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Exciton spectra of SnO₂ nanocrystals with surficial dipole layer

Baolong Yu *, Congshan Zhu, Fuxi Gan

Shanghai Institute of Optics and Fine Mechanics, Academia Sinica, P.O. Box 800 211, Shanghai 201800, People's Republic of China

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Abstract

Experimental results of absorption, luminescence and excitation spectra in both bare and coated SnO₂ nanocrystals are given. It is found that when the SnO₂ nanocrystals are coated by a layer of organic molecules, the absorption edge shifts to the longer wavelength direction as the particle size decreases, which is inconsistent with that of bare SnO₂ nanocrystals. It is demonstrated that the size and surface situations of nanocrystals have great influence on their spectroscopic properties. The experimental data are discussed in terms of the quantum confinement effects and dielectric confinement effects.

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Keywords: SnO₂ nanocrystal; Quantum confinement effect; Exciton

1. Introduction

Because nanocrystal radius is of the same order of the electron–hole separation, namely, the bulk exciton Bohr radius, it exhibits novel physical and chemical properties, especially, its linear and nonlinear optical properties hold scientists' wide interests in the world [1–3]. Because of smaller size and relative large surface area, the surrounding medium or matrix can greatly affect its optical behaviors [4,5]. In general, the energy levels of the naked nanocrystals shift to higher energies as the particle size decreases, the so-called absorption edge blue shift, this feature has been observed in CuCl [6], CdS [7], etc. Simple effective mass approximation model has been employed to qualitatively explain the observed blue

shift of the absorption spectrum [3]. However, this model gives quantitatively accurate results only for very large microcrystals, and ignores the influences of the surrounding matrix on the optical properties of microcrystals.

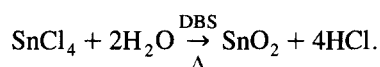
The rutile structure SnO₂ have wider band gap (3.60 eV) and smaller exciton Bohr radius ($a_B = 1.7$ nm) [8]. It is easier to reach the weak confinement region in SnO₂ nanocrystals which makes it more promising material for optoelectronics applications. Up to date, little report has been given for the spectroscopic studies of SnO₂ nanocrystals. In this paper, the SnO₂ nanocrystals both bare and coated samples were prepared by the method of colloidal chemistry. The absorption spectra, the fluorescence spectra, and the excitation spectra in both bare and coated SnO₂ nanocrystals were reported. Some new phenomena, such as red shift of the absorption band

* Corresponding author.

edge in coated samples when the particle size decreases which is inconsistent with that of the bare samples, stronger photoluminescence and fine structures in excitation spectra were observed at room temperature (RT).

2. Preparation of SnO₂ nanocrystals

The SnO₂ nanocrystals coated with a layer of dodecyl benzene sulfonic acid sodium salt (DBS) were prepared through the method of colloidal chemistry. The main reaction was presented as follows



This procedure has been detailed elsewhere [9]. Here the SnO₂ nanocrystals are coated by a layer of DBS, which play a role in protecting the SnO₂ nanocrystals from being condensed into larger powders, and spontaneously become chemically bounded to surficial Sn⁴⁺, which has verified by the infrared spectra. The radius of SnO₂ nanocrystals is 7 ± 0.4 nm (sample 1) and 15 ± 0.3 nm (sample 2), measured through transmission electron microscopy (TEM) and small angle X-ray scattering experiments on the D/Max- γ AX diffraction meter. Similarly, the bare SnO₂ nanocrystals in hydrosols were also synthesized, labeled as the sample 3 (radius 5 ± 0.4 nm) and the sample 4 (radius 2 ± 0.3 nm). The absorption spectra and the excitation spectra in both coated and bare samples were recorded on UV/VIS/NIR Lambda 9 spectrofluorimeter at RT. The luminescence spectra were measured by N₂-Laser Boxcar system.

3. Spectroscopic properties

3.1. Absorption spectra

Fig. 1 is the absorption spectra in both bare and coated SnO₂ nanocrystals. The absorption curves show long tails near the absorption edge (Fig. 2). The long tail could be due to the size distribution and the defects on its surfaces. The existence of tail makes the precise determination of the absorption

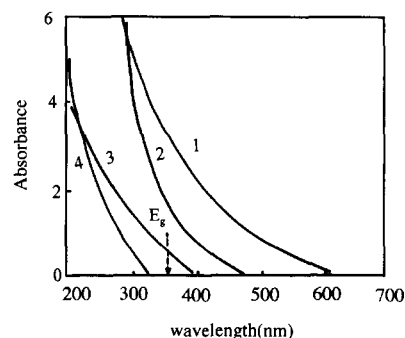


Fig. 1. The absorption spectra of SnO₂ nanoparticles curve 1 (radius 7 nm) and curve 2 (radius 15 nm) corresponding to the coated samples, curve 3 (radius 5 nm) and curve 4 (radius 2 nm) corresponding to the bare samples, E_g is the band gap of bulk SnO₂.

