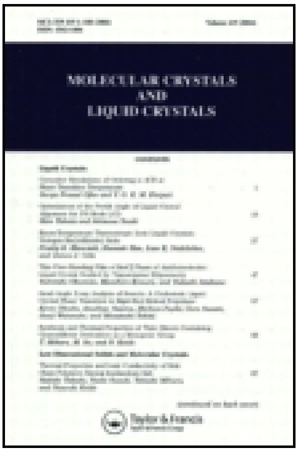

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Thermal Stability of CdSe/ZnS Quantum Dot-Based Optical Fiber Temperature Sensor

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Recently, Quantum Dots (QDs) have been widely studied due to their peculiar optical properties, and applied to various fields such as biomarker, LED device, Fluorescence Resonance Energy Transfer (FRET) sensor, and temperature sensor. In this study, we have prepared optical fiber temperature sensor using CdSe/ZnS QDs as sensing media. Carboxylated CdSe/ZnS QDs have been immobilized on the surface of optical fiber by EDC/ NHS crosslinking reaction. The PL spectra of QDs immobilized on optical fiber are dependent on the size of QDs and ambient temperature. Linear relation has been observed between PL intensity and temperature, and emission peak wavelength and temperature at the range of 25 and 135°C. The PL intensity of QDs has been greatly attenuated after repeated thermal cycle, resulting in poor thermal stability. But the temperature sensor with red QDs show constant slope of PL intensity vs. temperature after 5th cycle.

Keywords CdSe/ZnS Quantum Dots; optical fiber sensor; temperature sensor

1. Introduction

Quantum dots (QDs) are semiconductor nanocrystals and have been of great interest over past decades due to their peculiar electrical and optical properties [1]. QDs can be excited in a broad range of wavelenghts and have a narrow emission spectrum, and their emission peak was dependent on their size. As the size of the QDs increases, the emission peak moves to higher wavelength. This size tunning emission properties together with exceptionally high photostability over conventional organic fluorescent dyes characterizes QDs as promising candidates for the applications of light emitting diodes [2], lasers [3], solar cells [4,5], and biological labels [6,7]. Recently temperature dependent fluorescence property of QDs were studied [8,9] for the application of temperature sensor. PL intensity decrease and red-shift of PL spectral maximum with temperature increase have been observed. Temperature sensor can be prepared by using linear relation between PL intensity and temperature or wavelength change with temperature. Recently our group have studied optical properties of QDs and studied

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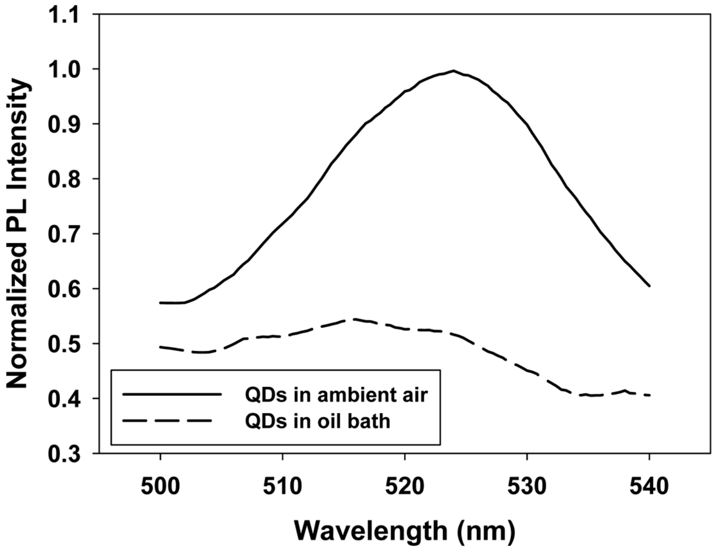


Figure 1. The PL spectra of QDs in ambient air and in oil bath. $\lambda ex = 450\,nm$.

