Role of chelating agent in chemical and fluorescent properties of SnO_2 nanoparticles*

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A modified polyacrylamide gel route is applied to synthesize SnO_2 nanoparticles. High-quality SnO_2 nanoparticles with a uniform size are prepared using different chelating agents. The average particle size of the samples is found to depend on the choice of the chelating agent. The photoluminescence spectrum detected at $\lambda_{ex} = 230$ nm shows a new peak located at 740 nm due to the surface defect level distributed at the nanoparticle boundaries.

Keywords: tin oxide, polyacrylamide gel, photoluminescence

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1. Introduction

Tin oxide (SnO_2) has been attracting a great deal of research interest due to its intriguing physicochemical properties. It has been established that SnO_2 has high chemical stability, remarkable resistivity variation in a gaseous environment, and a high exciton binding energy of 130 meV.[1] These outstanding properties make SnO_2 a promising candidate for the applications in gas sensors,[2] dye-based solar cells,[3] field emission displays,[4] and luminescent devices.[5] Nano-SnO_2 is of special interest, with many unique surface properties including luminescence and photocatalytic activity.[6,7] By investigating the photoluminescence spectra of pure SnO_2 nanoblades, Her *et al.*[8] reported a blue luminescence band at 2.8 eV related to a triplet-to-ground transition of a neutral oxygen-vacancy defect. For the nanostructured SnO_2 films, Gaidi *et al.*[9] reported a band at 3.2 eV attributed to defects close to the conduction band, a band-acceptor peak at 3.01 eV, a donor–acceptor pairs peak at 2.9 eV, and a broad peak at 2.48 eV connected to oxygen vacancy concentration. Although there has been substantial progress in this field, many issues such as the preparation method of SnO_2 nanoparticles and the origin of the luminescence still need to be further studied.

Recently, many efforts have been directed toward the fabrication of nano-SnO_2 to enhance the performances of materials in current applications. To date, well-defined nanostructures of SnO_2 with different dimensionalities such as nanowhiskers,[10,11] nanowires,[1,12] nanoparticles,[9,13] nanoblades,[8] nanotubes,[14–16] and nanofibers[17,18] have been obtained successfully. The polyacrylamide gel route is a promising method of producing nanoparticles, the basic reason for using chelating agents is that the corresponding crystal size may be adjusted under certain reaction conditions and with certain chelating agents.[19,20] Therefore, it is significant to prepare SnO_2 nanoparticles by using different chelating agents and study their luminescence properties. In this work, a modified polyacrylamide gel route is presented to synthesize SnO_2 nanoparticles with different average sizes.

2. Experiment

Stannic chloride, $SnCl_4{\cdot}5H_2O$, was dissolved in deionized water (0.015 mol/l). After the solution became transparent, a stoichiometric amount of citric acid or oxalic acid, which was used as the chelating agent to complex the cations, was added to the solution in the molar ratio 1.5:1 with respect to the cations (Sn). After that, 20-g glucose was dissolved in the solution. Finally, the acrylamide and N, N'-methylenebisacrylamide monomers were added to the solution and the pH value was adjusted to about 3 with aqueous ammonia. The resulting solution was heated at 90 °C on a hot plate to initiate the polymerization reaction, and a polyacrylamide gel was formed a few minutes later. The gel was dried at 120 °C for 24 h in a thermostat dryer. The obtained xerogel precursor was ground into powder and some powder was sintered at 400 °C for 5 h to prepare SnO_2 powders.

The phase purity of the samples was measured by means of X-ray powder diffraction (XRD) with Cu Kα radiation. The particle morphology was investigated by an INSPECT-F field-emission scanning electron microscope (SEM). Differential scanning calorimetry (DSC) analyses were performed

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by a Netzsch STA 449C simultaneous thermal analyzer. The luminescence properties were investigated at room temperature with a SHIMADZU RF-5301PC fluorescence spectrophotometer in the range of 200 nm–800 nm by using a 150-W xenon lamp as the excitation source.