band edge difficult. To determine the absorption band edge, we fit the absorption data to Eq. (1) [10].

$$\alpha(\hbar\omega) \propto (\hbar\omega - E_g')^{1/2}, \quad (1)$$

in which $\hbar\omega$ is the photon energy, α is absorption coefficient, and E_g' is the absorption band edge. Therefore, the E_g' of the coated SnO₂ nanoparticles can be the extrapolation of the Eq. (1) to be 2.76 eV (sample 1) and 3.10 eV (sample 2) (Fig. 2), which is significantly less than the band gap of bulk SnO₂ (3.6 eV). This result was in disagreement with the theoretical and experimental results on the optical properties of semiconductor nanocrystals reported in the former literature, which indicated that the absorp-

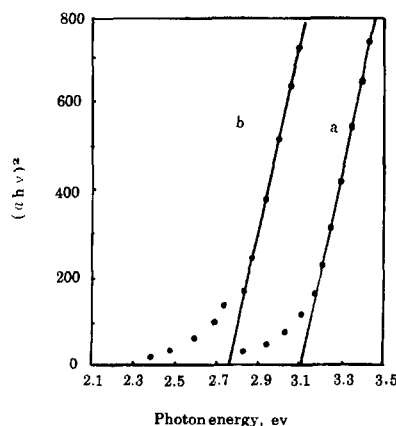


Fig. 2. $(\alpha - \hbar\omega)^2$ versus photon energy curve a (radius 15.0 nm), curve b (radius 7.0 nm).

tion band edge shifted to higher energy as the particle size decrease [3]. Similarly, the absorption edge of samples 3 and 4 are 3.7 eV and 4.1 eV, respectively. It can be seen that the absorption edge of bare SnO₂ samples are obviously larger than that of bulk SnO₂, and shifts to higher energy as the particle size decreases. It is worth pointing out that this difference of absorption spectra between coated and bare SnO₂ would arise from the coated layer. The discussion about the results mentioned above were as follows. As for the band edge shift of optical absorption of semiconductor nanocrystals, Takahara [11] described the energy of the lowest exciton energy as a function of effective radius \bar{R} and dielectric-constant ratio with effective-mass approximation (EMA) method, in effective Rydberg Units, given as

$$E'_g = E_g + \pi^2/\bar{R}^2 - A_1/\bar{R} - A_0, \quad (2)$$

where $\bar{R} = R/a_B$ (R is the radius), E_g is the band gap of bulk material, A_1 and A_0 are plotted in Fig. 2 of Ref. [11] as a function of dielectric-constant ratio ϵ_1/ϵ_2 (ϵ_1 and ϵ_2 are the dielectric constants of semiconductor material and surrounding medium, respectively). This is a new formula for the exciton energy which includes the dielectric confinement effects. Of course, when we put $\epsilon_1/\epsilon_2 = 1$, the Eq. (2) reproduce the previous results [12], namely,

$$E'_g = E_g + \pi^2/\bar{R}^2 - 3.572/\bar{R} - 0.246. \quad (3)$$

In Eq. (2), the second term is the quantum confined

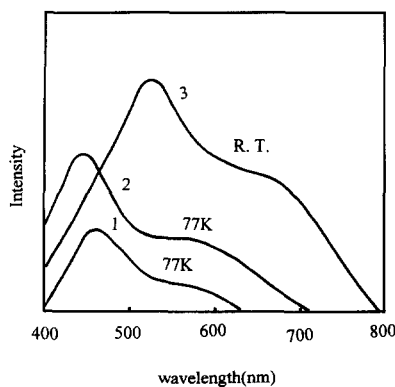


Fig. 3. Emission spectra of SnO₂ nanocrystals under excitation of 337 nm by N₂ laser. The curve 1 corresponding to the sample 3, the curve 2 corresponding to the sample 4, and the curve 3 corresponding to the sample 1.

