N-doped SnO₂ nanocrystals with green emission dependent upon mutual effects of nitrogen dopant and oxygen vacancy

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Abstract

A facile and economical chemical route was used to synthesize nitrogen-doped tin oxide (SnO₂) nanocrystals (NCs). Infrared and Raman spectral examinations reveal the existence of oxygen vacancies and local disorder. Temperature-dependent photoluminescence (PL) measurements display a broad band at 640 nm at room temperature that shifts to a higher energy at lower measurement temperature. Excitation wavelength-dependent PL spectra show that the band blue-shifts and its line width decreases as the excitation wavelength is reduced. The PL peak also blue-shifts when the annealing temperature is increased. Spectral analysis and theoretical calculation suggest that the PL band stems from the mutual effects of oxygen vacancies and nitrogen dopants. This PL investigation on N-doped SnO₂ NCs provides more insights about the optical properties and will promote further applications of SnO₂ NCs.

Keywords: SnO₂ nanocrystal; N-dopant; Oxygen vacancy; Photoluminescence

1. Introduction

Nanostructured tin oxide (SnO₂) has attracted considerable attention due to its excellent optical and electrical properties and has found applications in gas sensors, solar cells, photocatalysts, photodetectors and lithium-ion batteries [1–5]. However, to extend its applications, modification of the physical properties of this material is necessary. Doping can alter the electrical, optical and magnetic properties, and considerable efforts have recently been devoted to this. SnO₂ doped with extrinsic impurities shows improved conductivity [6,7], gas sensitivity [8,9] and photocatalytic capability [3]. It has also been reported that SnO₂ doped with a transition metal is a diluted magnetic semiconductor having a Curie temperature higher than room temperature [10,11].

Compared to other nitrogen-doped (N-doped) metal oxides, N-doped SnO₂ has not been investigated extensively [10–14], and the effects of N on the optical and electronic properties of SnO₂ nanostructures are not well understood. N-doped SnO₂ films have been fabricated by magnetron reactive sputtering in N₂ as the nitrogen source [12–14]. Some films exhibit p-type conduction [13] and enhanced photocatalytic activity due to the red shift of the band gap into the partial visible light region [12]. Compared to high-temperature synthesis, low-temperature chemical methods are more convenient because of their simplicity and low energy requirements. In this work, a facile and economical technique to synthesize N-doped SnO₂ nanocrystals (NCs) is described and their electronic structures are investigated by photoluminescence (PL). A green emission band which is observed to shift to a high energy with increasing excitation energy is attributed to optical transitions induced by both the oxygen vacancy (OV) levels at different depths and localized states arising from the nitrogen dopants.
2. Samples and experiments

SnO$_2$ NCs were fabricated at room temperature. Nitric acid and deionized water were mixed 1:2 v/v and tin powders with NC diameters on the order of micrometers were added to the solution. The solution was continuously stirred for 40 h and the white precipitate was collected by centrifugation and washed several times with deionized water and ethanol. The precipitate was dried at 80 °C in air for 40 h. After drying, the white powders were annealed in O$_2$ at temperatures of 500, 700, 900 and 1000 °C for 30 min.

Scanning electron microscopy (SEM) was performed with a field emission microscope equipped for energy-dispersive spectroscopy (EDS) to observe the morphology and grain size. The variations in the structural and crystallite size of the doped SnO$_2$ NCs with annealing temperature ($T_a$) were investigated by X-ray diffraction (XRD). Temperature-dependent PL spectra were acquired on a fluorescence spectrophotometer (Edinburgh FLS-920) with a 450 W xenon lamp as the excitation source. When we measured the PL spectra of the samples excited under different wavelengths, we used almost same excitation power and become stronger [15]. This implies a gradual decrease in the in-plane OVs and eventual disappearance. In the annealed samples, there is a broad Raman peak at 556.3 cm$^{-1}$, which has been suggested to have a disorder-induced consequence [18]. The IR mode at 253.9 cm$^{-1}$ upshifts by ~19 cm$^{-1}$ compared to that of the as-synthesized SnO$_2$ NCs. The presence of the IR mode at 302.1 cm$^{-1}$ indicates that the OV density is larger than 6% [19]. These IR active modes provide evidence of the

