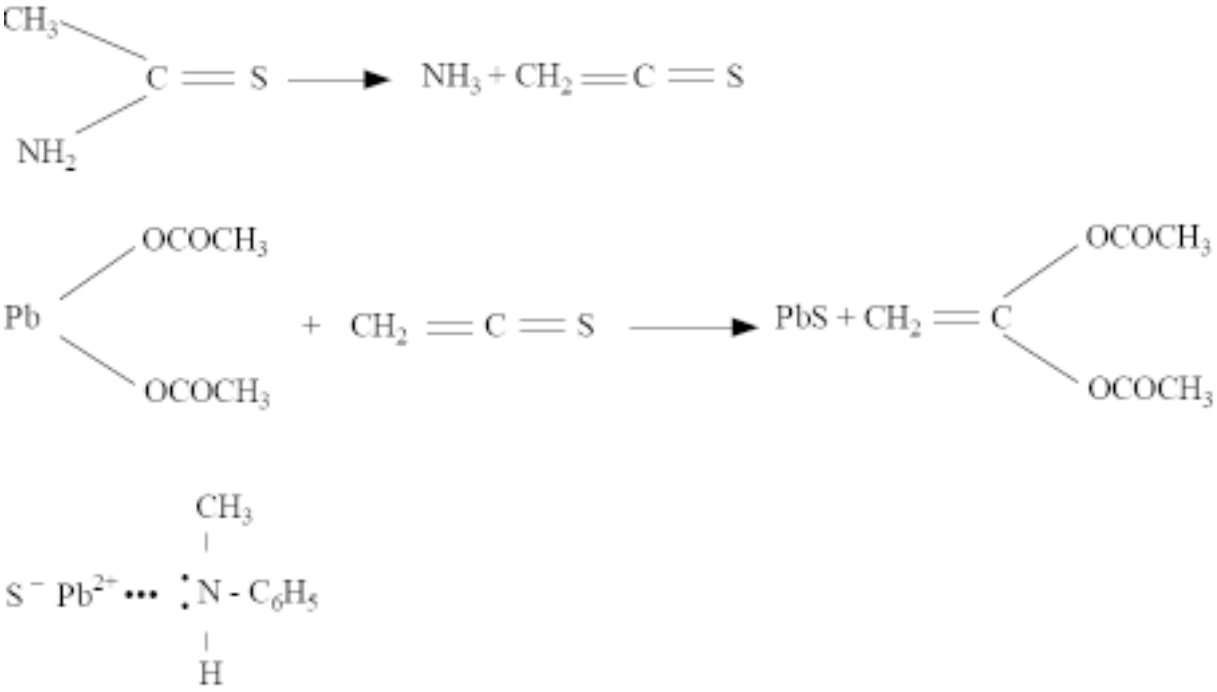
2.2. Characterizations

The N-Methylaniline capped lead sulphide nanoparticles were characterized by X-ray diffraction (XRD) using X'Per PRO (PANalytical), advanced X-ray Diffractometer with Cu *K*α radiation (λ = 1.5406 Å) in 2q ranging between 20° and 80° at the scanning rate of 0.017° per 20.67 sec's. Transmission electron microscope photographs were taken with JEM 3010(JEOL) transmission electron microscope with an accelerating voltage of 200 KeV. The FTIR spectrum was recorded using Perkin Elmer spectrophotometer in the wavelength region 4000 cm^{-1} – 450 cm^{-1}. Optical properties of N-Methylaniline capped PbS nanoparticles were measured using Perkin Elmer lamda5 UV-Visible spectrophotometer. The photoluminescence

spectrum is obtained from Flurolog- 3spectrometer (Jobin Yvon) range 200-900 nm. The synthesized material has been dispersed in ethanol for all characterizations.

3. RESULTS AND DISCUSSIONS

3.1. Formation mechanism of N-Methylaniline capped PbS nanoparticles



Formation of PbS nanoparticles capped by N-Methylaniline as follows, in the above reaction, lone pair of electrons present in the nitrogen atom of N-Methylaniline was donated to the vacant orbital of the Pb^{2+} in the PbS. The nitrogen atom forms a co ordinate bond with lead.