the possibility of using QDs as sensing media. We have prepared optical fiber temperaure sensor by immobilization of CdSe/ZnS QDs on the surface of optical fiber, and studied the variation of the PL intensity with temperature [10]. Linear relation between PL intensity and temperature was observed with the optical fiber immersed in oil bath for temperature control. In this work, optical fiber temperature sensor with QDs has been prepared and the PL intensity variation with ambient temperature was investigated. As the temperature of QDs was controlled in ambient air, the PL intensity of QDs was much higher than that of QDs in oil bath, which may be due to less interference by oil phase as shown in Figure 1. We have used three different sizes of carboxyl CdSe/ZnS QDs. The temperature of the QDs were varied between 25~135°C and PL intensity was measured with cyclic variation of ambient temperature.

2. Experimental

2.1. *Materials*

Qdot® ITK™ carboxyl quantum dots (Emission max 525, 605, 705) were purchased from Invitrogen. 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), N-hydroxysuccinimide (NHS), and 3-aminopropyltriethoxysilane (APTES) were purchased from Sigma Aldrich. Hydrofluoric acid (HF, 49%) was purchased from J.T.Baker. Sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) were obtained at DAEJUNG company. Ethanol (EtOH) and methanol (MtOH) were purchased from Duksan pure chemicals. Optical fibers, silica core diameter of $600 \pm 10\,\mu m$ and clad diameter of $660 \pm 10\,\mu m$, were purchased from Polymicro Technologies. All reagents were used without any further purification.

2.2. *Instrumental Analysis*

Fluorescence spectra of QDs were obtained by using Photoluminescence (PL) spectroscopy (Photon Technology International, NJ, USA). The excitation wavelength

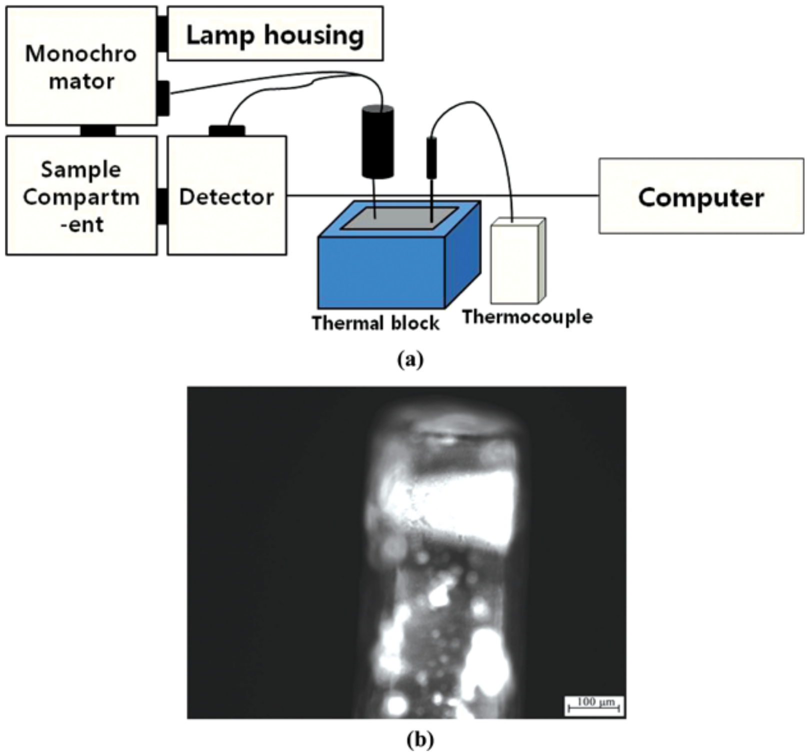


Figure 2. (a) Experimental setup for temperature control and PL analysis on QDs immobilized optical fiber. (b) Fluorescence microscopy image of immobilized QDs.

was 450 nm. Fluorescence image was obtained by using IM-1 2005 Ratio Fluorescence Imaging System (PTI) equipped with xenon lamp which is connected with a fluorescent microscope (Olympus IX71). Figure 2(a) shows the experimental setup for the temperature control and fluorescence spectrum analysis on the QDs. QDs were immobilized on the surface of optical fiber, and the ambient temperature was controlled by thermal block (Daihan Scientific, Seoul, Korea). A K – type thermocouple (HI8757, Hanna Inst) was inserted into the thermal block with the optical fiber to measure the temperature and PL spectra simultaneously. The optical fiber with QDs immobilized was connected through a fiber adaptor to spectrometer, and both excitation and emission light was transferred through the optical fiber.

