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UV–VIS spectroscopic study of one pot synthesized strontium oxide quantum dots ☆

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ABSTRACT

The properties of drastically change when matter makes transition from 1D, 2D, 3D, to 0D. The quantum dots (QDs) of strontium oxide (SrO) were synthesized by one pot chemical precipitation method using hexamethylenetetramine (HMT). The radius of SrO QDs was calculated from hyperbolic band model (HBM). The direct and indirect band gaps of SrO QDs were estimated from UV–VIS analysis. The particle size was found to be 2.48 nm. The quantum confinement effect in SrO QDs is discussed through exciton Bohr radius. The particle size from UV–VIS analysis is in excellent agreement with fluorescence and TEM.

1. Introduction

The optical and electronic properties of materials change drastically due to the quantum confinement of the charge carriers within the particle. SrO, an important wide band gap metal oxide (MOX) has attracted much attention. Jose et al. [1] reported the glass system of SrO for new broadband Raman gain media. Due to the inherent high-energy phonons in silicate-based glasses, usable rare-earth ions, which are optically active for optical amplification, are limited in silicate-based fibers. Because fluoride and heavy metal oxide glasses have low energy phonons and many rare-earth ions are optically active in them, these glasses have been studied as rare-earth hosts to expand amplification bandwidth in wavelength division multiplexing (WDM) systems [2]. There has been several method for the synthesis of MOX by low-temperature routes to obtain relatively homogeneous and small-sized grains. These methods include chemical precipitation, hydrothermal reaction and the sol gel method. Here we discuss chemical precipitation method for the synthesis of SrO QDs [3].

MOX nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites. Particle size is expected to influence three important groups of basic properties in any material. The first one comprises the structural characteristics, namely the lattice symmetry and cell parameters [4]. Bulk oxides are usually robust and stable systems with well-defined crystallographic structures. However, the growing importance of surface free energy and stress with decreasing particle size must be considered: changes in thermodynamic stability associated with size can induce modification of cell parameters and/or structural transformations [5] and in extreme cases the nanoparticle can disappear due to interactions with its surrounding environment and a high surface free energy [6]. Although, SrO is a dangerously radioactive isotope, it is a useful by-product of nuclear reactors from which spent fuel is extracted. Its high-energy radiation can be used to generate an electric current, and for this reason it can be used in space vehicles, remote weather stations and navigation buoys [7].

The optical conduction is one of the fundamental properties of metal oxides and can be experimentally obtained from reflectivity and absorption measurements. Due to quantum-size confinement, absorption of light becomes both discrete-like and size-dependent. In nano-crystalline semiconductors, both linear (one exciton per particle) and non-linear optical (multiple excitons) properties arise as a result of transitions between electron and hole discrete or quantized electronic levels. In the first case, depending on the relationship between the radius of the nanoparticle (R) and the Bohr radius (RB) of the bulk exciton, the quantum confinement effect can be divided into three categories; weak, intermediate and strong confinement regimes, which correspond to $R \gg$ RB, $R \approx$ RB, and $R \ll$ RB, respectively [8]. The effective mass theory (EMA) is the most elegant and general theory to explain the size dependence of the optical properties of nanometer semiconductors.

In the present work, SrO QDs are synthesized by one pot chemical precipitation method. The direct and indirect band gaps of QDs are determined through UV–VIS analysis. The quantum dot radius is computed from hyperbolic band model (HBM) using UV–VIS

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analysis. The effective mass approximation is used to find out the particle size in case of fluorescence spectroscopy. The confirmation is done through TEM.