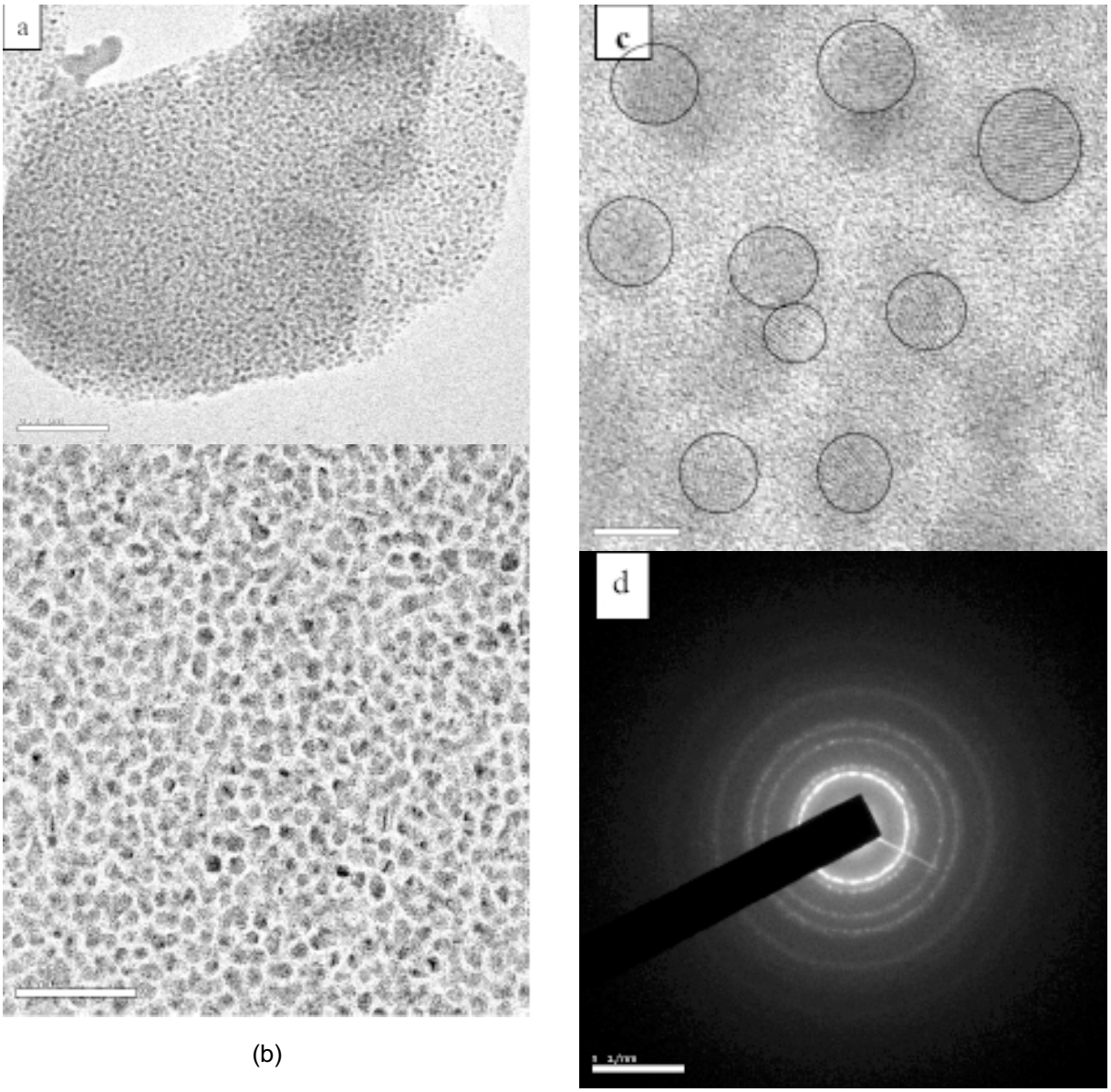
3.2. Structural and surface morphological studies

Fig. 1. shows the XRD pattern of N-Methylaniline capped PbS nanoparticles. The sharp peaks of the XRD pattern indicate that the synthesized PbS nanoparticles are well crystalline. All the diffraction peaks can be indexed to face centered cubic phase of PbS with calculated lattice constant *a*=5.936 Å. It is in good agreement with the standard value (JCPDS file no. 5-592) and no peaks due to impurities are found.

