Luminescent high temperature sensor based on the CdSe/ZnS quantum dot thin film*

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A high temperature sensor based on the multi-parameter temperature dependent characteristic of photoluminescence (PL) of quantum dot (QD) thin film is demonstrated by depositing the CdSe/ZnS core/shell QDs on the SiO_2 glass substrates. The variations of the intensity, the peak wavelength and the full width at half maximum (FWHM) of PL spectra with temperature are studied experimentally and theoretically. The results indicate that the peak wavelength of the PL spectra changes linearly with temperature, while the PL intensity and FWHM vary exponentially for the temperature range from 30 °C to 180 °C. Using the obtained temperature dependent optical parameters, the resolution of the designed sensor can reach 0.1 nm/°C .

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The recent progresses in quantum dot (QD) sensing techniques include the chemical and biochemical optical sensor[1], the temperature sensor[2,3], the current sensor[4], etc. In the previous work[2,5], the QD thin film was generally fabricated by a layer-by-layer electrostatic self-assembling technique in a microstructure fiber or a hollow core fiber. However, the temperature measuring ranges of those sensors are generally limited below 100 °C, while the QD sensor for over 100 °C high temperature detection has been investigated rarely.

In this paper, we first design a high temperature sensor with the QD thin film by the electrostatic self-assembling technique. And then the temperature sensing properties of photoluminescence (PL) spectra from the QD thin film are studied experimentally. In particular, by measuring the variations of the intensity, the peak wavelength and the full width at half maximum (FWHM) of PL spectra with the high temperature, the average sensitivity of the sensor reaches about 0.1 nm/°C when the temperature changes from 30 °C to 180 °C, which can meet some practical needs.

It is well known that the performance of the temperature sensor depends on the QD thin film. Generally, the wide band gap QD, such as CdSe and CdTe nanocrystal, is chosen to fabricate the sensing thin film. In our work, the CdSe/ZnS core/shell QDs are chosen due to their high luminescent stability and wide energy band. The CdSe/ZnS QDs and parameters in the experiment are provided by Hangzhou Najing Technology Co., Ltd.. The diameter of this kind of QDs is about 9 nm, and the red light in visible spectrum can be emitted at about 615 nm as shown in Fig.1. During the preparation of the QD thin film, the CdSe/ZnS QD solution with a concentration of 5 mg/mL is obtained firstly by dissolving them in ultraviolet (UV) curing glue. Then the QD solution is spread between two SiO_2 glass substrates and cured under 12 W UV light for 20 min. Finally the QD thin films with the thickness of about 250 μm are fabricated. The optical absorption spectra of the prepared QD thin film are measured using a UV-2550 spectrophotometer made in Japan, which is shown in Fig.1.

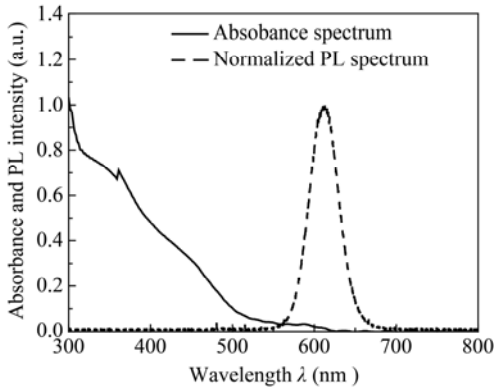

Fig.1 The absorption spectrum and PL spectrum of CdSe/ZnS QDs at room temperature

The setup of the temperature sensor is shown in Fig.2. In order to study the PL temperature response of the

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sensor, the sensor head with the CdSe/ZnS QD thin film is mounted into a ceramic heating furnace with an electronic temperature controller. Due to its broad absorption spectra, a solid state continuous wave (CW) laser with the central wavelength of 450 nm, the tunable power from 0 W to 1.5 W and the spot diameter of 2 mm is used as the excitation source. Light from the source excites the QD thin film deposited on the SiO_2 glass plate in the sensor head. The output optical signal from the sensor (including the excitation light and the emission light) is focused by a 5 cm lens to a 500 nm optical long-pass filter. After the residual excitation light is removed by the filter, the PL signal is collected into a multi-mode fiber connected to a spectrometer (USB-4000, Ocean Optics). In the experiment, the temperature is varied from 30 °C to 180 °C by steps of 5 °C, and it takes approximately 30 s to reach the new setting with the temperature kept constant for over 2 min at each step.

