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Synthesis of PbS Nanoparticles and Its Potential as a Biosensor based on Memristic Properties

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ABSTRACT

Quantum dots are nearly spherical nanocrystals that have unique optical property which are in intermediate in size between bulk semiconductor and individual atom. Lead sulphide (PbS) nanoparticles are synthesized by the reaction between lead nitrate and sodium sulphide. This paper proposes a detection method of bacterial sample based on memristic properties of semiconductor quantum dots. In this case, PbS nanoparticle is considered for its good fluorescent property. PbS nanoparticle were synthesized and characterized by UV –visible spectroscopy, PL, XRD, SEM and HRTEM. The antimicrobial activity of Pbs and CdS quantum dots are observed in this paper. The potential application of these quantum dots as a biosensor is examined by conjugating bacterial stain *E-coli* and *S. aureus* and examining the current –voltage characteristics with *E. coli*.

1. Introduction

Nanotechnology is an important field of science and technology. As the synthesis and characterization of nanoparticle has become possible, it opens a new door for the benefit of the society. Among them, quantum dots are the semiconductor nanocrystals which are having special optical properties due to their reduced size (2-10 nm). Synthesis and application of quantum dots are also in demand due to their unique optical as well as chemical properties. Lead sulphide (PbS) is an important IV-VI group semiconductor having narrow direct band gap 0.41 eV at room temperature (300 K). Research on PbS naoparticles are growing on demand because of its exciton Bohr radius which is 18 nm at room temperature. Having high dielectric constant (ε_0=169 at 300 K) as well as high carrier mobility leads to PbS nanoparticles exhibits strong quantum size effect despite of having relatively larger size (greater than 10 nm) along with the large band gap (3.2 eV - 4.4 eV) [1, 2]. As we know the nanoparticles having same order of exciton Bohr radius with larger band gap as comparison to bulk band gap (0.41 eV) leads to quantum confinement and the particles may be termed as quantum dots [1]. Due to their unique optical properties, till now PbS nanoparticles are tried to apply in optoelectronics devices such as light-emitting diodes, optical switches, solar cell etc. Electron microscopy like TEM, SEM studies shows that synthesis of nanoparticles without capping agent produces nanoparticles with relatively large size. In this work MPA (3-mercapto propionic acid) is used as capping agent to control the size of the nanoparticles. Capping agent plays a significant role in the growth of nanoparticles. It act as a stabilizer, which avoids agglomeration in the synthesis process. MPA enhances the process chemistry.

Water sanitation or water purification is still a major issue in developing countries. Even food poisoning or health hazard due to food borne pathogenic bacteria (*Escheria coli*, *Staphylococcus aureus*), viruses or parasites is also not less in India [2]. Keeping this in mind, nanomaterial research may be directed to sense these pathogenic bacteria as detection may be easy due to the similar average sizes of nanoparticles/quantum dots, proteins and viruses. Due to quantum confinement effect PbS nanoparticles are having unique electrical and optical properties, used in different electronic fields [3] however if quantum dots are synthesized then we can use these (PbS nanoparticles) for bacterial sensing purpose on the basis of memristive method in near future. Memristor acronym for memory resistor which is the fourth passive element of electrical circuit having ability of holding memory effect by trapping charge in flux linkage. In case of the memristor, it was shown by Strukov et al. that memristance arises naturally in nanoscale systems in which solid-state electronic and ionic transport are coupled under an external bias voltage. Their theoretical model reveals that size of memristance effect increases as the inverse square of device size. Similarly, the hysteresis type dependence of capacitance C on the applied voltage has been found in nanoscale capacitors having interface traps embedded nanocrystals/quantum dots [4-13].

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2. Experimental Methods

2.1 Chemicals and Reagents

All chemicals used for the experiment were of high purity and analytical grade. Lead nitrate $Pb(NO_3)$, sodium sulphide (Na_2S), PVA, nutrient agar were purchased from Sigma-Aldrich.

Microbial stain *Escherichia coli, Staphyloccus aureus* are obtained from Department of Bio-Engineering, Institute of Science and Technology, Gauhati University as well as Department of Biotechnology University of Science and Technology, Meghalaya.

2.2 Synthesis of PbS Nanoparticles

PbS synthesis is done by chemical method. 0.05 g of $Pb(NO_3)_2$ is dissolved in 25 mL of deionized water. Twenty-five milliliters of MPA with different concentrations (0.05, 0.1, 0.5 and 1 m) are then slowly added to the $Pb(NO_3)$ sample. The colour of the transparent solutions turns to black after adding MPA under nitrogen atmosphere. Finally, 25 mL of 0.01 M aqueous solution of sodium sulphide Na_2S is added to the above solution. The color of the final transparent colloidal suspensions turns from light brown to black by adding MPA with different concentrations.

