Quantum sized SnO_2 nanoparticles: Hydrothermal technique and optical properties

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By using ethylenediamine as both an alkali and ligand, quantum sized SnO_2 nanoparticles were successfully synthesized with a facile hydrothermal technique. The as-synthesized products were studied by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersed X-ray spectroscopy (EDX), ultraviolet-visible (UV-vis) absorption spectroscopy and room-temperature photoluminescence (PL) spectroscopy. X-ray powder diffraction pattern of the sample is quite similar with the standard pattern of tetragonal SnO_2 nanoparticles with average particle size was 3nm; SEM and TEM results shows that the spherical shaped with ultra-fine SnO_2 nanoparticles. The special photoluminescence property of the SnO_2 nanoparticles was attributed to the oxygen vacancies in the surface. Finally, the growth mechanism and special properties for the formation of quantum size SnO_2 nanoparticles was also discussed.

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1. Introduction

Tin oxide (SnO_2) is an important n-type metallic oxide semiconductor with wide band gap (3.6eV). Because of its unique electronic, optical, electrochemical and catalytic properties, SnO_2 were extensively used in solar cell, transparent conducting electrodes, solid-state sensors, rechargeable Li batteries and optical electronic devises [1-6]. For these applications, SnO_2 small particle size or large specific surface area is essential to high performance. The crystalline structure, the size and shape of the particles and the superficial characteristics are highly dependent on the followed route of synthesis. Until now, many methods have been developed to synthesize SnO_2 nanocrystallites, including sol-gel [7], chemical vapor deposition (CVD) [8], spray pyrolysis [9], solvothermal methods [10], laser abllation [11, 12], rapid oxidation of metal tin [13], thermal evaporation of oxide powders [14] and molten salt method [15]. Compared with other methods, the hydrothermal approach is a better alternative with the advantages of mild synthetic conditions, simple manipulation and low pollution. Even through the development of agglomerates is to be avoided, their growing is somehow inevitable else to the small diameter of the oxide particles and to the presence of the compounds involved in the mentioned procedure, mainly solvents. In the chemical methods reported in the literature the most common precursor used was $SnCl_4 \cdot 5H_2O$ with the oxidation state IV of tin in solution leading to the formation of SnO_2 nanocrystals [10]. Ethylenediamine acted as a template molecule, which was incorporated into the inorganic framework first and then escaped from it to form nanocrystallites with desired morphologies [16].

In this present work, quantum-size tin dioxide nanoparticles were prepared through ethylenediamine as both an alkali and ligand to coordinate with Sn ions by hydrothermal method. 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. Optical and microscopy studies are investigated.

2. Experimental procedure

2.1. Synthesis of quantum size of SnO_2 nanoparticles

SnO_2 nanoparticles were successfully synthesized by the following procedure. In a typical synthesis, dissolving 1.06g of tin chloride (hydrous $SnCl_4.5H_2O$) in 60 ml distilled water and 0.8ml of ethylenediamine was added to the above solution drop wise. The dropping rate must be well controlled for the chemical homogeneity. The resulting slurry-like white solution were poured into a stainless steel Teflon-lined autoclave and maintained at 190°C for 24h, and then cooling it down to room temperature naturally. The light brown precipitate was collected and washed with distilled water and absolute ethanol for several times to remove impurity, then dried at 60°C for 5 h in vacuum. The final product was used for further characterizations.

2.2. Characterization of quantum size SnO_2 nanoparticles

The size and purity of the as-synthesized sample was examined by X-ray powder diffraction (XRD) pattern was obtained using a Seifert (JSO DEBYEFLEX 2002)

diffractometer. XRD pattern was collected at room temperature using a continuous scan over an angular range of 2θ =20°– 70° with step size of 0.04° and scan rate of 1◦ min−1. Scanning electron microscopy (SEM) performed on a Hitachi S-4500 scanning electron microscope accompanied by energy dispersive X-ray analysis (EDX) attachment for the compositional analysis. Size and morphology of the as-synthesized sample further confirmed by Transmission electron microscopy (TEM) image, which was obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV. Ultraviolet-visible absorption spectrum was recorded in the range of 200–650nm on a Varian Cary 5E UV–Vis spectrometer. A Photoluminescence (PL) measurement was carried out on a Fluoromax-4 spectrofluorometer with a Xe lamp as the excitation light source.

