Synthesis of SnO$_2$ quantum dots by chemical precipitation assisted by ultrasound

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Abstract. SnO$_2$ quantum dots were successfully prepared via chemical precipitation assisted by ultrasound. X-ray diffraction analysis confirmed the rutile tetragonal structure of SnO$_2$ QDs with a crystallite size of 1.4 nm. The SEM micrographs of the obtained powder exhibited that the SnO$_2$ QDs are agglomerated particles of around 10 nm, while TEM images confirmed that the crystallite size are similar to the measured from XRD. The band-gap energy of the SnO$_2$ QDs measured from the UV–Vis reflectance spectrum of the SnO$_2$ QDs was 4.3 eV, displaying a significantly blue-shifting attributed to quantum confinement.

1. Introduction
Tin dioxide is an n-type semiconductor with band gap energy, $E_g$, of 3.6 eV and its calculated exciton Bohr radius $a_B$ is approximately 2.7 nm [1], thus the quantum dots (QD) of SnO$_2$ have smaller sizes than 2.7 nm. Recently, there has been growing interest in the properties of wide-band gap oxide QD SnO$_2$ semiconductors, because it has outstanding applications in various fields, as electrochemical Cd sensor [2], gas sensor [3], anode for sodium ion battery [4], and photocatalyst [5].

There are different physical and chemical methods that have been used to synthetize SnO$_2$ QDs as chemical precipitation [6], laser ablation [7], sonochemistry [8], hydrothermal [9], and microwave heating method [10]. Hence, synthesis of crystalline SnO$_2$ QDs by a fast and facile method is a challenging job. Herein, we develop a synthesis of SnO$_2$ QDs using chemical precipitation assisted by ultrasound in a heated ultrasonic cleaning bath commonly used in a chemical lab.

2. Experimental
All chemicals were of analytical grade and used without any further purification. A 25 ml of aqueous solution of 0.13 M of tin tetrachloride pentahydrate, SnCl$_4$·5H$_2$O (Aldrich), was prepared and then placed in an ultrasonic bath (Branson Model MT 1510) at 42 kHz and 75W and heated to 65 °C. After the solution was warm, then 4.5 ml of ammonia solution (Merck, 25%) was then added drop by drop to the above solution while sonicating, so that the final pH value of the solution was 9.5. The irradiation time was 150 min. The formation of a white tin oxide nanosol, presumably via the chemical reaction:

$$\text{SnCl}_4\cdot5\text{H}_2\text{O}_{(ac)} + 4\text{NH}_4\text{OH}_{(ac)} \xrightarrow{\Delta T=65^\circ/\text{Ultrasound}} \text{SnO}_2\downarrow + 4(\text{NH}_4\text{Cl})_{(ac)} + 7\text{H}_2\text{O}_{(ac)} \quad (1)$$

The nanosols were precipitated by centrifugation (Eppendorf Centrifuge 5810R) and washed several times using distilled water. Finally, the resultant white solid was dried at 70 °C for 24 h. The structure
and domain size of the nanoparticles were determined by X-ray diffraction using a Rigaku Miniflex II Desktop diffractometer operating with CuKα radiation (0.15045 nm wavelength) at 30 kV and 20 mA with a scan speed of 3° min⁻¹. The X-ray diffraction data were subjected to a general convolution process (Topas-Academic) allowing, in principle, any combination of appropriate functions to be employed for modeling the whole powder profile. These functions can represent the aberrations of the diffractometer as well as various contributions from the specimens; the technique is known as a ‘fundamental parameters approach’ [11]. It was used together with the Rietveld refinement method [12, 13] and gave the crystallite domain size of the SnO₂ QDs. The morphology of the nanoparticles was investigated by Field Scanning Electron Microscopy (FESEM) using a Zeiss ULTRA plus instrument. A JEOL FEG 2010-F Transmission Electron Microscope operated at 200 kV was used for recording the Bright Field (BF) and High Resolution Electron Microscopy (HREM) micrographs of the samples. UV–vis Diffuse Reflectance Spectroscopy (DRS) was measured by UV visible spectrometer (Perkin Elmer Lambda 750 double beam) equipped with 60 mm integrating sphere and spectalon was used as a reference. The powders were filled in a hole (10 mm in diameter and 3 mm deep) of a sample holder, and the surface was smoothed. The layer can be regarded as infinitely thick, as required by the Kubelka-Munk theory.

