Insights into the optical and anti-bacterial properties of biogenic PbSe quantum rods

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Received 2 August 2014; revised 13 October 2014; accepted 16 October 2014
Available online 21 November 2014

Abstract The detailed optical properties of lead selenide (PbSe) quantum rods biosynthesized in marine Aspergillus terreus were apprehended theoretically using ab initio calculations based on the experimental absorption spectrum. These studies indicate that the absorption coefficient of the biosynthesized PbSe quantum rods increases linearly with incident photon energies. The variation of other optical constants like extinction coefficient, refractive index and reflectance was comparable to that of the chemically synthesized counterparts. Further, the high dielectric constant and remarkable fluorescence of the biogenic PbSe quantum rods pronounce their application in opto-electronic devices in the Near Infra-Red and Ultraviolet spectral regime. The biosynthesized PbSe quantum rods were also found to possess appreciable anti-bacterial activity against various gram positive and gram negative bacterial species thus enhancing the relevance of the same for practical utility. Based on these results it can be concluded that biogenic PbSe quantum rods can be envisaged as potential candidates for bio-imaging, bio-sensing and other photo-voltaic applications.

1. Introduction

Biosynthesis of semiconductor quantum particles has of late allured the attention of researchers as eco-friendly, energy efficient and cost effective alternative for chemical synthesis means [1–5]. The greener synthesis approaches has further opened up prospectus for the development of efficient large scale synthesis of semiconductor quantum particles to exploit their superior quantum confinement effects in opto-electronic and photo catalytic applications [6,7]. Of particular technological relevance are the lead selenide (PbSe) quantum particles characterized by a narrow band-gap, large nonlinearity, high dielectric constant, lower effective mass for the electron and hole, large Bohr radii and fast response time [8] that mark them as ideal candidates for the fabrication of photo-voltaic devices and bio-sensing agents [9,10].

Literature survey reveals the preponderance of chemical routes for the shape controlled synthesis of PbSe quantum particles [11–13]. However all chemical synthesis approaches languishes the insistence of extreme reaction conditions and high operational cost, thus diminishing their cogency from the environmental point of view. To address these voids, the inherent metal detoxification mechanism in marine Aspergillus terreus was employed for the cost effective and...
green synthesis of PbSe quantum rods with properties in parallel with the chemically synthesized counterparts [14]. Biogenesis of crystalline rod-like structures of PbSe with aspect ratios between 5 and 10 was confirmed using TEM, SEM with EDAX and XRD studies. Further, the biogenic PbSe nano rods were also found to exhibit weak quantum confinement effects according to the theoretical interpretation by mass approximation method. Prior studies had also revealed the remarkable biocompatibility of the PbSe quantum rods biosynthesized by A. terreus [14].

Envisaging the potential of biogenic PbSe nano composites as exceptional quantum harnessing agents, it is important to comprehend the detailed optical characteristics of the same. The preceding sections enumerate the optical properties of PbSe quantum rods biosynthesized in marine A. terreus. Further, the bactericidal properties of these agents against various...
gram-positive and gram-negative human pathogenic bacteria are also elaborated.

2. Experimental details

Biosynthesis of lead selenide (PbSe) nanoparticles was initiated by a low cost green methodology under conditions akin to room temperature in marine *A. terreus* [14]. Optical characterization of the biogenic PbSe quantum rods was carried out using UV–Vis spectroscopy measurements performed on a Hitachi U-200 Spectrophotometer. Fluorescence measurements were carried out using Perkin-Elmer LS 50B luminescence spectrophotometer. Further, the antibacterial activity of the crude nanoparticle solution against various gram positive and gram negative human pathogenic bacteria like *Staphylococcus aureus*, *Bacillus cereus*, *Bacillus endophyticus*, *Salmonella typhi*, *Escherichia coli*, *Klebsiella pneumonia*, *Vibrio cholera* and *Vibrio parahaemolyticus* was carried out by filter paper bioassay [15]. For antibacterial activity, bacterial culture were inoculated in nutrient broth and incubated at 37 °C for 24 h. From the actively growing bacterial culture broth, 0.1 mL of the suspension (105 CFU/mL) was mixed with half strength nutrient broth (0.9 mL) and was immediately overlaid on the surface of the sterile nutrient agar plates (90 mm diameter). Sterile filter paper discs (Whatman No. 3: 10 mm square) were placed on these agar plates and then loaded with 50 μL suspension of the crude nanoparticles. These plates were incubated for 24 h and visually monitored for the zone of inhibition. Filter paper disc on nutrient agar plate with suspension containing standard antibiotic (500 μg/mL) was used as positive control. After incubation, the zone of inhibition was measured in millimetre across the filter paper.