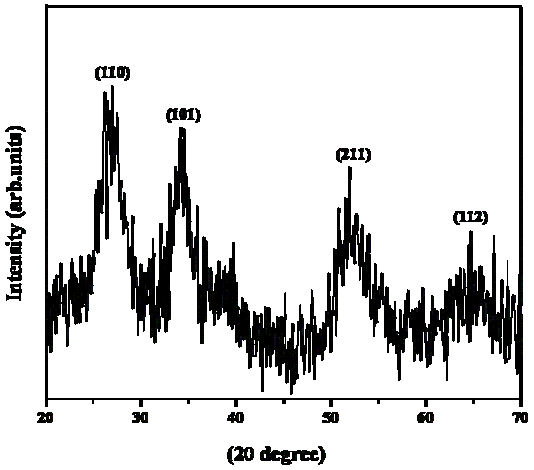

Fig. 1 XRD pattern of the as-synthesized SnO_2 nanoparticles.

3. Results

The X-ray powder diffraction pattern was recorded for the crystallographic identification of the as-synthesized sample as shown in Fig.1. The main diffraction peaks were observed at 26.7, 34.2, 52.0 and 64.8 degrees corresponding planes (110), (101), (211) and (112). SEM and EDX analysis provided the information about shape and elementary species of as-synthesized nanoparticles as show in Figs. 2 and 3. The size and morphologies of the as-synthesized nanoparticles were further investigated by TEM analysis as shown in Fig.4. Absorption spectrum of as-synthesized SnO_2 nanoparticles shows in Fig.5. Fig.6 illustrates the room-temperature photoluminescence of SnO_2 nanoparticles as-synthesized under aqueous condition.

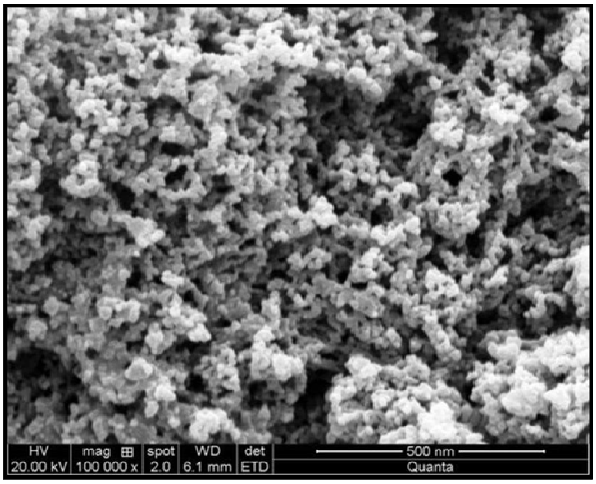

Fig. 2 SEM image of the as-synthesized SnO_2 nanoparticles.

4. Discussion

The XRD pattern of the product confirms that the formed material is tin oxide. All diffraction peaks can be indexed to the pure tetragonal SnO_2 crystalline phase. Moreover, no other characteristic peaks of the impurities, such as metallic Sn and other tin oxides were observed. The broad peaks are attributed to small size of nanoparticles according to the Scherrer's formula. The crystallite size diameter (D) of the SnO_2 nanoparticles has been calculated by equation:

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

where the λ is X-ray wavelength (0.1541nm for Cu-Kα), β is the full width at half maximum of the diffraction peak (FWHM) and θ is Bragg's diffraction angle. The average crystal size of the SnO_2 nanoparticles calculated to be ~3nm.

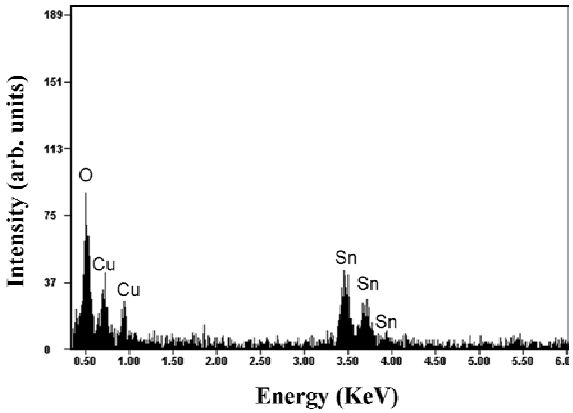

Fig. 3 EDX pattern of the as-synthesized SnO_2 nanoparticles.