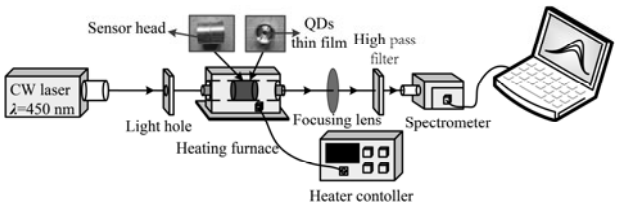

Fig.2 Schematic diagram of the temperature sensor system based on the QD thin film

Fig.3 shows the measured fluorescence spectra of the CdSe/ZnS QD thin film at different temperatures. We can see that the PL intensity decreases with the increase of the temperature, while the peak wavelengths and the FWHM of the emission spectra are increased with the increase of the temperature. Hence, there are three features in the QD emission spectra which could be used to detect the variation of the temperature, which are the intensity, the peak wavelength and the FWHM of the PL spectra.

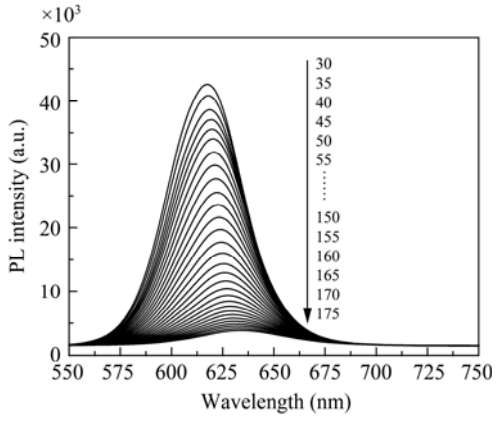

Fig.3 Measured PL spectra of the CdSe/ZnS QD thin film for different temperatures

Since the PL peak wavelength depends on the measured temperature as shown in Fig.3, the QD PL peak wavelengths corresponding to different temperatures should be obtained firstly. To reach this goal, a simple method is adopted to normalize the measured PL spectra, which matches the peak wavelength of each PL spectrum. Fig.4 shows the normalized PL spectra for different temperatures. From Fig.4, it is easy to extract the PL peak wavelength, and it can be seen that the PL peak wavelength shifts to the red side as the temperature rises. The PL peak wavelength is located at 617.6 nm at 30 °C, while it is 633.7 nm as the temperature increases to 180 °C. There is a 16 nm red shift in PL spectra when the temperature is raised from 30 °C to 180 °C. Thus, if the variation of the PL peak wavelength is linear and reversible with the temperature, the sensitivity of this temperature sensor reaches ~0.1 nm/°C. In fact, the PL peak wavelength certainly yields a linear change with the increase of temperature, which can be verified later.

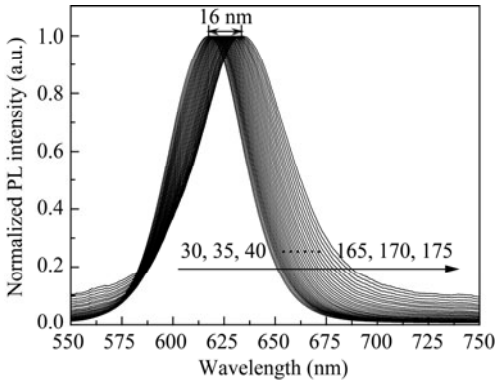

Fig.4 Normalied PL spectra of the CdSe/ZnS QD thin film for different temperatures

In theory, the temperature dependent red shift results from the shrinkage of the QD band gap energy and the increase of the QD size due to the heat expansion[5]. For the materials with wide band gap, such as CdSe/ZnS nanocrystal QD, where the exciton binding energy is much smaller than the energy band gap (E_g), E_g can be approximated as the energy of the first exciton peak observed in the optical absorption spectrum. The temperature dependency of the energy gap of the bulk semiconductor materials can be described by[6]

$$E_g(T) = E_{g0} - \alpha \frac{T^2}{T+\beta}, \tag{1}$$

$$E_g(T) = E_{g0} - \eta \frac{1}{e^{\gamma/T} - 1}, \tag{2}$$

where E_{g0} is the band gap at 0 K, β is approximately the 0 K Debye temperature, γ is the Einstein temperature, and α and η are the fitting parameters. With Eqs.(1) and (2), the fitting results are shown in Fig.5, and the corresponding fitting parameters can be obtained in Tab.1.

