SnO$_2$ quantum dots for nano light emitting devices

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We prepared SnO$_2$ quantum dots embedded in polyvinylpyrrolidone (PVP) matrix and report its operation as a Nano Light emitting device. The samples have been prepared via quenching technique where bulk ZnO powder is sintered at a very high temperature of 1000 °C and then quenched into ice cold polyvinylpyrrolidone solution. The specimen was then characterized using UV/VIS spectroscopy, X-ray diffraction study and high resolution transmission electron microscopy (HRTEM). These studies indicate the sizes of quantum dots to be within 9 nm. The prepared quantum dot samples have been evaluated as nano light emitting devices by exploring the variation of electroluminescence (light emission phenomenon) with supply voltage at room temperature.

Keywords: quantum dot, polyvinylpyrrolidone, quenching, nano LED.

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1. Introduction

The synthesis of semiconductor quantum dots and their different applications as various electronic and optoelectronic devices including different kinds of sensors, devices are among the top research areas at present [1–6]. Recently, many techniques [1–4] like molecular beam epitaxy (MBE), radio frequency sputtering (RF), liquid phase epitaxy (LPE), quenching etc. have been adopted to synthesize semiconductor quantum dots. But due to its manifold advantages [3,6] viz. like simplicity and low cost, quenching method draws the interest of current researchers. In the present investigation, we discuss the preparation of SnO$_2$ quantum dots in a polyvinylpyrrolidone (PVP) matrix (which embeds the quantum dots) by quenching method and their functioning as Nano light emitting devices which is a new area of nano research. The advantage of PVP over other polymer matrices viz. SBR latex matrix is that circular and uniform quantum dots can be fabricated on PVP. The prepared samples have been examined using different characterization methods to reveal their nano natures [2]. These studies infer the formation of quantum dots within the dimension of 8 nm. Next, the ability of SnO$_2$ samples to function as nano light-emitting diodes (LED’s) has been tested by performing etroluminescence studies at room temperature. Testing of SnO$_2$ quantum dots for nano LED, which has not been focused in any report earlier, is interesting, and technically very important.

2. Materials and method

To synthesize [3] SnO$_2$ quantum dots by quenching method, 4 gms of SnO$_2$ powder (99.99 % pure, E Merck) was calcined at ~ 1000°C for 10 hours and then quenched into 4 wt% aqueous solution of polyvinylpyrrolidone (PVP) matrix (99.9% pure, E Merck) kept at ice cold temperature followed by its moderate stirring (~ 175 rpm). This solution contains SnO$_2$ quantum dots embedded in a polyvinylpyrrolidone matrix (chemical structure is shown in Fig. 1). The film is developed on the laboratory glass slides by placing a few drops of SnO$_2$ quantum dot solution (embedded in PVP) on a clean slide and by stretching over it, another clean slide.

3. Results and discussions

The SnO$_2$ specimen was characterized by UV/VIS optical absorption spectroscopy (Perkin Elmer Lamda 35 1.24), X-ray diffraction study (Bruker AXS, X-ray source: CuK$\alpha$) and high resolution transmission electron microscopy (HRTEM) (JEM 1000 C XII).

Optical absorption spectroscopy [6] shows sharp blue shifted absorption edge of the prepared samples (Fig. 1). A blue shift is a distinct signature of quantum dot formation [1,3,4] (Fig. 2a). By considering shifted absorption

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edge (at 210 nm) of SnO\textsubscript{2} sample, average crystallite (particle) size has been estimated and found to be 10 nm by using the following hyperbolic band model [5]:

\[
R = \sqrt{\frac{2\pi^2\hbar^2E_{gb}}{m^* (E_{gn}^2 - E_{gb}^2)}},
\]

where \( R \) is quantum dot radius (\( 2R \) is the diameter and hence the particle size), \( E_{gb} \) is the bulk band gap, \( E_{gn} \) is quantum dot band gap (calculated from the sharp absorption edge which is 210 nm as shown in Fig. 1.), \( \hbar \) is Planck’s constant, \( m^* \) is effective mass. Similarly, from X-ray diffraction study (Fig. 3) average particle size (crystallite size) is calculated by using Scherrer formula [2],

\[
D = \frac{0.9\lambda}{W \cos \theta},
\]

\( \lambda \) is wave length of X-ray (0.1541 nm), \( W \) is FWHM (full width at half maxima), \( \theta \) (theta) is the glancing angle and \( D \) is particle diameter (crystallite size). Considering all the peaks [3] (2θ in degree) in the X-ray diffractogram, the average crystallite (quantum dot) size has been calculated to be 9 nm. Further, by analyzing the X-ray diffractogram with the help of ICDD (International Center Diffraction Data) it has been revealed that SnO\textsubscript{2} quantum dots are “wurtzite” in structure. HRTEM images of PVP film (c) and SnO\textsubscript{2} quantum dots (a) are shown in Fig. 3. It is evident in the HRTEM image (a) that SnO\textsubscript{2} crystallites (quantum dots) are circular in shape with sizes within 10 nm.

**Fig. 3.** HRTEM images of SnO\textsubscript{2} QDs in PVP matrix

SnO\textsubscript{2} sample sizes assessed from these three studies are reasonably similar, which is a distinct advantage over earlier reports [2, 3]. This matching occurs due to the formation of well uniformed and circular shaped quantum dots by using PVP matrix instead of PVA (polyvinyl alcohol) matrix [3]. All these characterizations infer that SnO\textsubscript{2} quantum dot sizes (diameters) are within 10 nm.

To test the operation of SnO\textsubscript{2} quantum dots as Nano Light emitting devices, the electroluminescence (EL) of the sample [5, 6, 19] at room temperature was determined (Fig. 4). SnO\textsubscript{2} has been shown to display appreciable electroluminescence at around 580 nm at room temperature and we believe that this emission is a result of the
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oxygen vacancy. It has been reported elsewhere that emission intensity is a function of bias voltage and the luminescence intensity increases at higher bias voltages [4, 18]. But the disadvantage is that, high bias voltages causes damage to the sample at longer operating times. This investigation obviously indicates that SnO$_2$ quantum dots can act as nano light emitting devices at a very low bias, which is our new achievement with fast response speed on the order of 10$^{-9}$ sec. Variation of EL intensity with bias voltage is plotted in Fig. 5. The data from the electroluminescence study of the quantum dots is given in Table 1.

![EL spectra (0.5 V) of SnO$_2$ samples](image1)

**Fig. 4.** EL spectra (0.5 V) of SnO$_2$ samples

![EL intensity Vs applied voltage](image2)

**Fig. 5.** EL intensity Vs applied voltage

4. Conclusion

SnO$_2$ shows appreciable electroluminescence at room temperature and the relationship between EL intensity and applied voltage up to 20 V appears to be almost linear. Thus, SnO$_2$ quantum dots can act as Nano light emitting devices at room temperature.
TABLE 1. Data from Electroluminescence (EL) spectra of SnO$_2$ quantum dots

<table>
<thead>
<tr>
<th>Sample</th>
<th>Applied voltage (V)</th>
<th>EL intensity (a.u)</th>
<th>Relative quantum efficiency (times)</th>
<th>Response speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$</td>
<td>2.5</td>
<td>145</td>
<td>3.2</td>
<td>Of the order of $10^{-9}$ sec</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>310</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>410</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>520</td>
<td>11.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>580</td>
<td>12.9</td>
<td></td>
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References