The SEM image of as-synthesized SnO_2 nanoparticles shows an agglomeration of spherical particles. The agglomeration effect was very prominently observed when we synthesized nanoparticles in aqueous media [17]. The energy dispersive X-ray (EDX) spectrum is used to confirm the composition of the prepared sample. The EDX pattern of the sample is indicates that high purity, which is in good agreement with the XRD result. The presence of Sn, O and Cu as the only elementary species in the sample, indicate that no any impurity in the sample. The presence of Cu is due to the copper grid. The spectrum was directly recorded by the EDX system attached to a scanning electron microscope (SEM). TEM image clearly indicates most of the particles morphology to be roughly spherical and ultra-fine particles. It is observed that in spite of agglomeration of nanoparticles, they have a narrow size distribution. The size of the SnO_2 nanoparticles was only about 3nm and is in good agreement with the values obtained from Scherrer's formula.

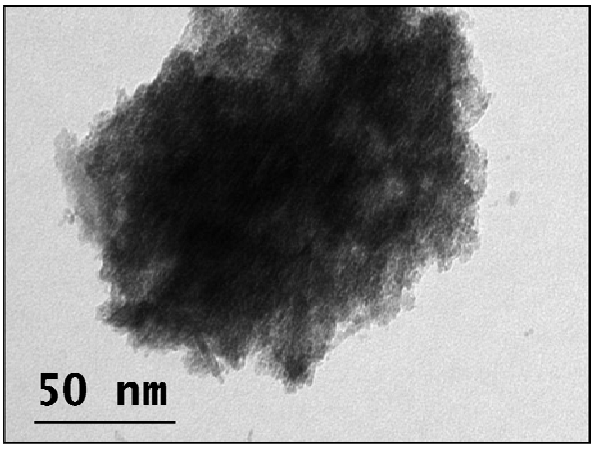

Fig. 4 TEM image of the as-synthesized SnO_2 nanoparticles.

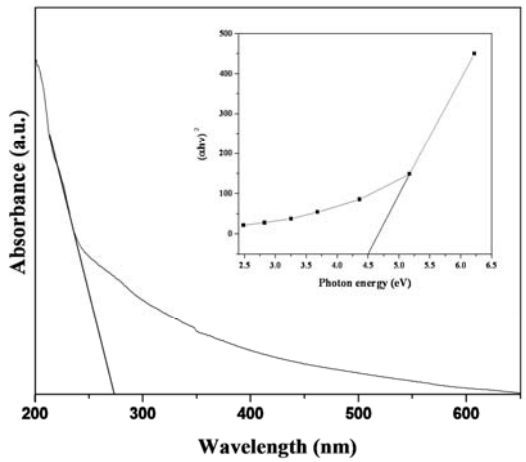

Fig. 5 UV-Vis absorption spectrum of the as-synthesized SnO_2 nanoparticles ($(\alpha h\nu)^2$ versus (hν) insert).

The direct band gap value of the SnO_2 nanoparticles synthesized by aqueous media presented in Fig.5. The data for Fig. 6 (inserted) was obtained by optical absorption measurement and plotting $(\alpha h\nu)^2$ versus photon energy (hν) using the following relation for direct energy gap [18]:

$$(\alpha h\nu)^2 = A\,(h\nu - Eg),$$

where α is the absorption coefficient, A and Eg are constant and band gap of the material, respectively. The quantum confinement effect is expected for semiconducting nanoparticles, and the absorption edge will be shifted to a higher energy when the particle size decreases [18]. The band gap of the as-synthesized SnO_2 nanoparticles is about (276 nm) 4.49eV, which is larger than the value of 3.6eV for the bulk SnO2 [19]. It is related to the size decrease of particles and we attribute it to the quantum confinement limit reaching of nanoparticles. Hence, the quantum confinement effect was well presented for the as-synthesized SnO_2 nanoparticles.

