Rose-like SnO$_2$ Nanostructures Synthesized via Facile Solvothermal Technique and their Optical Properties

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ABSTRACT

Rose-like SnO$_2$ nanostructures was successfully synthesized by using ethylenediamine as both an alkali and ligand via solvothermal technique. Quantum size nanocrystalline (2.25nm) was calculated and conformed by XRD and TEM analysis. Rose-like morphology was observed by SEM analysis. The quantum confinement effect was occurred by UV-vis spectroscopy. Room-temperature photoluminescence was carried out and investigated. The growth mechanism of the products is also discussed. The results show that the products have a rose-like SnO$_2$ nanostructure and consist of lot of tiny nanocrystalline, which are good candidates for gas sensor, solar cell and optoelectronic devices.

Keywords: Semiconductor, SnO$_2$, Nanocrystalline, Facile Solvothermal, Optical properties

1. Introduction

Recent studies have shown that many fundamental physical or chemical properties of semiconductor materials strongly depend on the size and morphology of the materials [1]. Nanostructured oxide materials are gaining increasing technical important for classic areas of application such as catalysts, passive electronic components or ceramic materials, and gas sensors [2]. Tin dioxide (SnO$_2$) in its pure form is an n-type semiconductor with a direct band gap of 3.6 eV between the full oxygen 2p valence band and the tin states at the bottom of the conduction band. It is particularly interesting because it has semiconducting properties and has been widely used as a catalyst for oxidation of organic compounds, as gas sensors, rechargeable Li-batteries [3] and optical electronic devices [4]. Particularly tin dioxide (SnO$_2$) is widely used as a gas sensor detecting reducing gases, such as H$_2$, CO, and H$_2$S, based on the resistivity changes with gas adsorption and desorption [5, 6]. Nanoparticles of oxide material are of considerable interest in the area of chemical sensing due to the improved sensitivity of nanostructures to the reducing gases compared to bulk oxide materials. The improved sensitivity of the

nanostructured oxides are due to the availability of high surface area and grain boundary sites in the nanostructured oxides. Ultra-fine powders are particularly important for many of these applications, because of their small crystallite size and high surface area.

To date, much work has been focused on SnO_2 nanomaterials due to their potential applications in numerous areas such as gas sensing, and many methods haven been proposed to synthesize SnO_2 nanocrystallites. However, achieving both good morphology and well-dispersed quality of SnO_2 nanoparticles is still a challenge.

In this paper, we report a rose-like nanostructure and consist of lot of tiny nanocrystalline was successfully synthesized by facile solvothermal technique by using mixture solvents (benzene: toluene (1:1)) and ethylenediamine as both an alkali and ligand. Ethylenediamine has always been a good candidate ligand because of its strong alkaliscence, weak polarity, reducibility, strong coordination interaction with metal ions and low boiling point. The structure and morphology information of the products was characterized by means X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Optical properties of the products were carried out UV-vis and Photoluminescence (PL).

2. Experimental procedure

2.1 Synthesis of rose-like SnO_2 nanostructures

A closed cylindrical Teflon-lined stainless steel autoclave with capacity of 100ml was used for the synthesis. All the reagents and solvents used were analytical grade and used without any further purification. 1.1g of $SnCl_4.5H_2O$ was taken into the beaker then 80ml of solvents (Benzene: Toluene (1:1)) were added. While stirring, 1ml of ethylenediamine was slowly added drop wise into the above solution. Slurry like white solution was formed, it poured into the autoclave which was kept in oven at 200°C for 24h. After the reaction, the autoclave was allowed to cool down naturally room temperature. The resulting brownish precipitates were carefully washed with distilled water and absolute ethanol repeatedly to remove impurities and then dried in vacuum at 60°C for 5h. The final products were characterized by the following methods.

2.2 Characterization of as-synthesized SnO_2 nanostructures

The crystal structure and size of the resulting products was characterized by X-ray powder diffraction (XRD, JSO-DEBYEFLEX 2002 X-ray diffractometer with Cu-Kα radiation, λ=0.1540nm). Optical properties of the products were carried out by Ultra-violet (UV, Varian Cary 5E spectrophotometer) and Photoluminescence (PL, Fluoromax-4 spectrofluorometer with a Xe lamp as the excitation light source). The morphology of the products was observed by scanning electron microscopy (SEM, Hitachi S-4500 scanning electron microscope) and size of the products was further confirmed by transmission electron microscopy (TEM, JEOL-3010 operating

at 200KV). Before TEM imaging, the products were ultrasonically dispersed in methanol.

