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Fabrication and Characterization of Quantum Dot-Based Optical Fiber Temperature Sensor

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In this study, we have prepared the optical fiber temperature sensor using CdSe/ZnS Quantum Dots (QDs) as sensing media. QDs have been immobilized on the surface of tapered fiber tip, and the dependence of fluorescence intensity on ambient temperature has been investigated. The surface of the optical fiber has been silanized using 3-aminopropyltriethoxysilane (APTES) which has amine functional group. QDs with carboxyl functional group have been immobilized by EDC/NHS coupling reaction. After drying with nitrogen blowing, QDs immobilization has been confirmed by photoluminescence spectroscopy (PL) and fluorescence microscope. Green, yellow, and red emission was observed depending on the size of QDs. The photoluminescence (PL) spectra were obtained with ambient temperature in the range of 25–125°C. Linear dependence of PL intensity on temperature has been observed from optical fibers where CdSe/ZnS QDs with green and yellow emission are immobilized. This shows that optical fiber temperature sensor can be fabricated using QDs as sensing media.

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

1. Introduction

Quantum Dots (QDs) have attracted an intense research activity in the last few decades due to their outstanding luminescent properties. Since the first breakthrough applications of water-soluble colloidal QDs [1,2], the majority of the researches on QDs has focused on their use as biological labels, optical sensors, and optoelectronic devices (i.e., LEDs, laser or solar cells) [3–5]. One of the most exciting properties of the QDs is that they can be excited in a wide range of wavelengths and have a narrow emission spectrum. Moreover, the center wavelength of the emission peak depends on the size of the QDs which allows a large choice of emission wavelengths. QDs also offer a great photostability and have a higher quantum yield than traditional organic fluorescent dyes, which attracts variety of bio-sensing applications.

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Recently, temperature dependence of colloidal QDs has been demonstrated. Temperature dependence of PL properties of QDs has been investigated in various conditions such as homogeneous solution phases, thin films, and sol-gel and polymer matrixes [6,7]. Generally thermal quenching of PL intensity and red shift of PL spectra of QDs has been observed [6,7]. The significant temperature dependence of PL intensity of QDs with insensitivity to oxygen reveals that QDs are attractive optical temperature sensing media [8]. However, no efforts have been made to fabricate optical temperature sensing devices by directly applying QDs. In this study, we have fabricated optical fiber temperature sensors which use QDs as sensing media. CdSe/ZnS QDs with different size distributions have been used. QDs have been immobilized on the surface of tapered optical fiber tips by silanization of optical fiber followed by EDC/NHS coupling reaction, and the dependence of fluorescence intensity of QDs immobilized on the surface of optical fibers on ambient temperature has been investigated. The surface modification of optical fiber and optical characteristics of QDs along with temperature sensor application have been discussed.

2. Experimental

2.1. *Materials*

Qdot® ITK™ carboxyl quantum dots in borate buffer were purhased from Invitrogen (NY). The emission maximum was observed at 525 nm, 605 nm, and 705 nm and their diameter was 10–20 nm. 3-aminopropyltriethoxysilane (APTES) and the borate buffer at pH 6.4 were purhased from Sigma Aldrich, and hydrofluoric acid (HF, 40%), hydrochloic acid, methanol were obtained from J. T. Baker, DAEJUNG company, and Duksan Pure Chemicals Co., Ltd., respctively. Optical fibers, silica core diameter of 661.70 μm and clad of 710 μm, were obtained fro Polymicro Technologies. All reagents were used without any further purification.

2.2. *Tapering of Optical Fibers*

The optical fibers were tapered to increase the power density of excitation and emission light for enhancing signal acquisition. The fiber tips were immersed in sulfuric acid at 100°C for an hour to remove 10 mm of polyimide buffer. The fibers were then rinsed and kept in boiled double-deionized water (ddH_2O) for an hour to clean the surface. Next, fiber tips were immersed again in 40% hydrofluoric acid (HF) for 4 hours while increasing the immersion depth gradually by using silynge pump to allow fiber tapering via capillary action. The fiber tips were then cleaned by ddH_2O, and allowed to air-dry.

2.3. *Silanization of Optical Fibers*

The tips were immersed in 1:1 mixture of concentrated hydrochloric acid (HCl) and methanol for 30 minutes at room temperature. After several rinses in ddH_2O, the fiber tips were immersed in concentrated sulfuric acid (H_2SO_4) for 30 minutes at room temperature. The tips were rinsed to remove all residues, boiled for 30 minutes in distilled water, and allowed to air dry. Next, the tips were immersed in 28.4 mg/ml solution of APTES in ethanol for 3 hours. The tips were then rinsed by ethanol and allowed to air-dry.