3. Results and discussion

The inherent biocompatibility and the remarkable band gap tailoring amenability of lead selenide (PbSe) quantum particles projects their potential application in effective fluorescence

![Figure 3](image-url) (A) Variation of reflectance (%) with wavelength. (B) Variation of refractive index with photon energy.
based biosensors. To better serve this purpose, the fluorescence ability of the biologically synthesized PbSe nanoparticles was checked with their fluorescence spectrum that displayed peak emissions at 425 nm and 475 nm (Fig. 1A). While chemically synthesized PbSe quantum particles arrayed a fluorescence emission in the IR region of the electromagnetic spectrum, the biogenic PbSe quantum rods were found to exhibit fluorescence in the visible region [16]. Fig. 1B depicts the fluorescence of the biogenic PbSe nanorods under short wavelength ultraviolet (UV) illumination.

Further, the absorption spectra (Fig. 2A) indicated the presence of absorbance peaks in the UV and Near Infra-Red (NIR) region of the electromagnetic spectra. The peaks were centred at 303 nm and 872 nm. The observed blue shift in the absorption peak in the UV region in comparison to that of the bulk PbSe could be attributed to the size effect in the biogenic PbSe QRs [17]. The absorption edge at lower wavelengths (<300 nm) indicates the presence of protein-capping that is reported to enhance the stability of the nanoparticles in solution and to prevent their aggregation. The absorption peak at 303 nm and 872 nm is characteristic of PbSe particles in the quantum size regime. The generation of such kinds of peaks could be due to the excitation of surface plasmons within the nanoparticles. Our results corroborate with previous studies of synthesis of PbSe QDs by hot solution method [18].

As PbSe nanorods are ideal candidates for optical sensing and bio-imaging, the knowhow regarding the optical constants is imperative. Although literature directs attention towards various attempts to study the optical constants of chemically synthesized PbSe quantum particles, the optical enumerations for biogenic PbSe quantum particles is scant. The absorbance data as obtained from UV–Vis spectroscopic studies were used to estimate the band gap, absorption and extinction coefficient, reflectance and dielectric constant of the PbSe nanofabrication. The absorption coefficient of PbSe nanorods in a hypothetical medium with a QR volume fraction of one was calculated by the Eq. (1)

\[ \alpha = \ln 10 \times \frac{A}{fl} \]  

where \( \alpha \) is the absorption coefficient, \( A \) is the absorption, \( f \) is the QR volume fraction, \( l \) is the cuvette length.

The variation of absorption coefficient with incident photon energy is depicted in Fig. 2B. It has been observed that the absorption coefficient increase almost linearly with the increase in the incident photon energy. The linear increase in absorption coefficient with photon energy could be attributed to the higher electron-hole pair generation and subsequent recombination when excited with photons of increasing wavelengths [19]. Our results attest the findings that excitation with photons of increasing wavelengths results in bond breaking and bond rearrangement, which in turn result in a change in the local structure in the lead chalcogenides. These include subtle effects such as shifts in absorption edge and the atomic and molecular reconfiguration which is associated with

![Figure 4](image-url)  

**Figure 4** (A) Variation of extinction coefficient, (B) real and imaginary part of dielectric constant with photon energy.
changes in absorption coefficient and absorption edge shift [20].

Further, the reflectance of the quantum rod sample was calculated in the wavelength range 200–1000 nm using the theory of reflectivity of light. As can be inferred from Fig. 3A, the reflectance of the PbSe nanorods increase in the wavelength range 300–400 nm and 800–1000 nm. This trend in the variation of reflectance is in concordance with prior literature [21].

The knowledge of accurate values of wavelength dependent refractive index and extinction coefficient is very important from the fundamental and technological context. Moreover, the refractive index is necessary for the design and modelling of optical components and optical coating. The wavelength dependent refractive index (n) and extinction coefficient (k) of the biogenic PbSe nanorods was calculated using Eq. (2) derived from the theory of reflectivity of light.

\[
n = \left[ \left( 1 + R \right) \left\{ \left( 1 + R \right)^2 - \left( 1 - R \right)^2 \left( 1 + k^2 \right)^{1/2} \right\} \right] / \left( 1 - R \right)
\]

where, \( R \) is the reflectance, calculated from the absorbance and transmittance of the sample.