2.3. *Preparation of QD Optical Fiber Temperature Sensor*

The QD optical fiber temperature sensor has been prepared using the method described in previous paper [10]. The optical fiber tip was tapered using HF etchant and carboxyl QDs were immobilized on the surface of optical fiber by silanization of optical fiber with APTES followed by EDC/NHS cross-linking reaction between silica and carboxyl QDs. Typically 10 mm length of optical fiber was etched. Figure 2(b) shows the fluorescence image of QDs immobilized on the surface of optical fiber.

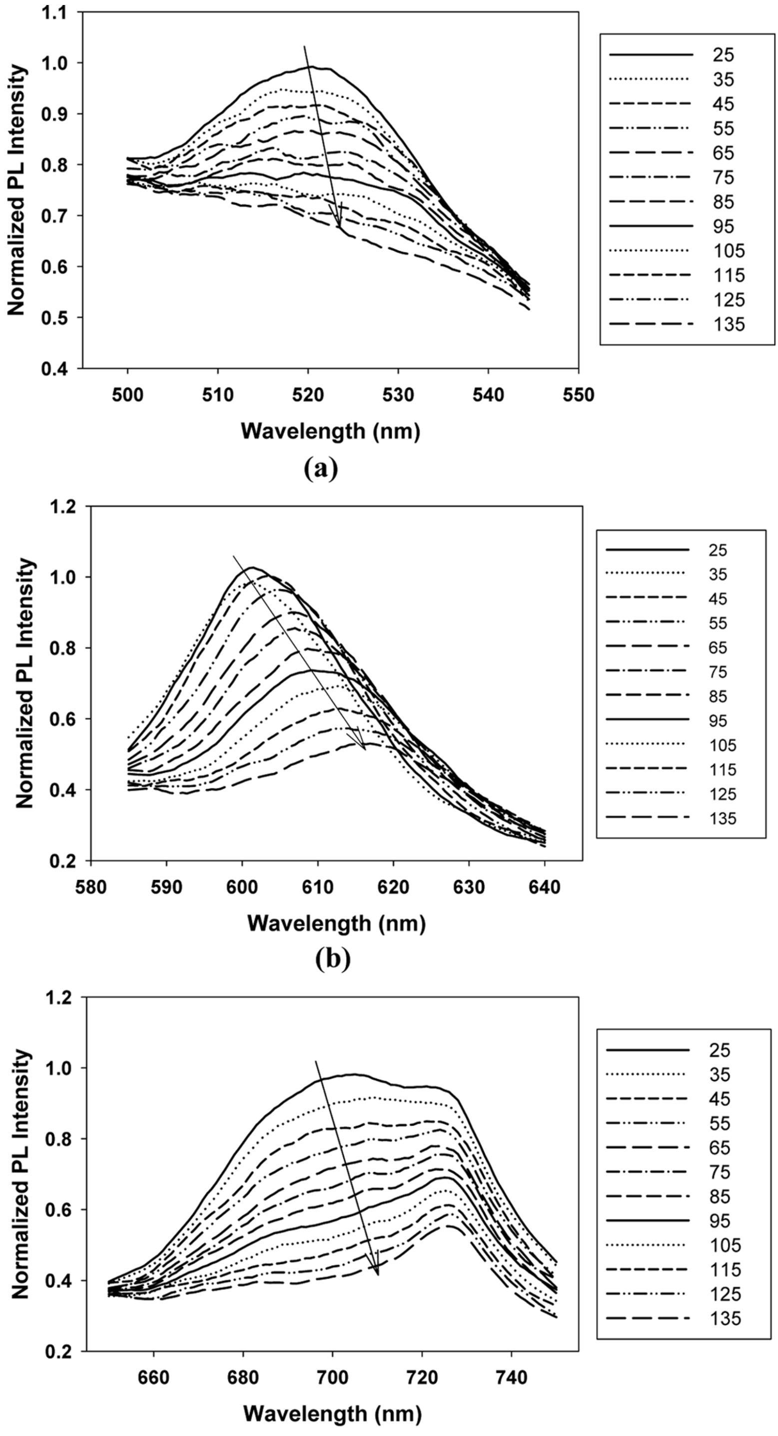


Figure 3. PL spectra of optical fiber temperature sensor with (a) Green QDs (525 nm), (b) Orange QDs (605 nm), and (c) Red QDs (705 nm).

3. Results and Discussion

Figure 3 shows the photoluminescence spectra of QD sensors at different temperatures in ambient air. The PL spectra were measured between 25~135°C. In the experiment, the ambient temperature was varied with increment of 10°C and ramping rate of 1°C/min using thermal block, and real temperature was measured using the thermocouple. The PL intensity of optical fiber without QDs was subtracted from PL intensity of optical fiber QDs for intensity calculation. The QDs immobilized on the optical fiber were excited by irradiation through optical fiber and reflected fluorescence light was detected through optical fiber connected to PL spectrometer. In Figure 3(c), the PL intensity increase at around 725 nm is due to background intensity from optical fiber. The figure