3. Results and discussion

Figure 1 shows the XRD patterns of SnO_2 samples prepared by using citric acid or oxalic acid as the chelating agent, respectively. For both samples, almost all diffraction peaks can be indexed in terms of the tetragonal rutile structure of SnO_2 (JCPDS No. 21–1250). Interestingly, the grain size of the samples is found to depend on the choice of chelating agent. The use of citric acid as the chelating agent produces an SnO_2 sample with relatively broad diffraction peaks compared with that of oxalic acid, as clearly shown from the enlarged peaks given in Fig. 1(b). The crystallite sizes of the samples were calculated using the Scherrer equation

$$D = \frac{k\lambda}{\beta \cos\theta}, \tag{1}$$

where $k = 0.9$ is the grain shape factor, and β is the full width of the diffraction peak. The calculated crystallite sizes of the samples prepared by using citric acid and oxalic acid as the chelating agent are 92 nm and 118 nm, respectively. This indicates that an SnO_2 sample with a smaller grain size can be obtained by using citric acid as the chelating agent.

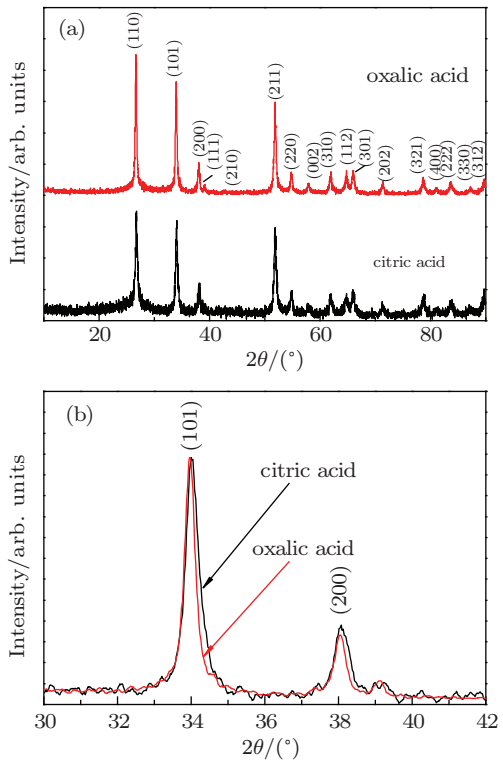


Fig. 1. (color online) (a) XRD patterns of SnO_2 samples prepared by using citric acid or oxalic acid as chelating agent. (b) Enlarged patterns around the peak (101).

Figures 2(a) and 2(b) display the SEM images of SnO_2 particles prepared by using citric acid or oxalic acid as the chelating agent, respectively, revealing that the particles are irregularly faceted with a narrow diameter distribution. The sample prepared with citric acid has an average particle size of 96 nm while the sample prepared by oxalic acid has an average particle size of 120 nm. Figure 3 depicts the corresponding particle size distribution statistically calculated from over 100 particles. The chelating agent is an important factor that affects the particle morphology.