3. Results and discussion

The phase and purity of the as-synthesized SnO_2 nanostructure were determined by the X-ray powder diffraction (XRD) pattern (Fig. 1) all the diffraction peaks can be perfectly indexed to the tetragonal structure of SnO_2. There is no any other peak corresponding to the impurity. The broadening peaks attributed that the small size of crystalline. The average crystalline size was calculated to be 2.25nm by using Debye-Scherer's equation.

$$D = 0.89\lambda/\beta\cos\theta$$

where λ is X-ray wavelength (0.1540nm for Cu-Kα), β is the full width at half maximum of the diffraction peak (FWHM) and θ is Bragg's diffraction angle. In Scherrer's equation, β represents the broadening due to particle size alone. In general the experimentally observed broadening (β_o) is the total contribution from particle size broadening [β] , instrumental broadening (β_i) and strain broadening (β_s) and is represented as

$$\beta_o = \beta + \beta_i + \beta_s$$

For our present case, we have considered $\beta \cong \beta_o$ (without considering β_i and β_s). Thus the measured particle sizes are always on the low side and the actual particle size is higher than the values obtained. However, the observed broad hump (and therefore large FWHM) suggests that the synthesized materials are nanocrystalline in nature with very small particle size.
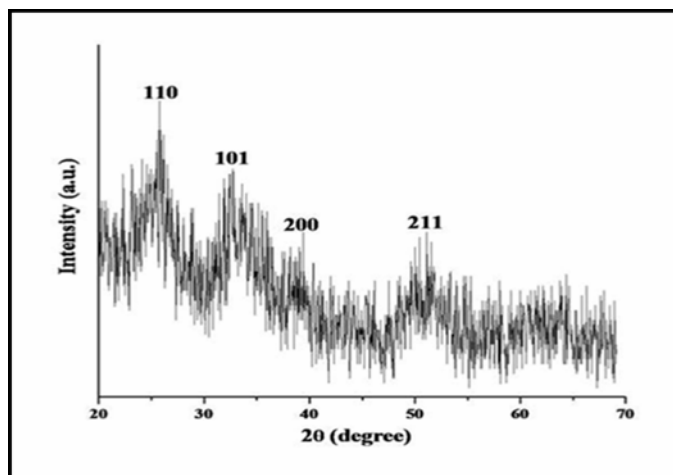

Fig. 1 XRD pattern of as-synthesized SnO₂ nanocrystalline.

UV-vis absorption spectrum was carried out in order to characterize the optical absorbance of the SnO_2 nanocrystalline. For semiconductor materials, the quantum confinement effect is expected if the semiconductor dimension become smaller than the Bohr radius (2.7nm) of the exciton, and the absorption edge will be shifted to a higher energy [7]. The absorption spectrum of as-synthesized SnO_2 nanostructure shows in Fig. 2.
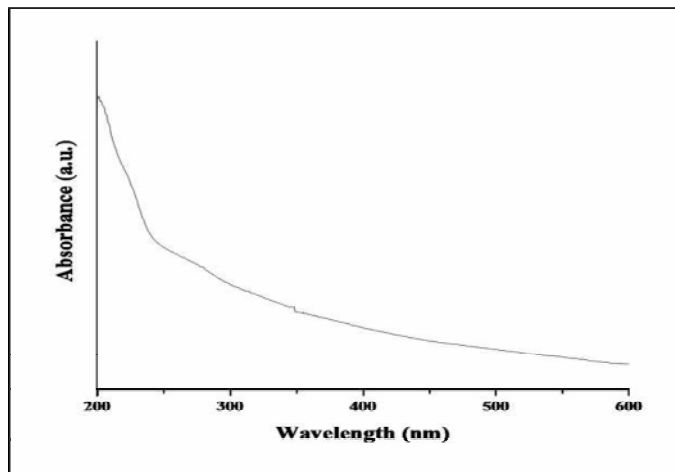

