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Self assembled surface adjoined mesoscopic spheres of SnO_2 quantum dots and their optical properties

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ABSTRACT

A simple one pot acidic solution single precursor synthesis method has lead to highly crystalline SnO_2 quantum dots (QD) that self assemble to form mesoscopic spheres. The precursor solvent and pH conditions were changed to optimise the crystalline quality, particle size and luminescence properties of SnO_2 QDS. X-ray diffraction and high resolution transmission electron microscopy clearly reveal the crystalline nature of SnO_2 particles of size about 2.5 nm with well defined lattice fringes and the surface adjoining to form mesoscopic spheres. Band gap enhancement due to quantum confinement effect has been observed. Blue luminescence and fast decay (1.2 ns) indicate creation of exciton and recombination with an oxygen vacancy centre. The results suggest that the optical properties follow the quantum size effect whereas the mesoscopic spheres of self assembled QDs lower the surface energy and provide large surface area for applications such as photovoltaic and gas sensing.

1. Introduction

Quantum dots of functional semiconductor like SnO_2 is of immense interest since novel properties exhibited by SnO_2 makes it a valuable material for wide ranging applications such as transparent conducting electrode, gas sensing, solar photovoltaic conversion, photo catalysis etc. SnO_2 is n-type semiconductor having wide band gap of 3.6 eV, high exciton binding energy of 130 meV [1,2,3,4,5,6,7] at room temperature and it shows high reflectivity in IR and good transparency in visible region. Due to such interest in SnO_2, there has been lot of reports in SnO_2 micro and nano structures with different morphology and study of their optical properties [8–13]. Three dimensional (3D) mesoscopic structure comprising 0D nanoscale building blocks (quantum dots) has the potential to offer more novel properties compared to similar solid structure due to much larger surface area and associated quantum confined optical properties. There have been very few reports of mesoscopic structures of SnO_2 [14–19]. Preparation of hierarchical structure of SnO_2 has been reported mainly for 1D/2D building blocks by complicated synthesis routes [20–24]. The present work describes a simple acidic solution single precursor synthesis method that leads to spontaneous self assembly in three dimensions in a ball like mesoscopic structure of monophasic spherical quantum dots of SnO_2. As the particle size approaches exciton Bohr radius, quantum confinement effect gets manifested in optical properties. Photoluminescence is a very useful probe for defects and surface states of QDs prepared in varied conditions. In the present study, important issues such as effect of pH of growth solution on crystallinity, luminescence and optical properties have been addressed to understand the processes and optimise the synthesis conditions to obtain best results. In addition, the quantum size effect on optical band gap of SnO_2 QDs has been investigated in self assembled mesospheres.

2. Experimental details

2.1. Synthesis

Tin oxide nanoparticles were prepared by simple low-temperature wet chemical method. Diluted solution (0.05 M) of tin chloride dihydrate ($SnCl_2{\cdot}2H_2O$) was prepared in DI water/ethanol/isopropyl alcohol and stirred for 2 h on magnetic stirrer with continuous heating at 40 °C. Few ml of HCL (conc.)/HNO_3/double diluted ammonia were added to the solution drop wise to maintain its pH as 1 or 7 or 10 respectively and again churned in magnetic stirrer for 1 h when nucleation of SnO_2 quantum dots with white/yellowish white colour becomes visible. The solution was kept in preheated oven at 90 °C for 24 h. Then the supernatant was decanted and the precipitate was washed with alcohol and DI water many times with subsequent ultrasonication and centrifugation. Precipitates washed with alcohol were dried in oven at 90 °C for 20 h. Different solvent and pH condition with changed acidic ligands were used to optimise the synthesis conditions. Best SnO_2 QDs were obtained with DI water and HNO_3 as

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solvent with solution pH maintained at acidic level 1 as measured by a pH meter.

2.2. Characterisation

The phase characterization of the synthesised product was done by X-ray diffraction (XRD) technique using Rigaku MiniFlex diffractometer with Cu Kα radiation. The average crystallite size (D) of the samples has been calculated from measured powder diffraction spectra using Scherrer equation as follows:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where k, λ, β, θ are the Shape factor (=0.9), X-ray wavelength ((λ = 0.15418 nm for Cu Kα), Braggs diffraction angle and the full width of half maximum (FWHM) of XRD peak respectively.

Morphology was studied using scanning electron microscopy using LEO 440 Pc based digital scanning electron microscope. The size, detailed morphology and lattice fringes of prepared quantum dots were observed on a high resolution transmission electron microscope (HRTEM) make FEI, model Tecnai G^2 TF30 STWIN. Samples for HRTEM were prepared by dispersing the powder in ethanol and ultra-sonicating for few minutes, and then droplets were placed on carbon coated Cu grids.

Photoluminescence (PL) excitation and emission spectra of the SnO_2 powders were measured with a LS-55 spectrometer. Time resolved decay was measured with Edinburgh instruments FLSP920 system using a hydrogen filled pulsed arc lamp (pulse width 700 ps) as excitation source with 40 kHz repetition frequency and time correlated single photon counting (TCSPC) technique.