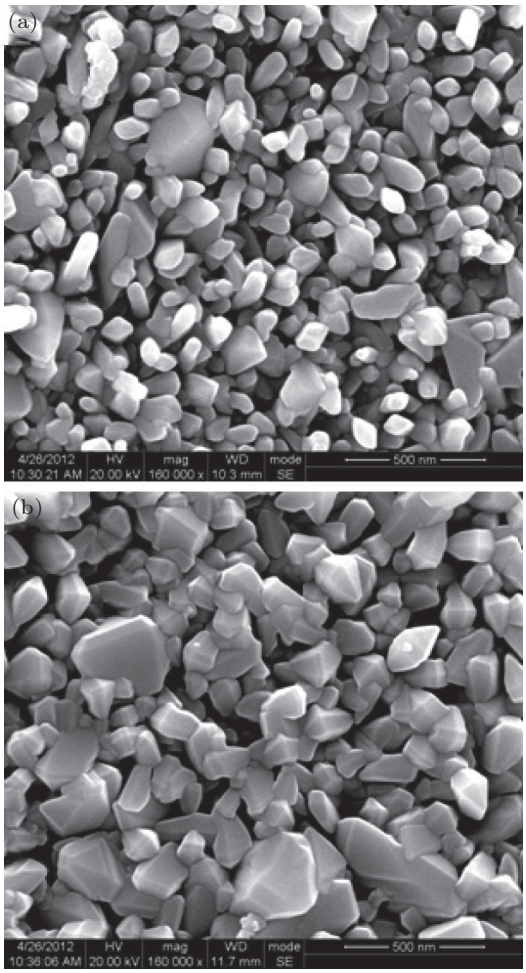


Fig. 2. SEM micrographs of SnO_2 particles prepared using (a) citric acid or (b) oxalic acid as the chelating agent.

To confirm the different particle size distributions with different chelating agents, the differential scanning calorimetry (DSC) curves of SnO_2 xerogel are shown in Fig. 4, revealing two exothermic processes. The weak exothermic peak at about 170 °C (oxalic acid)/200 °C (citric acid) is likely to be attributed to decomposition of micro-molecular organic compounds. The large exothermic peak at about 330 °C (oxalic acid)/354 °C (citric acid) is assigned to the decomposition of polyacrylamide's backbone and other residues.[21,22] As shown in Fig. 4, the chemical reaction finishes at about 380 °C (oxalic acid), resulting in the formation of SnO_2 powder. However, the modification of the SnO_2 precursor with a chelating

agent (citric acid) can result in an increased phase formation temperature. By considering the DSC patterns in Fig. 4 together with the SEM images in Fig. 2, we can see that the size of particles is not only determined by the chelating agents but also the temperature.

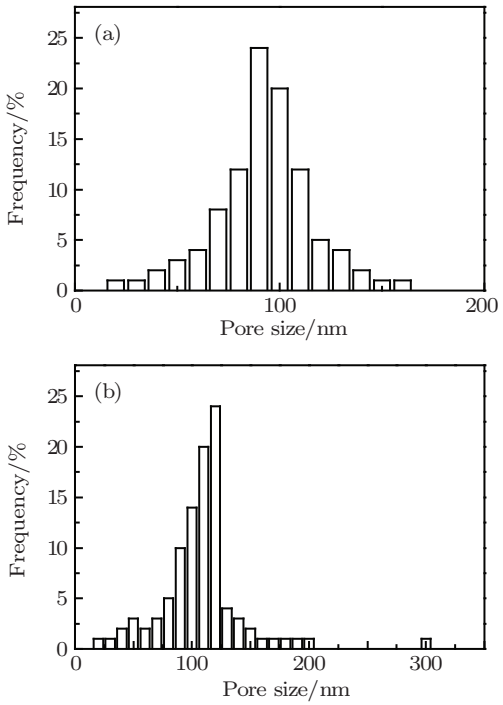


Fig. 3. Particle size distribution of SnO_2 samples prepared by using (a) citric acid or (b) oxalic acid as chelating agent.

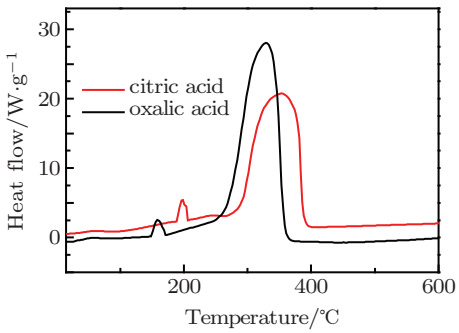


Fig. 4. (color online) Differential scanning calorimetry (DSC) curves of SnO_2 xerogel prepared by using citric acid or oxalic acid as chelating agent.