2. Experimental

The AR grade (SD Fine, India) chemicals were used in this work. The SrO QD was arrested by one pot chemical route approach. The reaction is shown below.

$$Sr(NO_3)_2 + C_6H_{12}N_4 \rightarrow SrO + C_6N_6 + 6H_2O$$

The 1 M HMT was dissolved in 5 ml double distilled water separately. After rigorous stirring, 1 M strontium nitrate was added in the solution. The HMT is used as a nitrate remover (precursor remover). The reaction was stood for 2 h at room temperature. The precipitate so obtained was vacuum filtered and filtrate was first dried at room temperature for 24 h and sintered at 100 °C for 3 h. The SrO QDs prepared in this way were characterized by UV–VIS analysis on a Perkin Elmer Spectrophotometer. The TEM analysis is used to know the particle size of SrO QDs. The fluorescence analysis was done on a FL Spectrophotometer (Model: HITACHI, F-7000). The slit width was adjusted to 5 nm. The sample for TEM analysis was prepared by carbon-coated copper TEM grids. The measurements were performed on a JEOL Model 1200EX instrument operated at an accelerating voltage of 120 kV.

3. Results and discussion

The analysis of UV–VIS spectra of SrO QDs shown in Fig. 1 was carried out with a view to explore their optical properties.

Fig. 1 shows that the% transmission is higher on lower wavelength side. It was seen that the strongest absorption appears at wavelength ~203 nm. At lower wavelengths edge absorption represents the quantum confinement effect present in the synthesized SrO QDs. Many applications of the materials depend upon its direct and indirect band gap values. The relation between absorption coefficient (α) and incident photon energy ($h\nu$) can be expressed as Eq. (1).

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad (1)$$

where A is constant and E_g is the band gap of the material. The exponent n depends on the type of the transition, its value is 1 for direct band gap and 2 for indirect band gap. The exact values

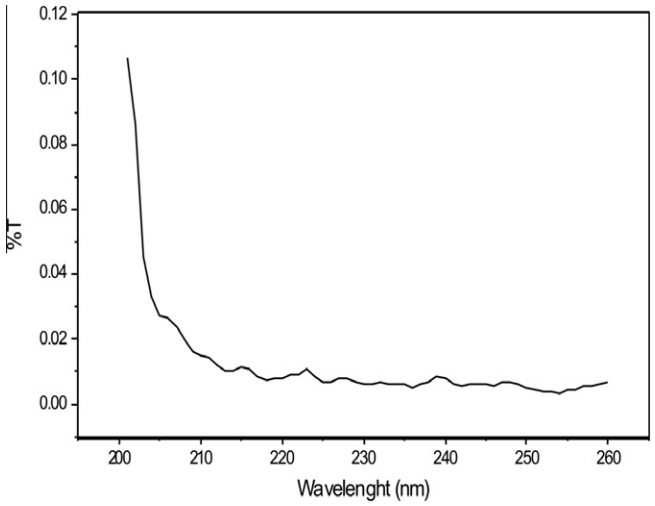

Fig. 1. UV–VIS Spectra of SrO QDs.

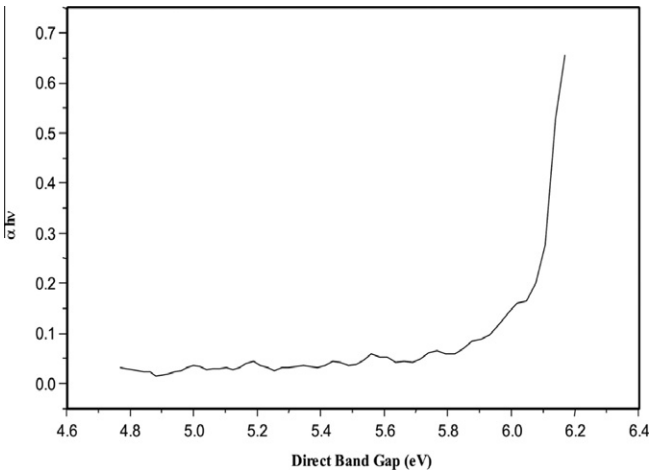

Fig. 2. Direct band gap of SrO QDs.

of direct and indirect bands are determined by extrapolating the straight-line portion of ($\alpha h\nu$) versus $h\nu$ graph to the $h\nu$ axis. The band gap of bulk SrO is 1.8 eV [9].

Fig. 2 shows the direct band gap of SrO QDs which is found to be at 6.14 eV (E_{nano}). This confirms the nanophase of material. It is also reflected from HBM analysis.