3. Results and Discussion

3.1 Material Characterization

3.1.1 UV –Vis Spectroscopy

The absorption spectrum of the PbS nanosample (Fig. 1) was recorded at room temperature using Systronic single beam UV –Vs spectrophotometer 117. The range is within 200 nm - 800 nm. The peak arises at 272 nm of wavelength. Thus after mixing of Pb^{2+} ions with MPA (having thiol group) a complex absorbing around 272 nm is immediately formed. Usually, a decrease in particle size causes an increase in the band gap and a blue shift occur. The band gap estimation is done using Tauc plot. From Tauc plot (Fig. 2), it has been seen that the band gap of PbS particle is 3.6 eV which is much larger than bulk PbS bandgap of 0.41 eV at room temperature. This signifies the quantum confinement of PbS.

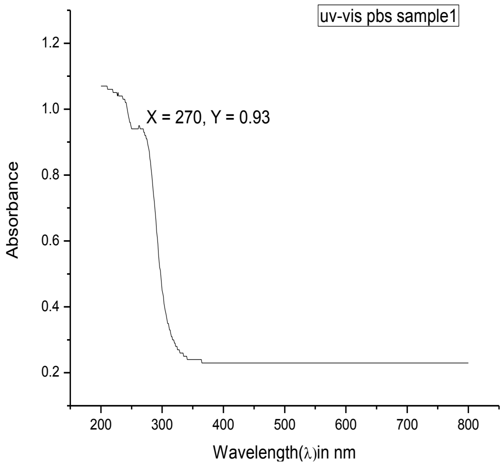

Fig. 1 UV-curve of PbS nanosample S_1

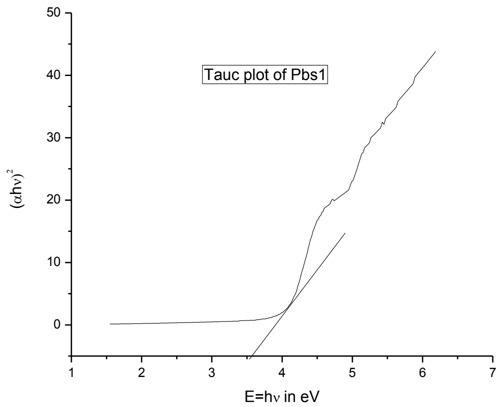

Fig. 2 Tauc plot for Sample S_1

3.1.2 PL Analysis

PL analysis is done at Department of Chemistry, Gauhati University F-2500 FL Spectrophotometer. The optical properties of synthesized lead sulphide nanoparticles were characterized by photoluminescence (PL) measurement. The PL spectrum of lead sulphide nanoparticles is shown in Fig. 3 shifts from 370 nm to 404 nm and is attributed due to nanosized particle.

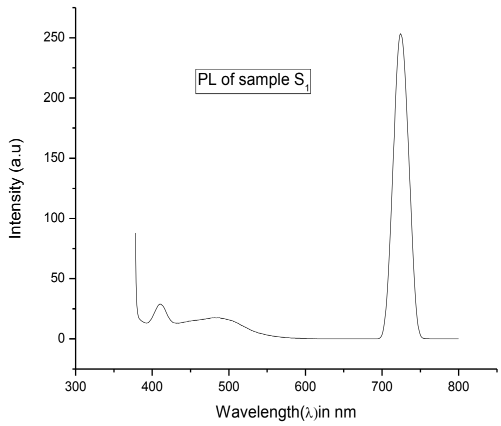

Fig. 3 PL analysis of sample S_1

3.1.3 XRD

X-ray diffraction graph of PbS sample is shown in Fig. 4. XRD is done by Phillips X-pert diffractometer equipped with a graphite monochromator using radiation source CuKα (λ=1.54 Å) and operating at 35 mA, 40 kV. The particle size of the PbS sample is estimated from the Debye-Scherrer formula. The average particle sizes obtained for sample S_1 is shown in Table 1. The XRD pattern is an agreement with the cubic structure of lead sulphide sample.