3. Results and discussion

Fig. 1a shows the XRD patterns of the as-synthesized and annealed SnO$_2$ NCs. All the peaks can be indexed to the tetragonal rutile phase of SnO$_2$. In the as-synthesized sample, the NCs are very small, as indicated by the broad XRD peaks. With increasing $T_a$ from 500 to 1000 °C, the diffraction peak becomes sharper, indicating a gradual increase in the NC size. According to the Scherrer formula, the average NC size is calculated to be ~2.2, 5.4, 40, 80 and 102 nm for the as-synthesized sample and samples annealed at 500, 700, 900 and 1000 °C, respectively. The XRD peak intensities also increase with $T_a$, implying a gradual improvement in the crystallinity. Fig. 1b depicts a representative SEM image of the SnO$_2$ NC sample annealed at 700 °C in O$_2$. The sample consists of many NCs with diameters between 10 and 80 nm. Although these NCs agglomerate, their boundaries are still distinguishable. EDS (inset) shows nitrogen and suggests that nitrogen has been incorporated into the SnO$_2$ NCs because absorption of nitrogen on the surface should be insignificant at a high temperature.

Fig. 2 displays the room-temperature Raman spectra obtained from the as-synthesized and annealed SnO$_2$ NC samples. The spectrum of the as-synthesized SnO$_2$ NCs in Fig. 2a shows two strong vibration modes at 578.2 and 234.5 cm$^{-1}$. The shoulder at 622.9 cm$^{-1}$ corresponds to the A$_{1g}$ mode but the position down-shifts compared to the mode at 633 cm$^{-1}$ for bulk SnO$_2$. This is due to the existence of bridging oxygen vacancies (OVs) [15]. The strong 578.2 cm$^{-1}$ vibration mode can be assigned to in-plane OVs localized on the NC surface [16]. The 234.5 cm$^{-1}$ mode corresponds to the E$_u$ TO mode attributed to sub-bridging OVs [15]. The E$_u$ TO mode is an infrared (IR) active mode and commonly inactive in Raman scattering. Its appearance can be ascribed to the relaxation of the Raman selective rule induced by the high concentration of surface defects such as OVs and lattice disorder [17].

In the Raman spectrum of the sample annealed at $T_a$ of 500 °C (Fig. 2b), four peaks at 253.9, 302.1, 556.3 and 627.8 cm$^{-1}$ can be observed but the peak at 578.2 cm$^{-1}$ disappears. As $T_a$ is increased, the NC size increases, causing the A$_{1g}$ mode at 627.8 cm$^{-1}$ to return to 633 cm$^{-1}$ (bulk) and become stronger [15]. This implies a gradual decrease in the in-plane OVs and eventual disappearance. In the annealed samples, there is a broad Raman peak at 556.3 cm$^{-1}$, which has been suggested to have a disorder-induced consequence [18]. The IR mode at 253.9 cm$^{-1}$ upshifts by ~19 cm$^{-1}$ compared to that of the as-synthesized SnO$_2$ NCs. The presence of the IR mode at 302.1 cm$^{-1}$ indicates that the OV density is larger than 6% [19]. These IR active modes provide evidence of the
existence of OVs and local disorder. Theoretical calculations have also disclosed that N is energetically favorable to substitute O sites in N-doped SnO$_2$ nanostructures due to the small formation energy [20]. As a result, some OVs are formed to attain charge neutrality [21] and it can be concluded that there are always OVs in both the as-synthesized and annealed NC samples.