shows that as the temperature increases the emission intensity decreases with red-shift of emission peak regardless of the size of QDs. The red-shift of PL spectra can be explained by the bandgap energy contraction of CdSe/ZnS QDs with thermal expansion of QDs. Figure 4 shows the PL intensity variation of QDs with temperature at the wavelength of 520, 600, and 700 nm. The figure shows that temperature sensor with green QDs show a gentle slope, while temperature sensor with orange and red QDs show steeper slopes, which is coincide with previous results [10]. The linear relation between PL intensity of QDs and temperature shows possible temperature sensing application of QDs. Figure 5 shows the emission-peak wavelength variation with temperature. Bastida *et al.* [9] recently show the linear relation of emission peak wavelength with temperature using CdTe QDs. In their experiment, nanocrystals of CdTe QDs were deposited on the optical fiber. In the figure, though the emission-peak wavelength increases linearly with temperature, the experimental data are more scattered than intensity-temperature data. Figure 6 shows the cyclic behavior of the optical fiber temperature sensor. The temperature was increased from 25 to 135°C and decreased back to 25°C, and this cycle was repeated many times. The temperature sensor with

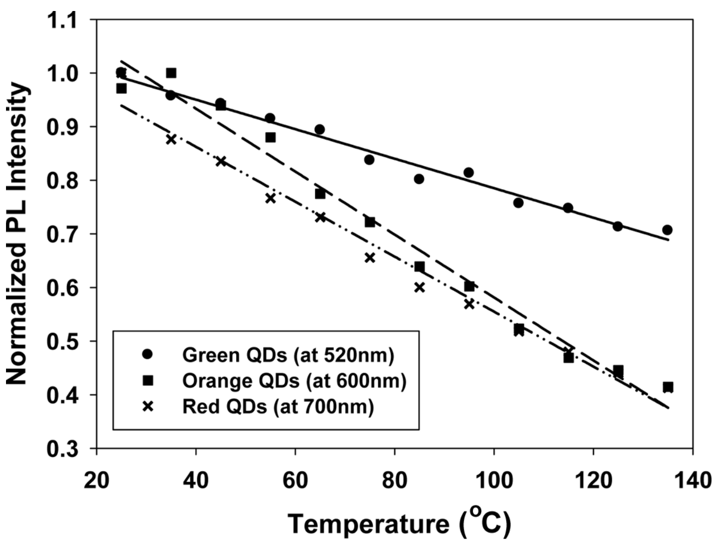


Figure 4. The PL intensity variation of QDs with temperatures at fixed wavelength: green QDs at 520 nm, orange QDs at 600 nm, and red QDs at 700 nm.