By considering absorption edge at 203 nm, the QDs radius was estimated by using the HBM (Eq. (2)) [10].

$$R = \sqrt{\frac{2\pi^2 h^2 E_{bulk}}{m^*(E_{nano}^2 - E_{bulk}^2)}} \quad (2)$$

where E_{bulk} is bulk band gap, E_{nano} is band gap of nanomaterial, m^* is effective mass of electron in bulk SrO. ($m^* = 0.24\ m_0$). The QDs radius was found to be 1.24 nm. Hence the particle size estimated as $2R$ is 2.48 nm.

Fig. 3 shows the indirect band gap of SrO QDs. It is found to be 6.1 eV by substituting the exponent value $n = 2$ in Eq. (1). The shifting of band gap from 6.14 to 6.1 eV confirms the presence of indirect band gap. The difference 0.04 eV may represent the energy of lattice phonon. The highest energy phonons correspond to intracellular vibrations, in our case found to be 0.04 eV that should not have seriously affected the size of the QDs [11]. There may be some effect of phonon energy but not strapping which affects the UV–Visible spectra. Thus the SrO QDs are defect free. The defects may not exist around the QDs' surface.

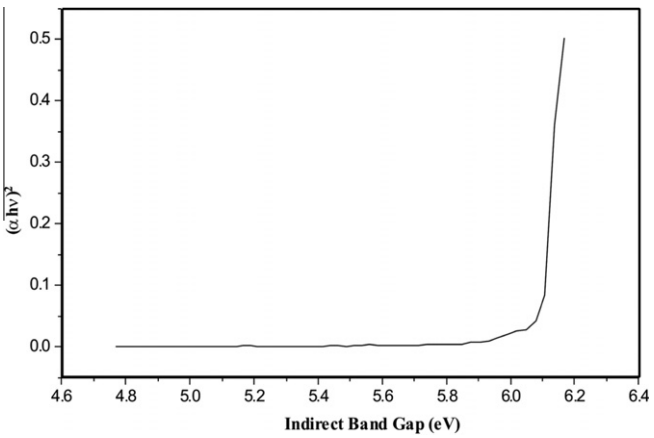

Fig. 3. Indirect band gap of SrO QDs.

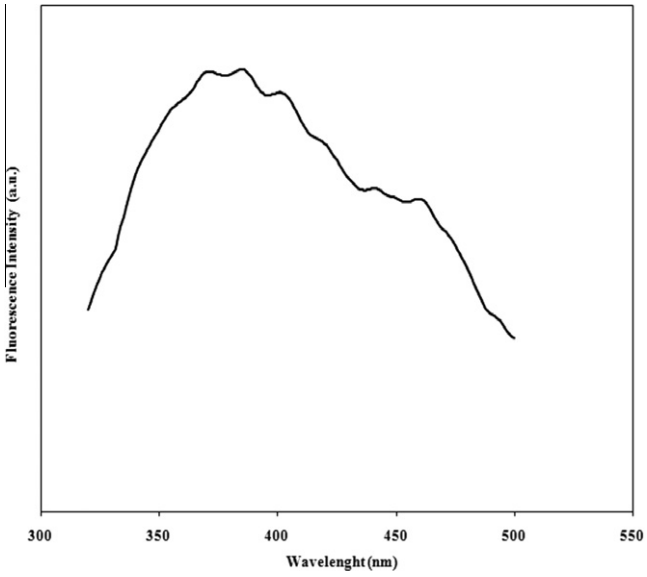

Fig. 4. Emission spectrum of SrO QDs under 254 nm excitation.