Fig.5 shows that both expressions in Eqs.(1) and (2) can yield the identical line shape with temperature. When the temperature is higher than room temperature (>27 °C), the band gap energy decreases linearly from 2.01 eV to

1.96 eV with temperature increasing, and β can be neglected. Moreover, these results are close to those of bulk CdSe material (α=3.7×10^{-4} eV/K, β=150 K) in a high temperature range from 30 °C to 180 °C as shown in Tab.1. This indicates that the dominant emission in the CdSe/ZnS core/shell results from the recombination of electrons and holes near the band edge of CdSe cores, while the emission energy variation related to the QD size due to thermal expansion is too small to have any measurable effect on the emission wavelength. Therefore, with these best-fit values in Tab.1, the peak wavelength shift of CdSe/ZnS QD in Fig.6 can be described by a linear function as

$$\lambda_{\text{peak}} = \lambda_0 + kT , \tag{3}$$

where the slope coefficient k is derived as 0.108 nm/°C, and there is a good correlation factor of R^2=0.9978. It is important to note that the slope coefficient k represents the sensitivity of the temperature sensor. Moreover, although the highest test temperature just reaches 180 °C due to the temperature limit of furnace, the practical measurement range can extend to the higher level.

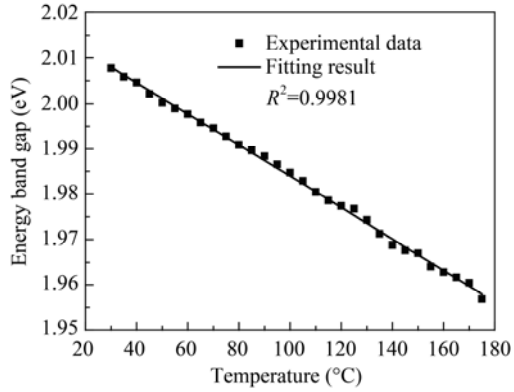

Fig.5 The experimental and fitting results of energy band gap as a function of temperature

Tab.1 The parameters used for fitting the energy band gap and the comparison of the fitting coefficients for CdSe/ZnS QDs in different papers

Parameter	In this paper	Lomascolo et al[7]	Joshi et al[6]	Gupta et al[3]
E_{g0} (eV)	2.084	2.129	2.198	2.121
α (×10^{-4} eV/K)	3.7±0.2	3.2±0.2	4.5±0.6	3.8±0.2
β (K)	151±20	220±30	195±70	150±20
η (×10^{-2} eV/K)	6.9±1.1	—	—	—
γ(K)	196±14	—	—	—

Besides the temperature dependence of QD emission peak wavelength, it can be also observed from Fig.3 that the intensity of the PL spectra decreases obviously when the temperature is increased from 30 °C to 180 °C. Fig.7 shows the PL intensity versus the temperature for the CdSe/ZnS QD sensing thin film. The analysis result indicates that the PL intensity of QD exponentially decreases when the temperature increases. Taking the radiative relaxation into account, in the thermally activated nonradiative process which means that the thermal escape from QD is caused by the carrier-longitudinal optical (LO)-phonon scattering and the carrier trapped by the surface defect states, the temperature dependence of the PL intensity can be described by[7]

$$I_{\text{PL}}(T) = \frac{N_0}{1 + A\mathrm{e}^{-E_a/k_B T} + B\left(\mathrm{e}^{-E_{\text{LO}}/k_B T} - 1\right)^{-m}} , \tag{4}$$