Figure 5 shows the photoluminescence (PL) excitation (λ_{em} = 379 nm) and the emission (λ_{ex} = 326 nm) spectra of the SnO_2 xerogels prepared by using citric acid or oxalic acid as chelating agent and sintered at 400 °C for 5 h. The excitation peaks at about 326 nm and 360 nm always occur in the SnO_2 powder, regardless of the chelating agent. The spectra were measured with the emission wavelength of 379 nm. The PL spectra of the SnO_2 samples consist of four peaks at about 379 nm, 417 nm, 450 nm, and 470 nm, as clearly seen from the inset of Fig. 5. The emission peak at 379 nm could be ascribed to the defects close to the conduction band.[9] The 417-nm and 450-nm peaks could be attributed to the donor–acceptor pair and band-acceptor transitions, respectively, which concern structural defects or impurities formed during the growth.[9] The emission peak at 470 nm (2.48 eV) is assigned to electron transition mediated by the defect levels in the band gap, such as oxygen vacancies.[9,23–26]

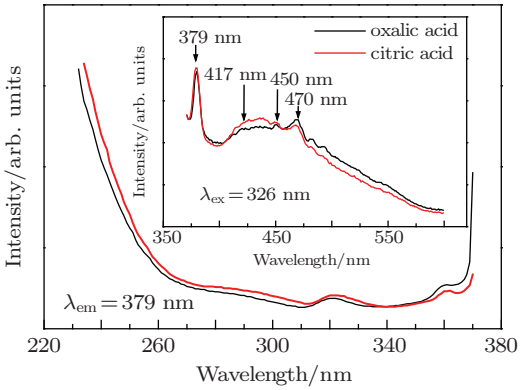


Fig. 5. (color online) Photoluminescence excitation (λ_{em} = 379 nm) spectrum of the SnO_2 xerogels prepared by using citric acid or oxalic acid as chelating agent. The inset shows the emission (λ_{ex} = 326 nm) spectra of the SnO_2 xerogels prepared by using citric acid or oxalic acid as chelating agent.

Figure 6 shows the excitation (λ_{em} = 740 nm) and emission (λ_{ex} = 230 nm) spectra of SnO_2 samples. The emission spectra show that the emission bands around 740 nm are observed when the excitation wavelength is 230 nm. This is possibly related to the surface Fs-centers (surface defects) distributed on the nanoparticle boundaries. It is found that the intensity of emission peaks strongly depends on the sample's particle size. When the particle size of the SnO_2 sample decreases, the relative intensity of 740-nm emission increases. This size-dependence of the emission peaks intensity is interpreted in terms of charge carrier recombination, in which the intensity increases with decreasing SnO_2 nanoparticle size because of the particles' higher surface-to-volume ratio.[9]

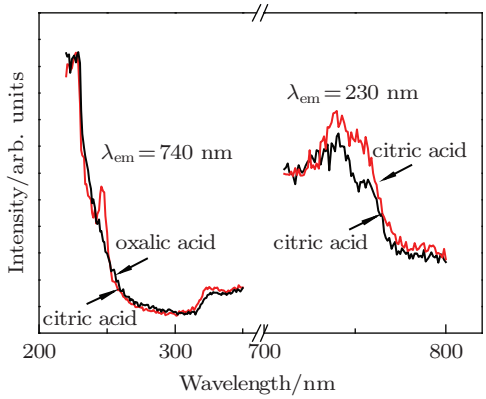


Fig. 6. (color online) Excitation (λ_{em} = 740 nm) and emission (λ_{ex} = 230 nm) spectra of SnO_2 samples.

4. Conclusions

In this work, a polyacrylamide gel route to synthesize SnO_2 nanoparticles is presented. It is found that the average

particle size of the samples depends on the choice of chelating agent. The photoluminescence spectra of the samples consist of two emission bands for both SnO_2 samples prepared by using citric acid or oxalic acid as the chelating agent. One emission band is composed of three emission subbands peaking at 417 nm, 450 nm, and 470 nm, while the other is centered at 379 nm. The emission intensity increases with the decrease of the particle size.

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