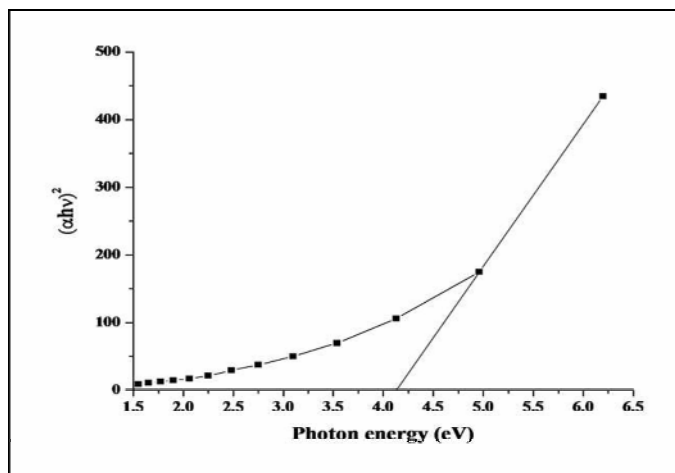*Fig. 2 UV-vis absorption spectrum of as-synthesized SnO_2 nanocrystalline.*

Fig. 3 The spectrum of $(\alpha h\nu)^2$ versus photon energy (eV).

The value of the absorption edge of the sample was 296nm (about 4.18 eV). The optical band gap energy can be estimated by using the following equation for a semiconductor:

$$\alpha = K \, (h\nu - E_g)^{n/2} / \, h\nu$$

where α is the absorption coefficient, K is a constant, E_g is the band gap and n is equal to 1 for a direct transition. The band gap can be estimated from a plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$).

The intercept of the tangent to the plot will give a good approximation of the band gap energy for this direct band gap material (shown in Fig. 3) [8]. The band gap of the as-prepared SnO$_2$ nanocrystalline calculated to be 4.18 eV is larger than the value of 3.62 eV for the bulk SnO$_2$ due to the contribution of quantum size effect of the present SnO$_2$ nanoparticles [9].

Fig. 4 shows the photoluminescence emission spectrum of as-synthesized SnO$_2$ nanocrystalline. The oxygen vacancies mostly present in three charge states of Vo^o, Vo$^+$ and Vo^{++} [10]. As the Vo^o is a much shallow donor, it is believed that most oxygen vacancies will be in their paramagnetic Vo$^+$ state under flat-band conditions [11]. The recombination of surface trapped hole with an electron in deep trap (Vo$^+$) to form a Vo^{++} center gives rise to visible emission when a conduction band electron recombines with the Vo^{++} center. In the spectrum (Fig. 4), there are three strong emission peaks at 423, 468 and 510, three week emission peaks at 451, 482 and 492 and three shoulder emission peaks at 458,463 and 472. The one of the strong emission peak at 468nm can be assigned to oxygen-related defects [12]. The other peaks also may be attributed to near band-to-band transition and oxygen-related defects.
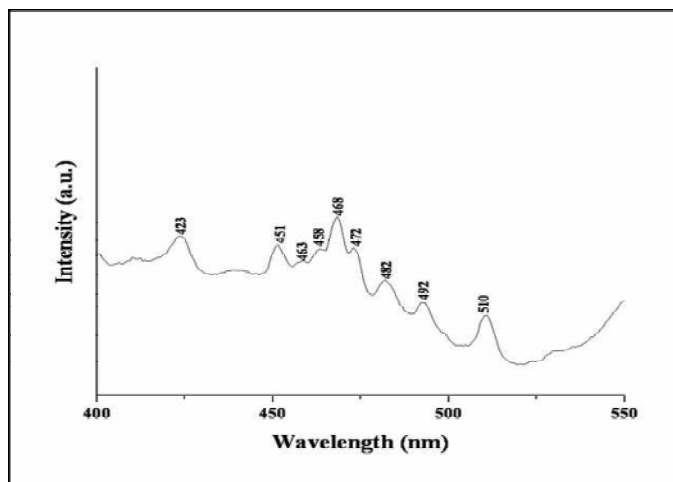

Fig. 4 Photoluminescence spectrum of as-synthesized SnO$_2$ nanocrystalline.