The TEM observation for N-Methylaniline capped PbS nanoparticles is shown in Fig. 2a. The resolution of this image was taken at the scale of 100 nm. From the micrograph, it is seen that the size distribution of the N-Methylaniline capped PbS nanoparticles are uniform. The localized TEM micrograph of N-Methylaniline capped PbS nanoparticles is shown in Fig. 2b. The resolution of this image was taken at the scale of 50 nm. It clearly shows that these particles are unaggregated in the entire film. The average size of the PbS nanoparticles, observed from TEM is 5 nm which are in uniform size distribution. The morphology of the N-Methylaniline capped PbS nanoparticles are spherical. The average size of the N-MA capped PbS nanoparticles is smaller than the excitonic bohr radius (18 nm) of bulk PbS, which is confirmed by TEM.

Fig. 2c shows the HRTEM image of the N-Methylaniline capped PbS nanoparticles. The resolution of this image was taken at the scale of 5 nm. The existence of lattice planes from the HRTEM image further confirms the crystallinity of N-Methylaniline capped PbS nanoparticles. It can be clearly seen that the morphology of the N-Methylaniline capped PbS nanoparticles are exactly spherical and all the particles are easily distinguishable. It demonstrates that all the particles are free from agglomeration.

Fig. 2e shows the SAED pattern of an area containing some nanoparticles. The rings of the SAED pattern indicate that the synthesized PbS nanoparticles exhibit monodispersity in the particle size. The



(b)

Fig. 2. (a) TEM image (Scale bar 100 nm). (b) Localized TEM image (Scale bar 50 nm). (c) and (d) HRTEM(Scale bar 5 nm) images of N-Methylaniline capped PbS nanoparticles, (e). SAED pattern of N-Methylaniline capped PbS nanoparticles.

rings of the SAED pattern can be indexed with the cubic phase of the XRD pattern of the N-Methylaniline capped PbS nanoparticles.

3.3. Optical properties of N-Methylaniline capped PbS nanoparticles

UV visible spectrum has been widely used to characterize the semiconductor nanoparticles. As the particle size decrease, absorption wavelength (λ_{max}) will be shifted to shorter wavelength, since the band gap increases for the nano sized particles. This is the quantum confinement effect of the semiconductor nanoparticles. The absorption co-efficient of the bulk PbS is 3020 nm. UV Visible pectrum of N-Methylaniline capped PbS nanoparticles is shown Fig. 3a. In this spectrum, λ_{max} is observed at 350 nm. This indicates that the absorption shift towards the shorter wavelength, because of the particle size reduction. From this spectrum, it is observed that the N-Methylaniline capped PbS