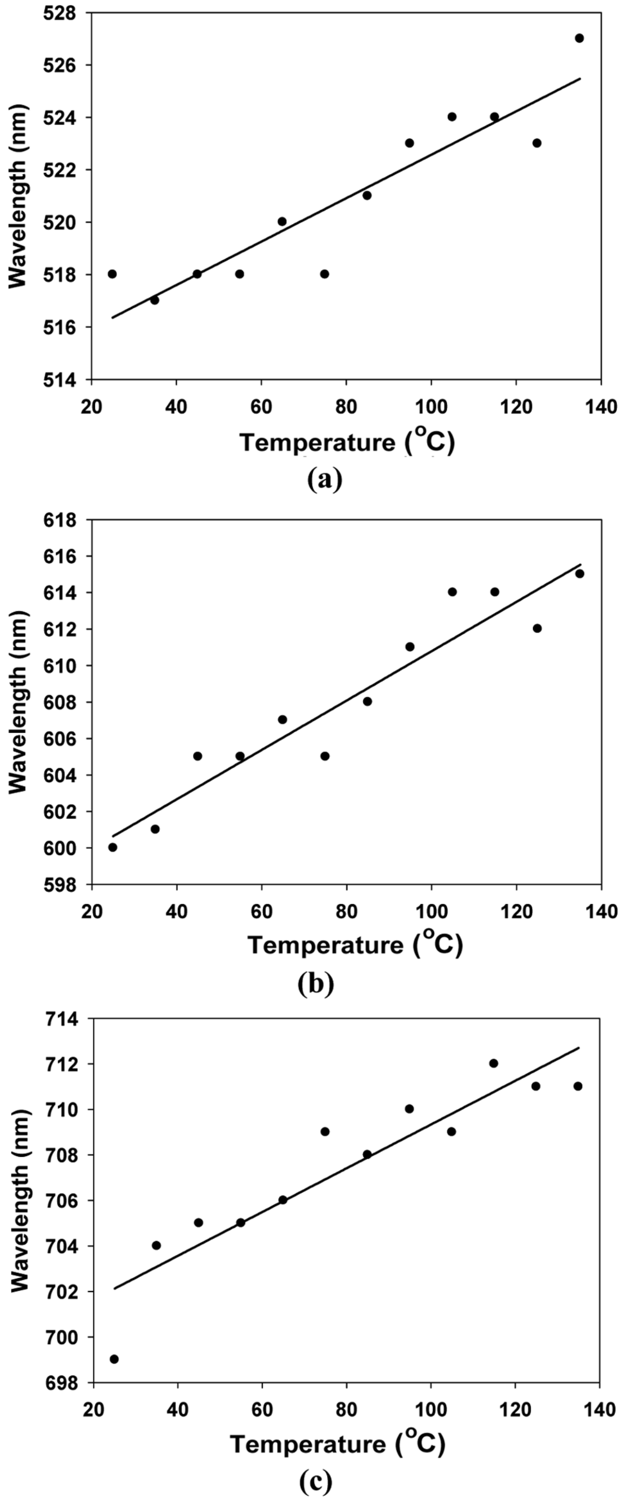
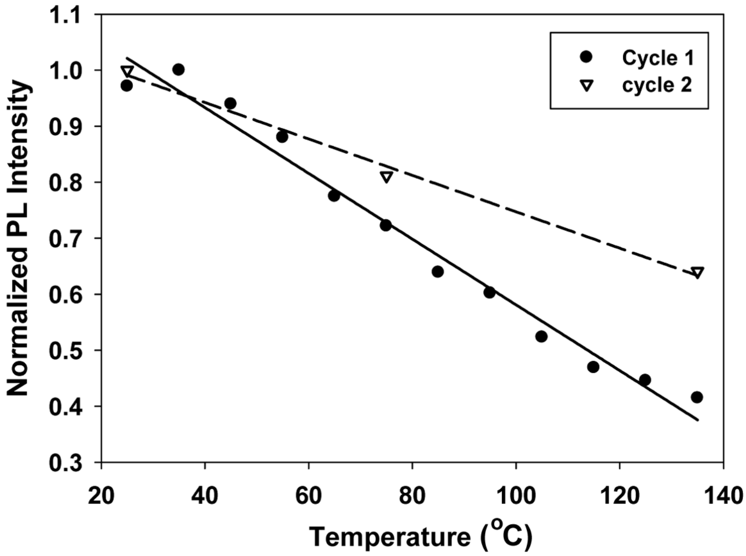
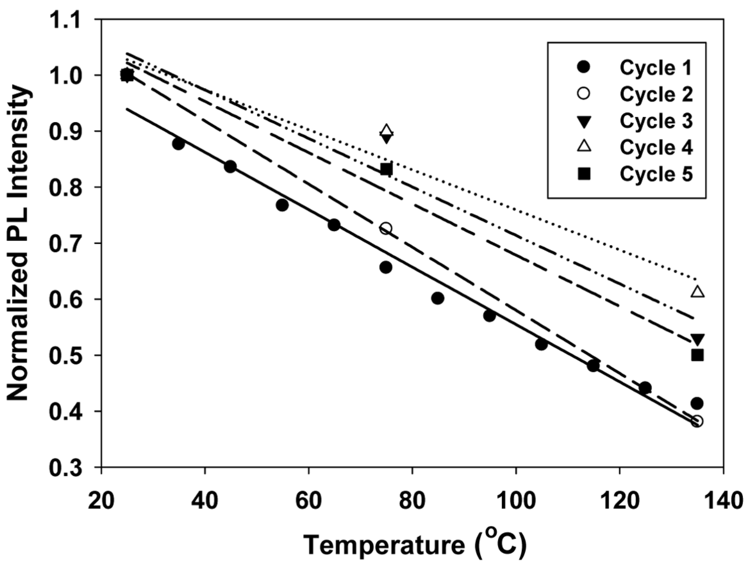