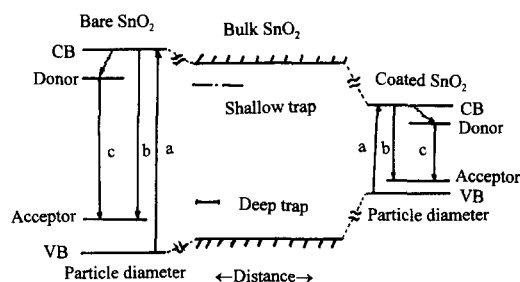


Fig. 4. Schematic energy diagram for SnO₂ nanocrystal, (a) absorption, (b) H-band emission, (c) L-band emission.

energy, leading to the absorption band edge blue shift as the size of particle reduces; the third and fourth terms arise from the surface polarization effect, called dielectric confinement energy, leading to red shift. Compared to the absorption band edge of bulk material, red and blue shifts take places simultaneously, and compete each other. As for the SnO₂ nanocrystals, when coated by DBS which has a smaller dielectric constant ($\epsilon_1 \approx 1.5$) than that of SnO₂ ($\epsilon_2 \approx 13.5$), the dielectric confinement effect emerges [11], the screening effect is reduced and the Coulomb interaction between charged particles within microcrystals become enhanced, resulting in enhancement of the exciton binding energy and the exciton oscillator strength, thus the surface polarization energy becomes the key factors of influencing the absorption band edge, meanwhile, the quantum confinement energy would become the subordinate factor, the less the particle size and the more the difference between ϵ_1 and ϵ_2 , the more the red shift. But for the bare SnO₂ nanocrystals, the key factors of influencing the absorption edge is the quantum confinement energy due to absence of the dielectric confinement effects. Therefore, the absorption edge shifted to a higher energy region (blue shift) as the particle size of the SnO₂ nanocrystals decreases, which was consistent with the results reported by Chestnoy et al. [3].

3.2. Luminescence spectra

The Fig. 3 is the photoluminescence spectra of the samples 1, 3 and 4. The excitation source is a N₂ Laser at 337 nm, where exist two broad bands, H-band and L-band. The curves 1 and 2 correspond-

ing to the luminescence spectrum of bare SnO₂ are similar to that of the bulk crystal at 77 K [13], its H-band is produced by the recombination of electron on the conduction band with the hole bound on the acceptor energy level (or the recombination of electron on the donor energy level with the hole on the valence band), whereas L-band is the recombination of electrons on the donor energy level with the hole on the acceptor energy level (Fig. 4). The luminescence band shifts toward the longer wavelength direction with the increasing size of particle due to the fact that the energy gap between the donor energy level and the acceptor energy level depends on the particle size, and finally it coincides with the luminescence wavelength of the bulk crystal.

The intensity distribution of luminescence produced by the recombination of the electron bound on the donor energy level with the hole bound on the acceptor energy level can also be obtained based on the calculation of the above state density $g(E_1)$. Assuming that the transition probability of each energy level is the same, the luminescence intensity I_{a-b} will be

$$I_{a-b}(\hbar\omega) \propto \int dE_1^a \int dE_1^d \frac{g(E_1^a)}{1 + \exp[-\beta(E_1^a - E_{IF}^d)]} \times \frac{g(E_1^d)}{1 + \exp[-\beta(E_1^d - E_{IF}^d)]} \times S[\hbar\omega - (E_g - E_1^a - E_1^d)], \quad (4)$$

where E_1^a , E_1^d are the acceptor and the donor energy level respectively, E_F^a , E_F^d is the Fermi energy level of the acceptor and the donor respectively, which are

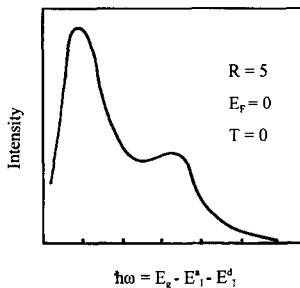


Fig. 5. Luminescence intensity due to the acceptor–donor recombination.

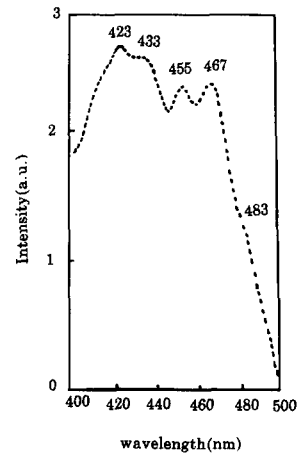


Fig. 6. Excitation spectrum of coated SnO₂ nanocrystals (radius 7.0 nm). Emission wavelength: 520 nm.

all calculated by starting from the top of the energy levels, $\beta = 1/KT$, S is the step function:

$$S(t) = \begin{cases} 0 & t > 0, \\ 1 & t < 1. \end{cases}$$

Fig. 5 gives the calculation results for $R = 5$ nm, $E_1^a = E_1^d = 0$ and $T = 0$, whereby it can be seen that there are two peaks for the luminescence of acceptor–donor recombination, which is in agreement with those obtained experimentally.