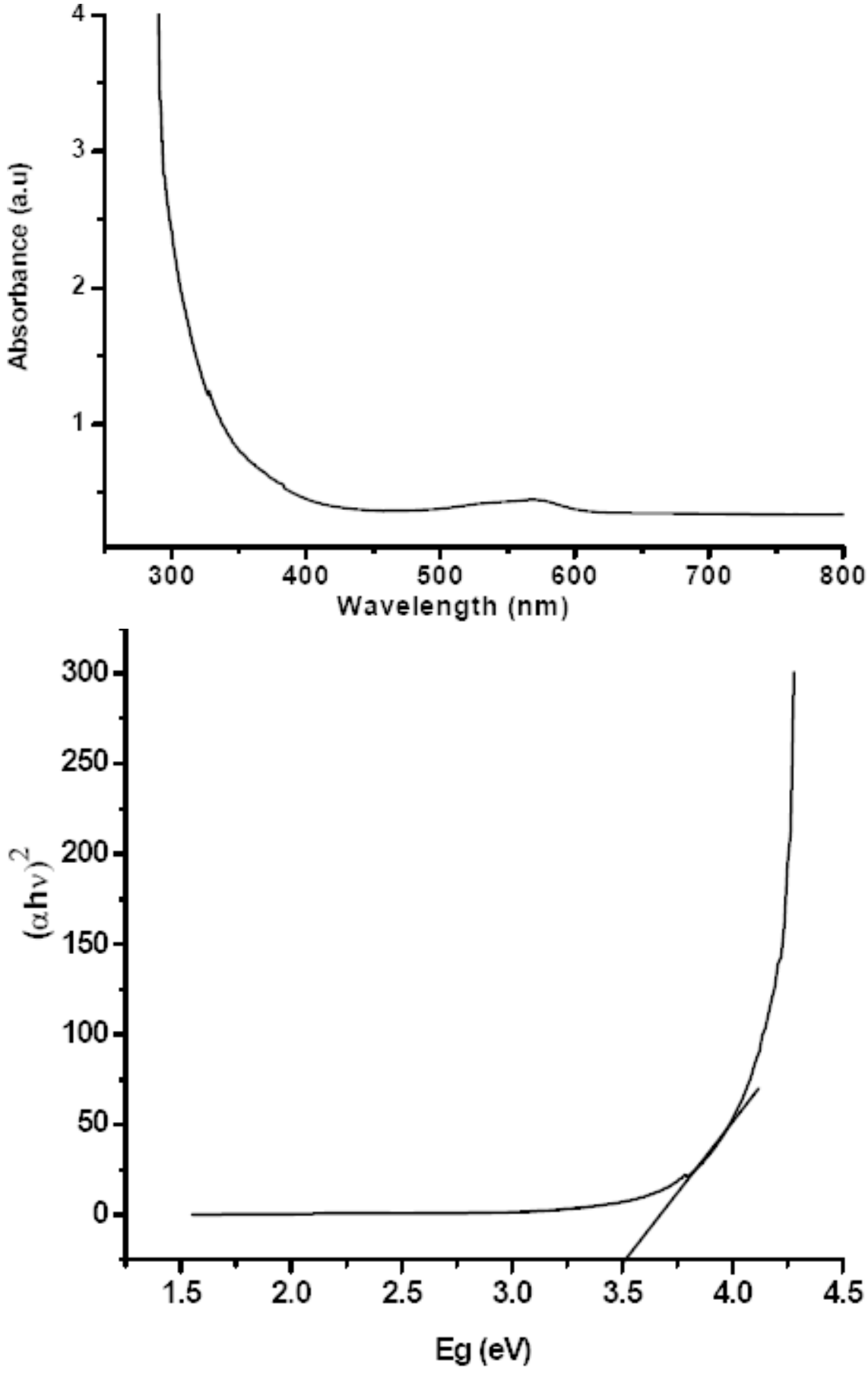


Fig. 3. (a) UV Visible spectrum and (b) of N-Methylaniline capped PbS nanoparticles.