Optical absorption characteristics of SnO_2 quantum dots were studied using Avantes Avaspec 3648 UV–vis spectrometer with a 1 cm quartz cell at room temperature. The sample was prepared by dispersing powder in glycerol and ultrasonicating for half an hour. The optical absorption coefficient α of a direct band gap semiconductor like SnO_2 close to the band edge can be expressed by the following equation:

$$\alpha = \frac{k(h\upsilon - E_g)^{1/2}}{h\upsilon} \quad (2)$$

where k is a constant, E_g is the band gap. The band gap can be estimated from the tauc plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ (photon energy) by extrapolating the linear part of the plot to the energy axis.

3. Results and discussion

X-ray diffraction patterns of SnO_2 powders prepared using different solvent and at different pH are shown in Fig. 1(a–d). All the diffraction peaks could be indexed to Bragg diffractions of the rutile structured SnO_2 with tetragonal lattice constant a = 4.74 Å and c = 3.19 Å, which match well to the reported value for SnO_2 crystal (JCPDS card no. 41-1445). The broadening of XRD peaks suggests that the SnO_2 crystals are of very small size. The average crystallite size was calculated based on the Scherrer equation, $D = 0.9\lambda/\beta\cos\theta$ and found to be in the range of 2.5–7 nm depending upon the solvent and pH value of the solution which also affected the crystallinity of the SnO_2 QDs. The crystallinity of SnO_2 QDs varied with precursor solvents and the pH of the solution. It is also found that the XRD peaks become sharper with annealing at higher temperature indicating increase in crystallite size. Table 1 enlists the different sample nomenclature using different solvent and pH routes to SnO_2 synthesis and the respective particle size calculated from XRD pattern using Scherrer formula. The optimum room temperature synthesis conditions to obtain good crystalline SnO_2 QDs was acidic (HNO_3) solution (pH 1) and morphological studies were carried out on the sample S6 accordingly.

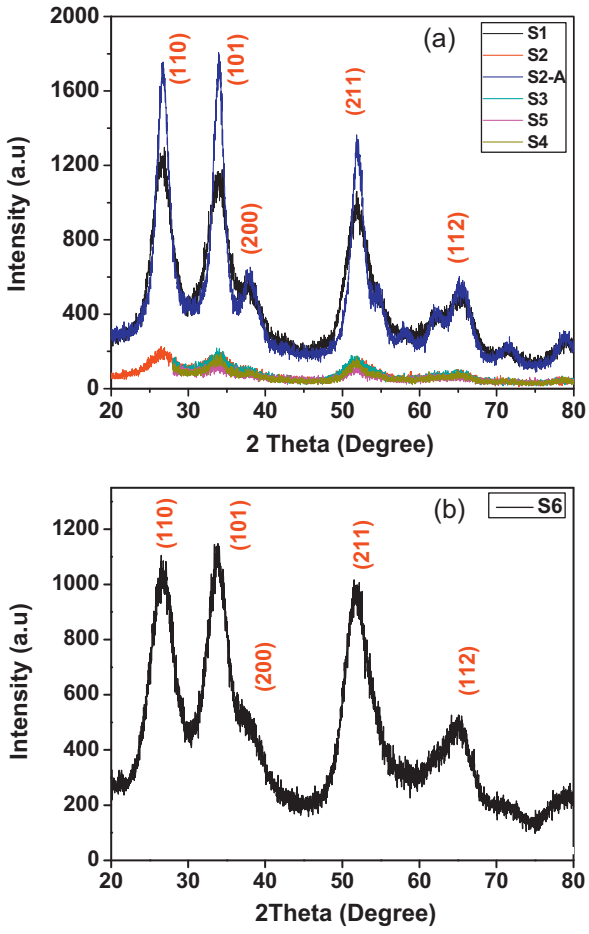

Fig. 1. XRD spectra of SnO_2 quantum dots prepared under different solvent and pH conditions, (a) with solvent as DI water and HCl with pH 1 (S1) and pH 10 as synthesised (S2) and annealed (S2-A), with pH 10 and solvent as IPA (S4) and ethanol (S5), with pH 7 and solvent as ethanol and DI water (S3) and (b) with optimised pH 1 and solvent as DI water and HNO_3 (S6).

Fig. 2 shows the scanning electron micrograph of SnO_2 nanoparticles synthesised using solvent as water and HNO_3 and pH maintained at 1 (S6). The micrographs indicate the presence of spherical balls of diameter ranging in few hundred nanometers indicating self assembled mesoscopic structure of much smaller particles as indicated by XRD analysis (particle size = 2.5 nm). Formation of similar mesoporous microspheres of SnO_2 via nanoparticle assembly has been reported [10] using hydrothermal carbon microspheres as sacrificial templates. Herein the SnO_2 QDs nucleate, grow and self assemble into microspheres without any template in a simple one pot acidic solution synthesis process. To understand the constituents of the mesoscopic balls in greater detail, HRTEM was carried out for the same sample (S6) which is shown in Fig. 3. From high resolution transmission electron

Table 1
SnO_2 nanoparticles prepared with different pH and Solvents.

Sample name	pH	Solvent	Particle size (from Scherrer's equation)
S1	1	DI water and HCl	2.8 nm
S2	10	DI water and HCl	2.5 nm
S3	7	Ethanol and DI water	5 nm
S4	10	Isopropyl alcohol	2.83 nm
S5	10	Ethanol	7.7 nm
S6	1	DI water and HNO_3	2.5 nm
S2-A	10	S2 annealed at 500 °C	4.5 nm