The molar extinction coefficient was calculated according to the Eq. (3):

\[
k = \frac{\pi \lambda}{4} \frac{a}{n}
\]

where \( a \) is the absorption coefficient, \( \lambda \) is the wavelength.

The plot of refractive index (n) against the incident photon energy (Fig. 3B) intuits that the refractive index (n) increase almost linearly with increase in photon energy for photons with wavelengths in the UV and NIR regions. Further, it was examined that the refractive index (n) of the material had a notable negative drift in the visible region of the electromagnetic spectrum. The extinction coefficient (k) of the PbSe QRs was found to increase linearly after the incidence of photons with energy greater than 2.5 eV (Fig. 4A). The increase in the values of n and k could be due to the presence of large number of unsaturated defects or bonds in the biogenic PbSe QRs and their inherent localized states [21].

Dielectric constant, a parameter that signifies the electron storage potential of materials, was calculated using the following Eqs. (4) and (5)

\[
e' = n^2 - k^2
\]

\[
e'' = 2nk
\]

These parameters plotted against incident photon energy (Fig. 4B) array that the biosynthesized PbSe quantum rods possess higher dielectric constant (>20); pronouncing their inherent electron-hole mobility’s at room temperature. The aforementioned pattern was comparable to that observed for the other optical constants and was typical for photons in the UV and NIR region of the electromagnetic spectrum. The variation in the real and imaginary part of dielectric constant with increase in photon energy could be explained by the presence of structural defects and localized states which

### Table 1 Zone of inhibition of the PbSe QRs and standard antibiotic.

<table>
<thead>
<tr>
<th>Bacteria</th>
<th>Zone of inhibition (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Control</td>
</tr>
<tr>
<td>Gram (+) bacteria</td>
<td></td>
</tr>
<tr>
<td>Staphylococcus aureus</td>
<td>26</td>
</tr>
<tr>
<td>Bacillus cereus</td>
<td>31</td>
</tr>
<tr>
<td>Bacillus endophyticus</td>
<td>30</td>
</tr>
<tr>
<td>Gram (−) bacteria</td>
<td></td>
</tr>
<tr>
<td>Salmonella typhi</td>
<td>34</td>
</tr>
<tr>
<td>Escherichia coli</td>
<td>28</td>
</tr>
<tr>
<td>Klebsiella pneumoniae</td>
<td>32</td>
</tr>
<tr>
<td>Vibrio cholerae</td>
<td>33</td>
</tr>
<tr>
<td>Vibrio parahaemolyticus</td>
<td>32</td>
</tr>
</tbody>
</table>

Figure 5 Comparison of the zone of inhibition between (A) Gram positive Bacillus cereus and (B) Gram negative Escherichia coli for control and biogenic PbSe quantum rods (sample).
give rise to a local potential. However, since the bonding in lead chalcogenides being covalent in nature does not result in large changes in the local potential at higher photon energies. The results appear to previous findings [21] and also attest that the real and the imaginary part of dielectric constant are proportional to the refractive index and absorbance respectively [22].

Bacterial biofilms are one of the major disadvantages that impede the use of biogenic nanoparticles as thin films and in membranes for analyze detection in solution. The filter paper bioassay for anti-bacterial activity of the biogenic PbSe quantum rods dispensed on filter paper discs, revealed the formation of distinct zones of inhibition by gram positive and gram negative bacterial pathogens. The results and images of the inhibition zones are presented in Table 1 and Fig. 5, respectively. It was observed that the biogenic PbSe nanorods had an anti-bacterial activity comparable to that of standard antibiotics against pathogens like B. cereus and E. coli (Fig. 5). Thus it can be inferred that the biogenic PbSe quantum rods can serve as a broad spectrum antibacterial agent.

4. Conclusion

Lead and selenium tolerant A. terreus is a potential fungus for the extracellular biosynthesis of PbSe quantum rods. Analyses of the optical properties of biogenic PbSe reveal properties in par with the chemically synthesized counterparts that project the potential of this biogenic nano fabrication in high efficiency opto-electronic applications. Further, the antibacterial activity of the biogenic PbSe quantum rods adds relevance. Hence it can be concluded that the PbSe quantum rods biosynthesized in marine A. terreus possess significant optical and anti-bacterial properties and thus is a promising semiconductor nanofabrication for bio sensing and bio imaging applications.

Acknowledgments

Authors are thankful to the Department of Metallurgical and Materials Engineering and the Department of Chemistry, National Institute of Technology Karnataka for extending their facilities.

References