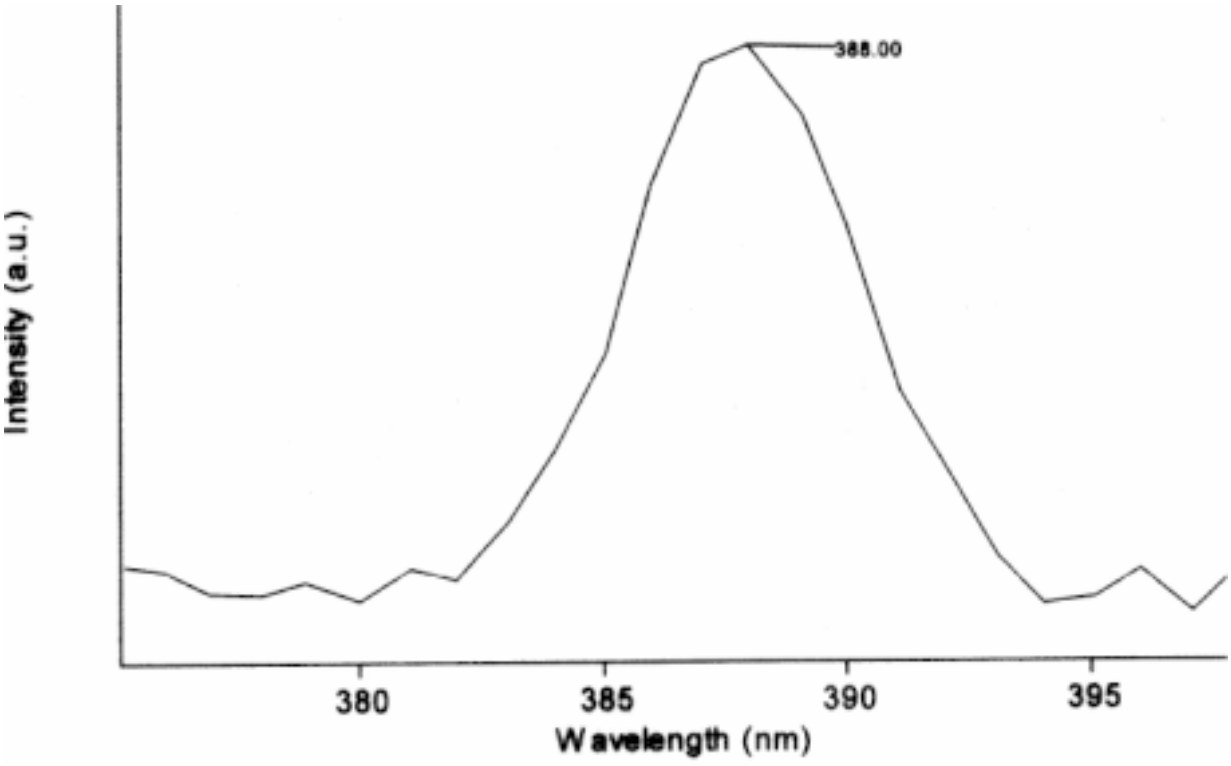


Fig. 4. Photoluminescence spectrum of N-Methylaniline capped PbS nanoparticles.

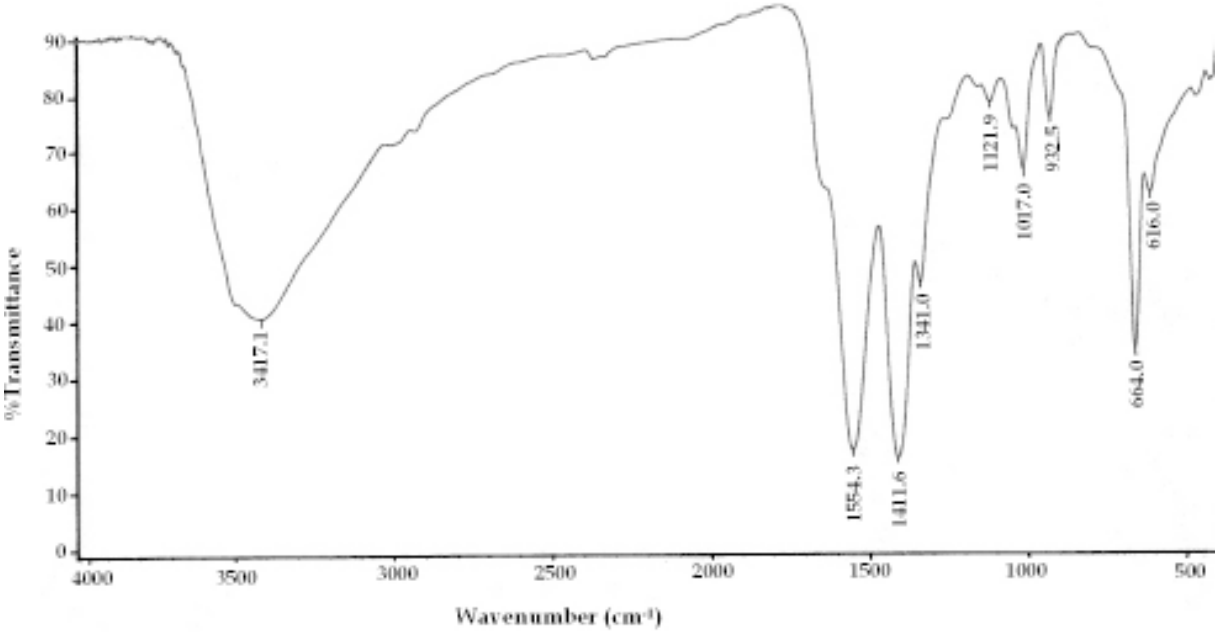


Fig. 5. FTIR spectrum of N-Methylaniline capped PbS nanoparticles.

nanoparticles exhibit the significant blue shift. This is an indication of strong quantum confinement. From UV spectrum, the band gap of the N-Methylaniline capped PbS nanoparticles have been calculated as 3.56 eV. It shows that the optical band gap of this material was highly enhanced. This reveals that, when the size of the particle is reduced to very low, the energy states separation is too high (i.e, energy gap). Further, it is confirmed by plot of E_g vs $(\alpha h\gamma)^2$ is shown in Fig. 3b.