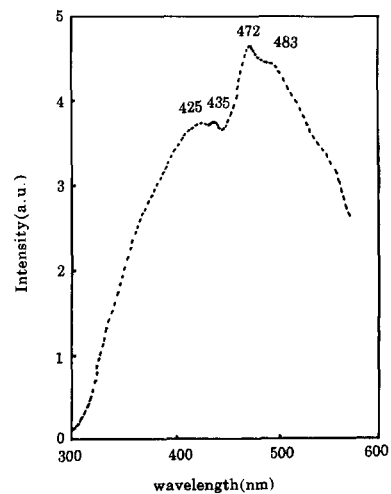


Fig. 7. Excitation spectrum of coated SnO₂ nanocrystals (radius 7.0 nm). Emission wavelength: 580 nm.

3.3. Excitation spectra

Figs. 6 and 7 are the excitation spectra of sample 1. The excitation spectra of sample 2 are similar to sample 1. An interesting phenomenon never observed before was the fine structures of exciton transitions due to the quantum confinement effects. As well known, the excitation spectrum reflects the structure characteristics of energy level, from which we can obtain more information about exciton transition. Furthermore, the excitation spectrum has higher sensitivity than that of absorption spectrum [14], it makes the measurements of the exciton transition possible. The excitation spectra with fine structures shown in Figs. 6 and 7 are strong evidences of quantum confinement effects. However, in absorption spectra, due to inhomogeneous broadening arising from the temperature, solvent effects, and size distribution, it smeared out discrete levels in Fig. 1. In weak confined regime, Hanamura [15] analyzed theoretically the oscillator strength and the third-order optical polarizability due to exciton effects in semiconductor nanocrystallites, he obtained the energy E_n of the dipole allowed exciton with $l = m = 0$ in quantum sphere,

$$E_n = E_g - E_b + \hbar^2 \pi^2 n^2 / 2MR^2, \quad n = 1, 2, 3, \dots \quad (5)$$

where E_g is the band gap of bulk material, R is the radius of nanocrystal, $E_b = \mu e^4 / 2\hbar \epsilon_0^2$ is the exciton binding energy, $M = m_e + m_h$ and $\mu = m_e m_h / (m_e + m_h)$ are the total and reduced mass of exciton. If the surface polarization energy arising

from surface modification was considered in exciton energy, the Eq. (5) would be improved as follows:

$$E_n = E_g - E_b + \hbar^2 \pi^2 n^2 / 2MR^2 + E_p, \quad n = 1, 2, 3, \dots \quad (6)$$

where E_p is the surface polarization energy. For sample 1: $R = 7.0$ nm, $E_g' = 2.76$ eV (obtained from Fig. 2); for bulk SnO₂: $E_g = 3.6$ eV, $a_B = 1.7$ nm, the surface polarization energy E_p was approximately obtained from Eq. (1), $E_p = -A_1/\bar{R} - A_0 = E_g' - E_g - \pi^2/\bar{R}^2 = -0.919$ eV. The calculated results using Eq. (6) and experimental results are shown in Table 1. From Table 1 we can see that the higher quantum number n , the stronger the influence of the quantum confined effect on the exciton transition energy. The conclusion of Takahara [11] is only for the $n = 1$ exciton. There are also two wider excitation band in Figs. 6 and 7, which is in agreement with those of the emission spectra shown in Fig. 3.

4. Conclusion

We have studied the spectroscopic properties of SnO₂ nanocrystals in weak confinement regime. Through the measurements of absorption spectra and excitation spectra of coated SnO₂ nanocrystals, the red shift of absorption band edge as the particle size decreases and fine structures of the optically allowed transition were found for the first time. Because of the influences of the quantum confinement effects and dielectric confinement effects, the stronger photoluminescence of coated SnO₂ nanocrystals was recorded at room temperature.

Acknowledgements

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Table 1

Comparison of exciton transiting energy between theory and experiment

Theory ^a	Experiment ^b , emission wavelength	
	520 nm	580 nm
$E_1 = 483$ nm	483 nm	483 nm
$E_2 = 473$ nm	467 nm	472 nm
$E_3 = 456$ nm	455 nm	
$E_4 = 435$ nm	433 nm	435 nm
$E_5 = 411$ nm	423 nm	425 nm

^a $R = 7.0$ nm, $E_p = -0.919$ eV, $E_g = 3.6$ eV, $E_b = 0.13$ eV, $M = 4.24 m_0$ [13].

^b $R = 7.0$ nm.

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