The PL properties are interesting because different optoelectronic properties are expected from N-doped SnO$_2$ nanostructures. Fig. 3a shows the measurement-temperature ($M_T$)-dependent PL spectra of the SnO$_2$ NC sample annealed at $T_a$ of 700 °C in O$_2$ excited by the 320 nm line of a xenon lamp. Two bands at 400 and 500–650 nm are observed. The former consists of three sharp peaks as shown in Fig. 4 (circle). They are assigned to the band-acceptor and donor–acceptor pair transitions as well as phonon replica, respectively [22,23]. Here, we focus our attention on the latter, the broad PL band. The profile of this band and its change with $M_T$ are completely different from those of the undoped SnO$_2$ NCs [24]. With increasing $M_T$, its intensity decreases and peak position red-shifts. At room temperature, the PL band shifts to 640 nm and its intensity decreases drastically. The PL shift displays a similar trend with $M_T$ in the as-synthesized and other annealed samples. In the SnO$_2$ nanoribbons, a clear double-peak PL band is observed at 480 and 620 nm, but each subpeak position hardly changes as $M_T$ varies [24]. This implies that this PL band should not originate from the mutual effects of OVs and oxygen interstitial postulated previously. Instead, the $M_T$-dependent PL red shift should arise from the stress induced by the surface shrinkage effect [25], even though the PL origin is unclear.

Fig. 3b presents the excitation-wavelength ($\lambda_{ex}$)-dependent PL spectra of the sample annealed at $T_a$ of 700 °C and measured at 10 K. The PL peak exhibits a monotonic blue shift from 530 to 500 nm and the intensity increases gradually as $\lambda_{ex}$ decreases from 330 to 290 nm. The full-width at half-maximum (FWHM) diminishes as well. Since the band gap of the NC sample is ~345 nm (3.60 eV), the quantum confinement effect of small size NCs can be ruled out as the origin of the green band. It is known that variations in the OVs with depth can lead to a blue shift in the PL peak with decreasing $\lambda_{ex}$ [26], but the FWHM increases because more OVs are excited. Here, the FWHM decreases and so this PL band should not be only related to OVs at different depths. Annealing in O$_2$ can lead to variations in the oxygen interstitials with depth, also causing the FWHM to increase with decreasing $\lambda_{ex}$. This means that oxygen interstitials cannot cause the observed PL. Since our Raman and EDS results reveal the presence of both OVs and N dopants in the NC samples, the observed
PL band may be a mutual effect of both the OVs and N dopants.

OVs and N dopants at different depths have different defect levels in the forbidden band gap. In the NC samples annealed at different $T_a$, the depth distributions of the OVs and N dopants are different. The deeper they are, the higher are the corresponding energy levels. To investigate this further, the PL spectra of the NC samples annealed at different $T_a$ are shown in Fig. 4. The peak position blue-shifts and FWHM increases with increasing $T_a$. Since substitution of O by N creates an OV in the SnO$_2$ NC and high-temperature annealing in O$_2$ makes the OV position deeper, the PL blue shift is mainly caused by the increased depth of the OVs. It can thus be inferred that the observed PL originates from the mutual effects of both the OVs and N dopants. With increasing $T_a$, the OVs migrate towards the interior and the N dopants remain unchanged in the lattice position, except that some N atoms escape from the NC surface. Consequently, the PL spectrum blue-shifts with increasing $T_a$, as shown in Fig. 4. The inset in Fig. 3b shows two PL excitation (PLE) spectra. When the excitation wavelength reaches the strong PLE spectral position at 290 nm (Fig. 5), the high energy levels ($\sim$500 nm emission) will have a higher population of electrons, which are not only from the defect levels with the 290 nm excitation but also from the transition from the conduction band to the high energy levels with the $\sim$500 nm emission. Thus, with decreasing excitation wavelengths, the PL peak intensity increases and the FWHM decreases as illustrated in Fig. 3b. To obtain experimental confirmation, the time-resolved PL decay curves at 500 and 530 nm excited by 290 and 330 nm at 10 K, respectively, are displayed in Fig. 6a and b. The decay curves can be fitted by two stretched exponential components (A and B) according to the following function [27]:

$$I = I_1e^{-t/\tau_1} + I_2e^{-t/\tau_2}$$

where $I_1$ and $I_2$ are the PL intensities of the components with decay times of $\tau_1$ and $\tau_2$, respectively. The PL decay lifetimes are thus calculated to be (0.9, 9.4) and (1.6, 16.2) ns, respectively. The standard deviation are obtained to be (0.1, 0.4) and (0.1, 0.7) ns, respectively. We can see that good agreement is achieved between the fit result and experimental data. As the monitoring wavelength decreases, the intensity ratio of component B to A increases from 0.64 (39/61) to 3.17 (76/24). As shown in Fig. 5, since component B with a long lifetime is associated with the transition between the defect levels (the red arrow from level 1 to 2), the increase in this transition component will increase the intensity of the PL peak with the transition from level 2 (high energy defect level) to the valence band (ground state). At the same time, since little electron transition occurs between levels 1 and 3 and the electron population in level 3 mainly comes from the conduction band, this reduces the PL intensity on the low energy side with the radiative transition from level 3 (low energy defect level) to the valence band (ground state). As a result, the 500 nm PL peak narrows compared to the 530 nm PL one. Hence, when the excitation wavelength approaches 290 nm, the 500 nm PL peak has higher intensity and narrower line width than the 530 nm PL one, as shown in Fig. 3b.

To theoretically confirm our assignment of the PL origin, an ab initio computational study is performed on the electronic properties of the surface of N-doped SnO$_2$ crystal with OVs and N-dopants at different depths. The calculation is carried out using the density functional theory with the generalized gradient approximation of the potential functional proposed by Perdew et al. [28] under package CASTEP [29], in which a plane-wave norm-conserving pseudopotential method [30] is used. The kinetic energy cutoff is 450 eV to represent the single-particle wave functions and slabs are adopted to investigate the surface properties of the NCs. The surface is represented by a slab 1.44 nm thick carved along the (110) direction. The periodic structure for the calculation in the CASTEP...
package is reconstructed by using a $0.637 \times 0.670 \text{ nm}^2$ supercell in the on-plane direction and adopting 1 nm thick vacuum slabs to separate the periodically repeating SnO$_2$ slabs. In every supercell, an N atom is the dopant and an oxygen vacancy is created in the initial structure at different depths. The geometry of the configuration is optimized using the BFGS minimizer in the CASTEP package with default convergence tolerances: $2 \times 10^{-5}$ eV for energy, 0.5 eV nm$^{-1}$ for maximum force and 0.0002 nm for maximum displacement [31]. Fig. 7 shows the densities of states (DOSs) of the three configurations: (a) one shallow N-dopant and one shallow OV per supercell, (b) one deep N-dopant and one deep OV per supercell and (c) one shallow N-dopant and one deep OV. The DFT calculation is known to underestimate the energy band but the band feature is still available [24,32]. Obviously, these DOSs are inconsistent with those of SnO$_2$ nanoribbons with different amounts of OVs/oxygen interstitials [24]. The results are indicative of the role of the N dopant. According to the comparison between the DOS curves (b) and (c) with curve (a), by increasing the depth of the OV, the top of the valence band (position A) is lowered (the red arrow toward left side) and meanwhile, the energy (peak position) of the impurity level B changes only slightly (the dashed green circle) and the energy of the impurity level C is enhanced (the red arrow toward right side). This suggests that the transition from C to A or from B to A has a higher energy if the OV is deeper. This effect persists even though the position of the N dopant is not changed (the blue arrows toward left and right sides). To further confirm the optical transition, we plot the curves of the imaginary part of dielectric function as a function of energy for configurations (a), (b) and (c).

matrix element increases and especially its FWHM decreases (from peak 1 to 2). This explains very well the PL results in Fig. 3b.

4. Conclusion

In conclusion, N-doped NCs are synthesized and annealed in O$_2$ at different temperatures, and Raman scattering and EDS reveal the existence of OVs and N dopants in the NCs. The synthesized NCs exhibit an optical emission band that varies with measurement temperature, excitation wavelength and annealing temperature. Spectral analyses and theoretical calculations suggest that the observed PL is closely related to both OVs and N-dopants. The optical transition induced by the OV/N-dopant levels is proposed to be responsible for the PL band. This PL investigation on N-doped SnO$_2$ NCs provides more insights into the optical properties of these materials and will promote further applications of SnO$_2$ NCs.

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