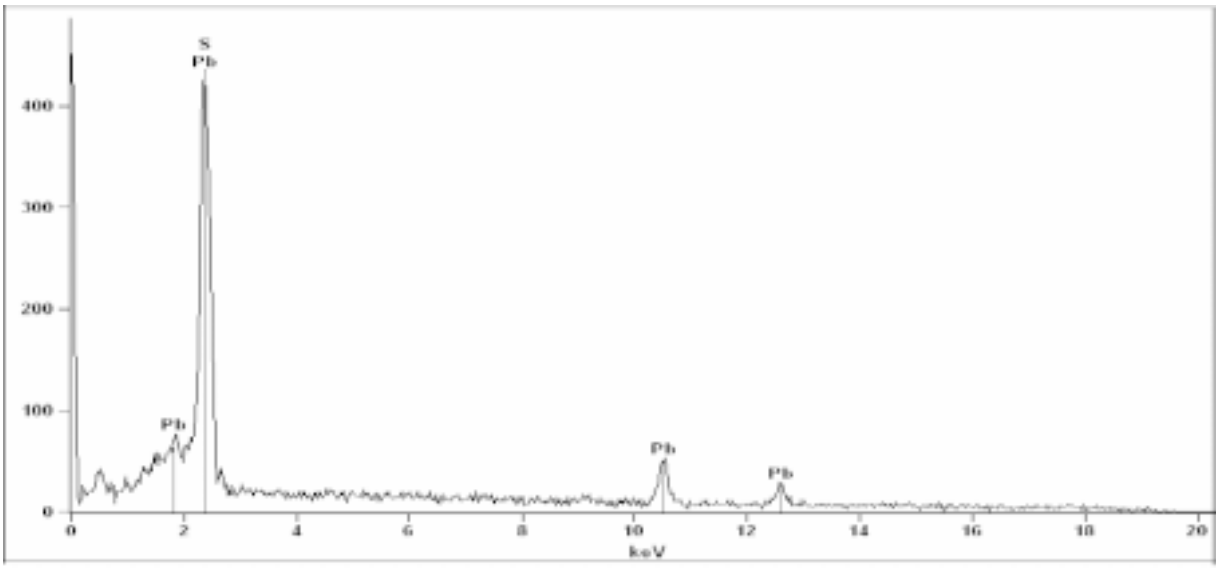


Fig. 6. Energy dispersive X-Ray absorption (EDAX) analysis of N-Methylaniline capped PbS nanoparticles.

Fig. 4. shows the photoluminescence spectrum of N-Methylaniline capped PbS nanoparticles. The emission wavelength is peaking at 388 nm. This emission wavelength peak shifted towards to the blue when compared to the bulk PbS. This emission is due to the recombination of electron and hole pair. Intensity of the photoluminescence has been increased due to the surface passivation of PbS nanoparticles by N-Methylaniline molecules. This blue shift of the N-Methylaniline capped PbS nanoparticles demonstrate the strong quantum confinement. The absorption wavelength was observed at 350 nm (in Fig. 3) and the emission wavelength was observed at 388 nm. The difference between the absorption and emission peak wavelength is 38 nm. This indicates the emission associated with the transition of electrons from trap state to conduction band (or valence band).

3.4. Spectroscopic investigations of N-Methylaniline capped PbS nanoparticles

The FTIR spectrum of N-Methylaniline capped PbS nanoparticles is shown in Fig. 5. In this spectrum, N-H asymmetric absorption band occur at 3417 cm^{-1}. This shows that N-Methylaniline molecules were binded with PbS nanoparticles. The region 3417 cm^{-1} gets broadened due to the presence of quinonoid ring formation. Other two peaks at 1554 cm^{-1} and 1341 cm^{-1} can be attributed C=N and C-H stretching respectively.

Fig. 6. shows the EDAX analysis of the synthesized product. It reveal the presence of Lead and Sulfur in the product. Strong signals were observed for Pb and S. Further it demonstrates that the synthesized product is PbS.

4. CONCLUSION

PbS nanoparticles capped with N-Methylaniline have been synthesized in gram quantities. The particle size observed from TEM is around 5 nm which are in uniform size distribution. The particles exhibit spherical morphology. Further, N-Methylaniline helps to synthesize the PbS nanoparticles below Bohr radius. The optical properties of the synthesized N-Methylaniline nanoparticles are highly enhanced and it shows the significant blue shift. Synthesized PbS nanoparticles can be used in quantum confinement applications.

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