Figure 5. The emission-peak wavelength variation of QDs with temperature: (a) Green QDs, (b) Orange QDs, and (c) Red QDs.



(a)



(b)

Figure 6. The cyclic behavior of PL intensity of the QDs. The temperature was increased from 25 to 135°C and decreased back to 25°C: (a) Orange QDs and (b) Red QDs.

orange QDs shows decreased slope of PL intensity vs. time at second cycle, and PL intensity could not be detected at 3rd cycle as shown in Figure 6(a). The PL intensity of temperature sensor with green QDs could not be detected even after one cycle. But the PL intensity of temperature sensor with red QDs could be detected until 5th cycle, and the slope was not changed much as shown in Figure 6(b). It has been speculated that as the temperature increases over 100°C, the QDs on the surface of optical fiber becomes aggregate, and this significantly attenuate the PL intensity of QDs with repeated thermal cycle, and resulted in poor thermal stability. And as the size of QDs increased, the stability of PL intensity over thermal cycle increased.

4. Conclusion

CdSe/ZnS QD temperature sensor has been prepared. Using the EDC/NHS reaction, carboxyl QDs was immobilized on optical fiber and the PL intensity variation of QDs with temperature was studied. As the temperature increases the emission intensity decreases linearly with red-shift of emission peak regardless of the size of QDs. The emission-peak wavelength increases linearly with temperature though the experimental data are more scattered than intensity-temperature data. Generally, the PL intensity of QDs decreased with repeated thermal cycle, but as the size of QDs increased, the stability of PL intensity over thermal cycle increased.

Acknowledgment

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