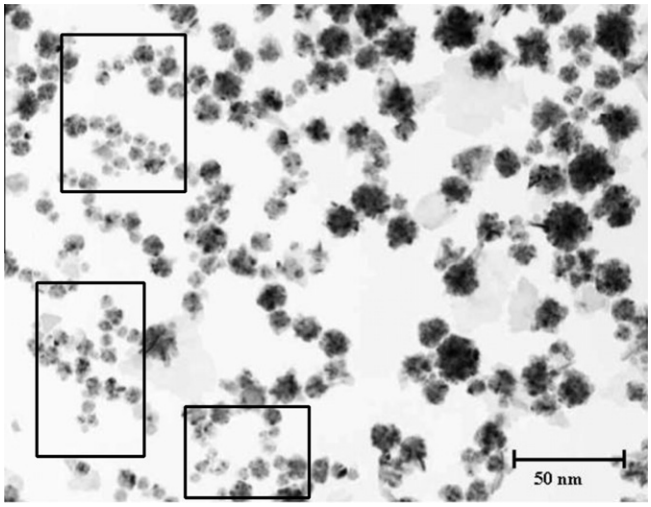

Fig. 5. TEM image of SrO QDs.

The exciton Bohr radius of SrO QDs was estimated as in reference [8]. In this study it was found to be 1.983 nm. This value is greater than the quantum dot radius. This is in agreement with $R \ll$ RB, which shows the presence of strong quantum confinement regime in SrO QDs.

In order to calculate the particle size, fluorescence measurements were made at an excitation wavelength of 254 nm and fluorescence observed from 320 to 500 nm, displayed in Fig. 4. The fluorescence is the exciton recombination, which directly probe the optical band gap of the particles. This emission frequency is perceived as fluorescence and depends on the size of the band gap, which can be altered by changing the size of the QD as well as changing the surface chemistry. It is important to note that the smaller the QD, the higher the band gap energy. This size tunable absorption and emission property of QDs is extremely valuable for quantum dot analysis. QDs are fluorescent semiconductor nanocrystals, range in size from 2 to 25 nm in diameter and contain approximately 200–10,000 atoms leading to the effects of quantum confinement [12].

The particle size was calculated using the effective mass approximation (EMA) assuming exciton confinement in particle with. The optical band gap and particle size are correlated with Eq. (3) [13].

$$E_g = E_{bulk} + \frac{h^2}{8r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{e^2}{4\pi\varepsilon_0\varepsilon_r\gamma_e} \quad (3)$$

where r is the radius of the particle, γ_e is the Bohr exciton radius and E_{bulk} is the band gap of bulk SrO, ε_r is relative dielectric constant, ε_0 is dielectric constant of air. m_e^* effective mass of electron in SrO, m_h^* is effective mass of hole. These calculations resulted in the radius of particle of SrO QDs. r is found to be 1.33 nm, $2r$ = 2.67 nm gives the particle size.

The TEM image of SrO QDs is shown in Fig. 5. This shows that the QDs are spherical in shape. The small amount of agglomeration of QDs is observed in the micrograph. The average particle size is observed to be ~3 nm. The average particle size estimated from UV–VIS analysis and fluorescence spectroscopy is in good agreement with the TEM investigation. Micic et al. [14] reported the EMA break down at a lower particle size. This observation is not evidenced in the present case. Imaging a small dot through electron microscopy technique is not enough to say it is in a quantum dot state [15]. The optical absorption is a technique that allows one to directly probe the band gap of QDs. The band gap edge of a material should be blue shifted if the material is confined. This blue-shifted spectrum confirmed the formation of QDs. In our case, the intense absorption is observed at 203 nm.

4. Conclusions

The nanosize SrO QDs were successfully synthesized by chemical route. The direct and indirect band gap values for SrO QDs were found to be 6.14 eV and 6.1 eV, respectively. The radius of SrO QDs was computed by HBM and found to be 1.24 nm. Thus the particle size was 2.48 nm. The energy of lattice phonon may be observed as 0.04 eV. The exciton Bohr radius of SrO QDs was estimated to be 1.983 nm. This value is greater than the quantum dot radius. This is in agreement with $R \ll$ RB. This indicates the presence of strong quantum confinement regime in SrO QDs. The average particle size from TEM analysis was observed to be ~3 nm. This agrees with UV–VIS analysis and fluorescence spectroscopy.

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