3. Results and Discussion

Tin oxide has a tetragonal structure with the space group $P4_2/mnm$ (136) and lattice parameter of $a=4.737\text{Å}$ and $c=3.185\text{ Å}$ [14]. Sn and O ions are located at $(0, 0, 0)$ and $(0.307, 0.307, 0)$, respectively. Figure 1 shows that all diffraction peaks can be indexed as belonging to the tin oxide phase. Domain sizes were determined from the broadening of the $x$-ray diffraction lines by assuming a Voigt function [15]. The average domain size for sample of SnO₂ QDs synthesized assisted by ultrasound radiation was found to be approximately 1.4 nm.

![XRD pattern of SnO₂ QDs](image)

**Figure 1.** XRD pattern of SnO₂ QDs (squares). Fitted pattern is shown as solid curves and tick marks indicate expected position of diffraction peaks for a modeled tetragonal SnO₂ structure. The lower part of the panel shows the difference plot between the experimental and fitted patterns.

The sample dried was a translucent rock like appearance and the morphology of the SnO₂ QDs was studied by FESEM, and Figure 2(a) shows a typical micrograph at low magnification for the obtained sample, it looks a stone with a smooth surface. But at high magnification shown in Fig. 2(b) indicates the presence of agglomerated particles with a narrow size distribution and a particle size of around 10 nm.
Figure 2. FESEM images at low (a) and high (b) magnification of SnO$_2$ QDs synthesized assisted by ultrasound irradiation for 150 min. Scale bars indicate magnifications.

Fig. 3 shows HRTEM images of the SnO$_2$ QDs, they are slightly agglomerated, and clearly show a single crystalline structure with a crystallite size of around 2 nm, which agrees with XRD measurement.

![HRTEM images of SnO$_2$ QDs](image)

Figure 3. HRTEM images of SnO$_2$ QDs.

SnO$_2$ exhibited a direct band gap [16]. Accurate $E_g$ estimation for studied SnO$_2$ QDs was obtained by using the equation for a direct transition [17]:

$$\alpha(h\nu) \approx B(h\nu - E_g)^{1/2}$$  \hspace{1cm} (2)

A UV–Vis diffuse reflectance spectrum of the obtained SnO$_2$ QDs powder is shown in Fig. 4a. The band gap of SnO$_2$ QDs may be estimated from the Kubelka–Munk function $F(R)$ which is proportional to the absorption coefficient ($\alpha$), which is estimated by the following equation [18]:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{k}{s}$$  \hspace{1cm} (3)

where $R$ denotes the reflectance. Figure 4b shows the modified Tauc plot of $(F(R) h\nu)^2$ vs photon energy ($h\nu$) for SnO$_2$ QDs. Extrapolation of this line to the photon energy axis yields the band gap as shown in Fig. 4b. The band gap of the SnO$_2$ QDs is about 4.3 eV. The band gap of semiconductor, with crystallite size smaller than the exciton Bohr radius, increases due to quantum confinement [1].
Figure 4. a) UV–Vis diffuse reflectance spectrum of SnO$_2$ QDs obtained by chemical precipitation assisted by ultrasound. b) Modified Tauc plot: $(F(R) h\nu)^2$ vs photon energy $(h\nu)$ for SnO$_2$ QDs.

4. Conclusions
The method of the synthesis for the SnO$_2$ QDs is straightforward, inexpensive and consumes less material than other methods that eliminate chemicals to the environment. X-ray diffraction analysis confirmed the rutile tetragonal structure of SnO$_2$ QDs with a crystallite size of 1.4 nm. The SEM micrographs of the obtained powder exhibited that the SnO$_2$ QDs are agglomerated of particles of around 10 nm, while TEM images confirmed that the crystallite size are similar to the measured from XRD. The band-gap energy of the SnO$_2$ QDs measured from the UV–Vis reflectance spectrum of the SnO$_2$ QDs is 4.3 eV, so was significantly blue-shifted due to quantum confinement.

Acknowledgments
The authors wish to thank the General Research Institute of the National University of Engineering (IGI-UNI) for a financial support.

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