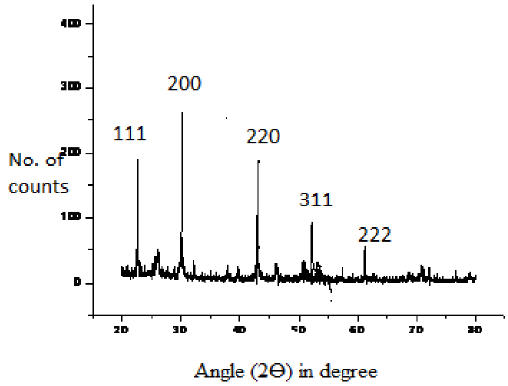

Fig. 4 XRD of PbS sample S_1

Table 1 XRD data of PbS nanosample S_1

No. of peaks	2θ (degree)	FWHM β	d (Å)	(hkl)	Crystal structure (nm)
1	22.63	1.0	3.92	111	8.47
2	30.04	1	2.96	200	8.59
3	43.0	1.34	2.10	311	6.67
4	60	0.9	1.51	222	10.65

3.1.4 Scanning Electron Microscopy (SEM)

SEM analysis is used for examining size and morphology of PbS nanoparticles. The images are analysed and shown in Fig. 5 by using ZEISS SIGMA VP field emission scanning electron microscope. The image shows that it is very small ranging 10-20 nm. Some of few are aggregated. The synthesized nanoparticle with *S. aureus* is also seen in SEM images.

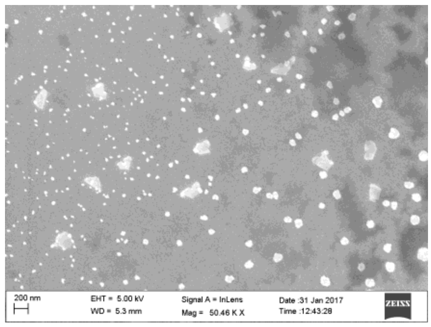

Fig. 5 SEM images of PbS nanoparticle with *S.aureus*

3.1.5 HRTEM

High resolution transmission electron microscope gives the direct imaging such as crystallographic structure and lattice imperfection of various kind of materials on atomic scale. The image Fig. 6 shows that particles are nearly round or oval in shape. The size of the particles are in the range of 10-13 nm. The size estimation of as-synthesis nanoparticles are characterized by transmission electron microscope (make: JEOL (Japan), model: JEM 2100). Thus all characterization results confirms the formation of lead sulphide (PbS) nanoparticles.

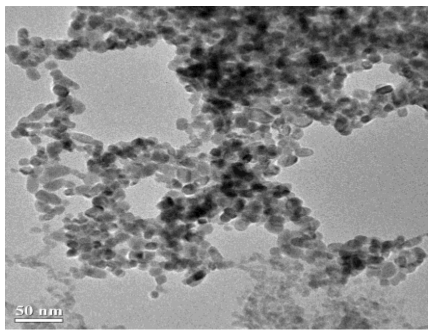

Fig. 6 HRTEM image of sample S_1

3.2 Antimicrobial Activity of PbS Nanosample

The antimicrobial activity of PbS nanosample is analyzed by well diffusion method against *S. aureus* and *E. coli* (Fig. 7). The Muller Hinton Agar plates were prepared and 3 mL of each culture were added to individual plate and spread uniformly. Wells of 5 mm are made and

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sterilized the needle. 30 µL of 0.1 M PbS nanosample is used in the well with bacterial strain *Staphylococcus aureus*. Then the plate is kept under incubator (after good sealing) at 37 °C for 24 hours and zone of inhibition is noted.

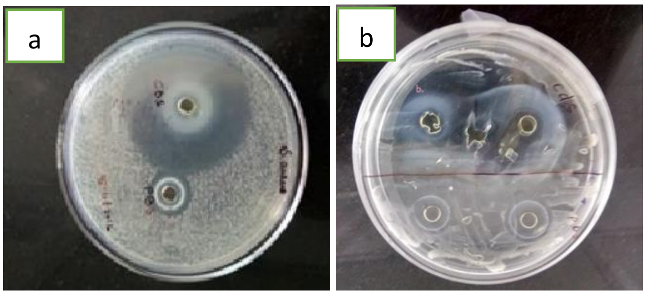

Fig. 7 Antibacterial effect of S_1 with a) *S. aureus* and b) *E. coli*

3.3 Current –Voltage Charcteristics

The electrical characterization is carried out by fabricating electrochemical devices with thin films of PbS/3MPA nanoparticles. Thin films are of average thickness 100 nm and of active area (12.56 mm^2) spin coated on ITO coated glass (25 mm x 25 mm x 1 mm) of surface resistivity 10-25 Ω/sq. which is used as the bottom electrode and Cu being used as the top electrode (Fig. 8).