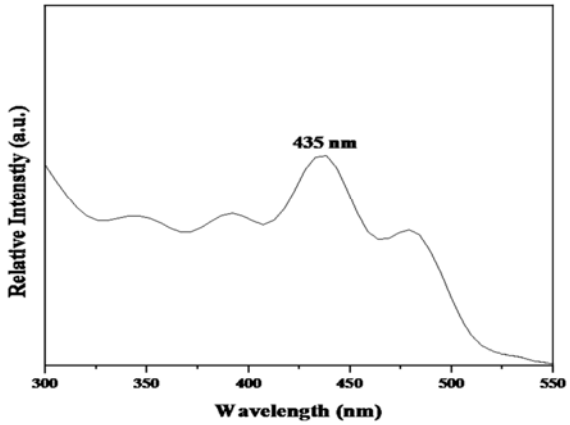

Fig. 6 PL spectrum of the as-synthesized SnO_2 nanoparticles.

In generally, the oxygen vacancies are the most common defects in the poly or nanocrystalline oxide and are used to be the radiative center in the luminescence process. The oxygen vacancies mostly present in three charge states of Vo^o, Vo^+ and Vo^{++} [20]. 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 [21]. 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 our study, there is one strong broad emission peak and one weak emission peak was observed at 435, 478nm in visible region. In addition, two shoulder emission peaks were observed at 345, 390nm. The earlier reports supposed that the broad peaks around visible region 400–500nm can be assumed to be due to the formation of a Vo^{++} luminescent center in the SnO_2 nanoparticles [22]. Therefore, in our study the strong broad peak at 435nm

attributed that related to the oxygen vacancies in the sample [23].

In water solvent, the synthesis consisted of hydrolysis of the precursor $SnCl_4.5H_2O$. In the process Eq. (1), the Cl^- ion was replaced by OH– to produce Sn-OH, which in turn produces Sn $(OH)_2$, and finally SnO_2 was formed according to the scheme shown below

$$\begin{array}{lll} SnCl_4 + H_2O & \longrightarrow & Sn^{4+} + Cl^- + H^+ + OH^- \longrightarrow (Sn^{4+} + OH^-) + (H^+ + Cl^-), \\ (Sn^{4+} + OH^-) & \longrightarrow & 4SnOH \longrightarrow 2\ SnO_2 \end{array} \quad (1)$$

It is well known that ethylenediamine is a strong coordination that can coordinate with Sn^{4+} and a strong alkali reagent. The quantum-size SnO_2 nanocrystallites during the hydrothermal process was supposed as followed: as the ethylenediamine was added into the precursor solution, the complex of $Sn_n(ethylenediamine)_m^{4+}$ were formed immediately and white slurry was observed. Meanwhile, OH– groups were released. During the hydrothermal process, the complex of $Sn_n(ethylenediamine)_{m-x}(OH)_x^{(4-x)+}$ were dissociated and SnO_2 nanocrystallites formed gradually. It was thought that the formation of $Sn_n(ethylenediamine)_m^{4+}$ complex decreased the reactivity between Sn ion and OH– group and resulted in the formation of quantum size SnO_2 nanocrystallites. From the above results, the possible mechanism for formation of the SnO_2 nanocrystallites would be meaningful to provide the methodology to synthesis novel nanomaterials.

5. Conclusions

We have synthesized quantum sized SnO_2 nanoparticles by using ethylenediamine as both a coordination and an alkali reagent by facile hydrothermal technique. The as-synthesized SnO_2 nanoparticles average particle size was 3nm, which was confirmed by XRD and TEM studies. SEM image shows that the spherical shaped nanoparticles. The quantum confinement effect was confirmed by UV-vis spectrum. PL study attributed to the oxygen vacancies in the surface. It was supposed that the formation of complexes between Sn^{4+} and ethylenediamine decreased the releasing rate of Sn^{4+} and induced the formation of quantum sized SnO_2. From the above experimental results, it can be concluded that the properties of SnO_2 nanoparticles, which are good candidates for gas sensor, solar cell and optoelectronic devices.

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