where $I_{\text{PL}}(T)$ is the PL intensity at temperature T, N_0 is the initial carrier population of emitting states, m is the number of LO phonons involved in the thermal escape of the carriers from QD, E_a is the activation energy of surface defect states, E_{LO} is the LO phonon energy, and $A=\tau_{\text{rad}}/\tau_a$ and $B=\tau_{\text{rad}}/\tau_o$ represent the ratios of the radiative lifetime τ_{rad} in QD to the capture time (τ_{rad}) and the scattering time (τ_o) from emitting centers by the nonradiative recombination centers, respectively. Since E_{LO} is taken as 25 meV from Raman spectra on CdSe QDs in previous work[8], the experimental data is fitted to Eq.(4) by fixing E_{LO}. The best fitting curve is reproduced by the experimental data for A=1.25, B=12, E_a=15.4 meV and m=7.1. These results are similar to those obtained by D. Valerini[7] and P. Jing[9]. Thus, it is reliable to use the PL intensity of the CdSe/ZnS core/shell QD thin film to measure the high temperature.

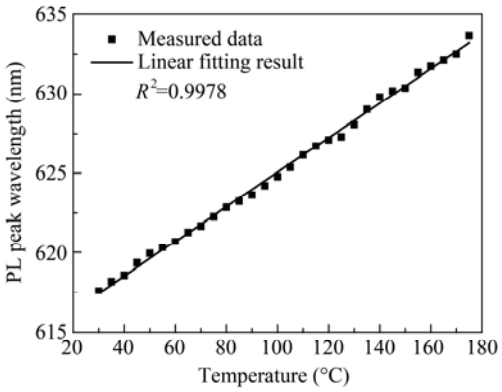

Fig.6 Dependence of the emission peak wavelength on temperature

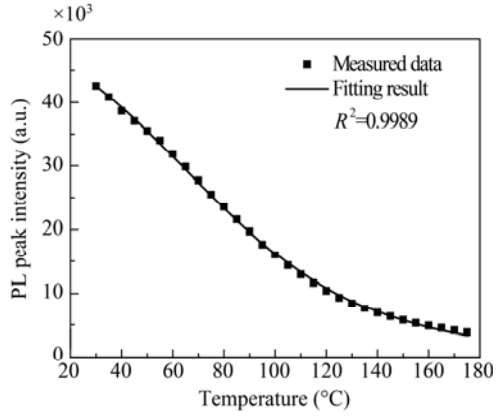

Fig.7 Dependence of the PL intensity on temperature

By further analyzing Fig.3, it can be also found that the PL bandwidth of the QD thin film decreases when the measured temperature increases. Taking advantage of the emission feature, the emission bandwidth can be also used to detect the measured temperature. The experimental results of FWHM of PL spectrum for CdSe/ZnS core/shell QD thin film, which are obtained from Gaussian best fitting of the spectra, clearly show in Fig.8 that the FWHM exponentially increases with temperature. The exponential fitting has a good correlation factor of R^2=0.9996. As a sensing parameter, the average sensitivity of the sensor can reach 0.076 nm/°C. In general, the PL broadening is composed of inhomogeneous and homogeneous terms, and results from the exciton scattering with acoustic and LO phonons[9].

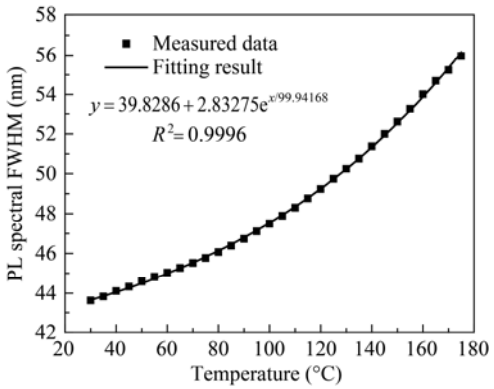

Fig.8 Dependence of FWHM of PL spectrum on temperature

A high temperature sensor based on the CdSe/ZnS QD thin film with a thickness of about 250 μm is set up. The intensity, the peak wavelength and the FWHM of PL spectra with the increase of the test temperature (from 30 °C to 180 °C) are measured and analyzed. By fitting the experimental data, the results show that the peak wavelength of the PL spectra changes linearly with temperature, while the PL intensity and FWHM vary exponentially. Moreover, using those temperature dependent optical parameters, the resolution of the designed sensor can reach about 0.1 nm/°C. More importantly, the measured temperature can be expressed by the multi-parameter variation of the QD PL spectra, which can improve the measured accuracy.

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