The morphology of the as-synthesized SnO_2 samples was carried out by SEM analysis. Rose-like morphology was observed shows in Fig. 5. Ultra-fine nanocrystalline were aggregated and showed as rose-like morphology. The result shows that the products have a rose-like nanostructure and consist of lot of tiny nanocrystalline. The average crystalline size was calculated to be ~2.25nm.
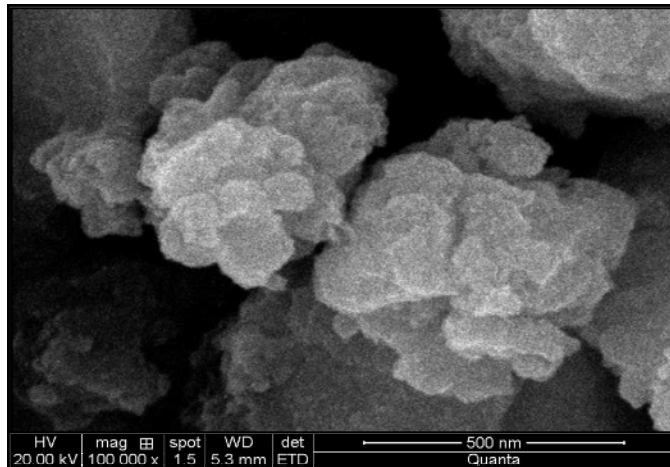

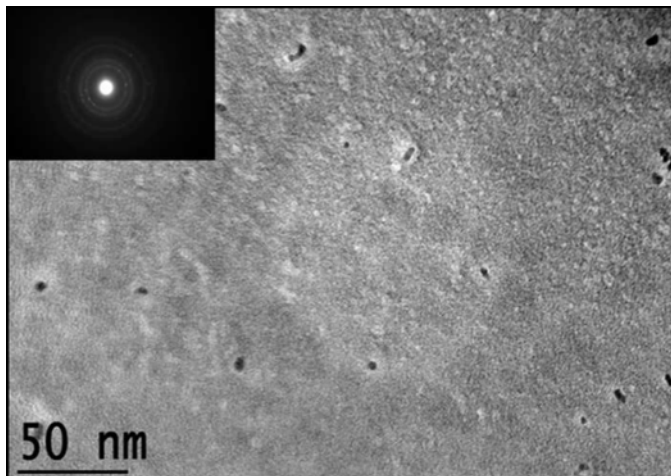*Fig. 5 Rose-like morphology of as-synthesized SnO₂ nanostructures.*

Fig.6 TEM image of as-synthesized SnO₂ nanocrystalline.

The crystalline size was further confirmed by TEM analysis, well-dispersed SnO_2 nanocrystalline shows in Fig. 6. It is clearly observed that the as-synthesized SnO_2 nanocrystalline are extra-fine, with an average grain size of 2.25nm. This result is similar to that obtained from XRD analysis. The SAED pattern rings

revealed (inserted in Fig. 6) that the obtained SnO$_2$ nanoparticles are highly crystalline in nature.

It is well known that ethylenediamine is both a strong coordination that can coordinate with Sn^{4+} and a strong alkali reagent. The mechanism for the formation of the SnO$_2$ nanocrystalline would be meaningful to provide the methodology to synthesis novel Nanomaterials: as the ethylenediamine was added into the precursor solutions, the complex of Sn$_n$(ethylenediamine)$_m$$^{4+}$ were formed immediately and white slurry was observed. Mean while, –OH groups were released. During the solvothermal process, the complex of Sn$_n$(ethylenediamine)$_{m-x}$(OH)$_x$ $^{(4-x)+}$ were dissociated and quantum size SnO$_2$ nanoparticles formed gradually.

4. Conclusion

We have synthesized rose-like nanostructures of quantum sized SnO$_2$ nanocrystalline by using ethylenediamine as a both a coordination and an alkali reagent via facile solvothermal technique. The crystalline size was estimated by XRD and conformed by TEM analysis. The morphology of the SnO$_2$ nanostructure was carried out by SEM analysis. The optical properties were carried out by UV-vis and PL studies. The possible mechanism was discussed for formation of quantum size SnO$_2$ nanocrystalline. From the above experimental results, it can be concluded that the properties of SnO$_2$ nanocrystalline, which are good candidates for gas sensor, solar cell and optoelectronic devices.

Acknowledgement

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