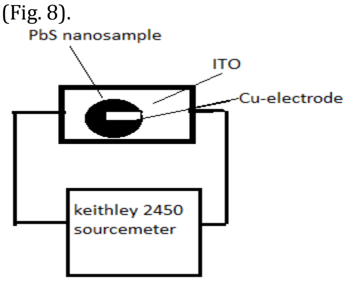

Fig. 8 Schematic diagram of I-V measurement

3.3.1 Voltage Gap Act as Sensing Parameter

Current voltage characteristics is taken with the help of Keithley 2450 source meter and from the Fig. 9. It shows that PbS nanosample behaves memristically. Thus it shows a hysteresis pattern while taking voltage variation from -2V →0V→+2V→2V without using bacterial stain.

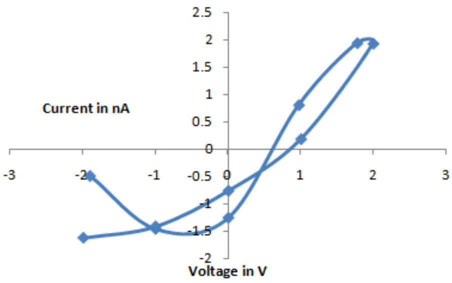

Fig. 9 I-V characteristics of sample S_1

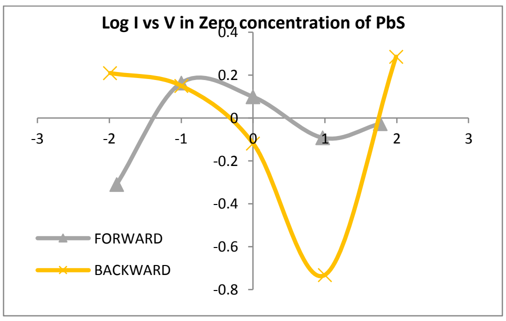

Fig. 10 Log I variation with the applied voltage

If we take logarithmic of current with variation of voltage, then voltage gap (V_g) is obtained between current minima of both forward as well as backward curves. This is also observed by Carrara et al. [5]. Fig. 10 shows the LogI vs applied voltage characteristics. Now whenever bacterial sample (*E. coli*) is added and current voltage chacteristics is recorded for PbS nanosample. It again shows the memristive behaviour as shown in Fig. 11.

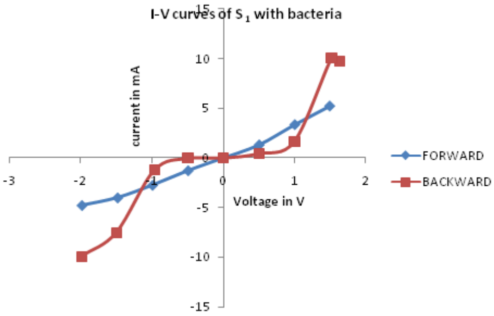

Fig. 11 I-V charcteristics of sample S_1 with bacteria

In this study PbS nanoparticle is synthesized by chemical method. HRTEM images showed that PbS nanoparticles are of the size 10-20 nm. Then PbS nanocomposites are tested for antimicrobial activity using *E. coli* and *S. aureus*. The diameter of the zone of inhibition are 14 mm for *E. coli* and 15 mm for *S. aureus*. The MPA containing PbS nanosample showed antibacterial activity against *E. coli* and *S. aureus* sample. SEM images showed that the bacteria are less presence with PbS nanosample. Thus PbS nanoquantum dots acts as antibacterial agents against food borne pathogen *E. coli* and *S. aureus*. From the current voltage characteristics it is clear that the nanoparticles obey Mem-nature. Sample S_1 without bacteria *E. coli* acts as the meminductive and with bacterial conjugation it acts as the memristive. Thus there is occurrence of voltage difference of pinching. This difference of voltage may act as the sensing parameter for bacterial detection purpose.

4. Conclusion

The present study depicts the synthesis of PbS/MPA nanocomposites and their utilization as active material of memdevices. However, if nanocomposites are functionalized with *E. coli* antigen, memristic behaviour of the device gets affected and voltage difference between current minima (i.e voltage gap) is observed. Thus voltage gap can acts as the sensing parameter for bacterial detection as it varies with *E. coli* concentration in mem devices which may be studied in near future in sensing purposes.

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