2.4. *Immobilization of CdSe/ZnS Quantum Dots on Fibers*

The silanized optical fibers with amine functional group were further reacted with carboxyl group conjugated QDs by EDC/NHS coupling reaction. The fiber tips were incubated overnight in a mixture of 200 µl 100/100 mM EDC/NHS (prepared in 0.1 M borate buffer, pH 7.4) and 5 µl (8 µM) of QDs, and kept in dark at room temperature.

2.5. *Instrumental Analysis*

Atomic force microscopy (AFM) images were obtained using XE-100 in non-contact mode (Parksystems, Gyeonggi, Korea). Steady-state fluorescence excitation and emission spectra were obtained by using spectrofluometer (Photon Technology International, Lawrenceville, NJ, USA). The optical fiber with QDs immobilized was connected through fiber adaptor to spectrometer, and both excitation and emission light was transferred through the optical fiber. The optical fiber temperature sensor was dipped into an oil-circulating bath equipped with a temperature controller (JeioTech Co., Seoul, Korea). Figure 1 shows the system for measuring PL spectra and temperature controller.

3. Results and Discussion

3.1. *Excitation and Emission Scan of QDs*

Figure 2 shows the excitation and emission spectra of QDs. For excitation scan, the emission wavelength was observed at 525 nm, 605 nm, and 705 nm (Fig. 2(a)). The emission scans of green, yellow, and red QDs were obtained at the excitation wavelength of 450 nm (Fig. 2(b)). The fluorescence of QDs shows distinguished red shift which is observed when the size of QDs increases.

3.2. *Immobilization of QDs on Optical Fiber*

Figure 3(a) shows the general scheme of the silanization of optical fibers by APTES and the immobilization of QDs by EDC/NHS coupling reaction. The reaction has been used for amide linkages between a carboxylate and an amine group. EDC/NHS-coupled reactions are known to be about 20-fold efficient compared to using EDC alone [9]. The surface of silica after cleaning contains hydroxyl group, and this can react with ethoxy silane by hydrolysis and condensation reaction. The amine group in APTES later can be reacted with carboxyl group in QDs by introducing

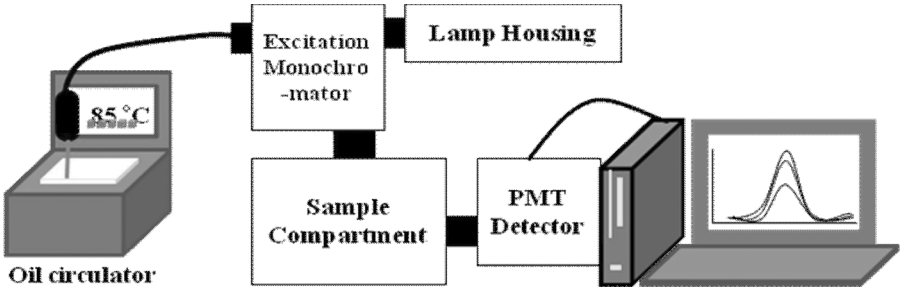

Figure 1. System for PL spectra of QDs and temperature controller.

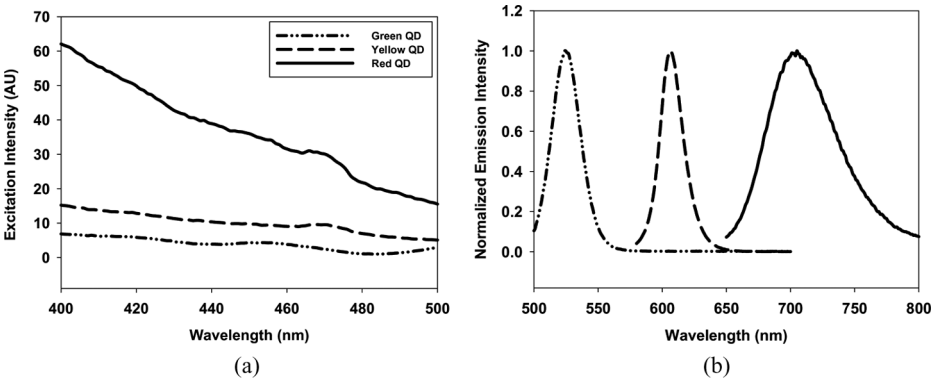

Figure 2. The fluorescence spectra of QDs. (a) Excitation scan and (b) emission scan with excitation wavelength at 450 nm.

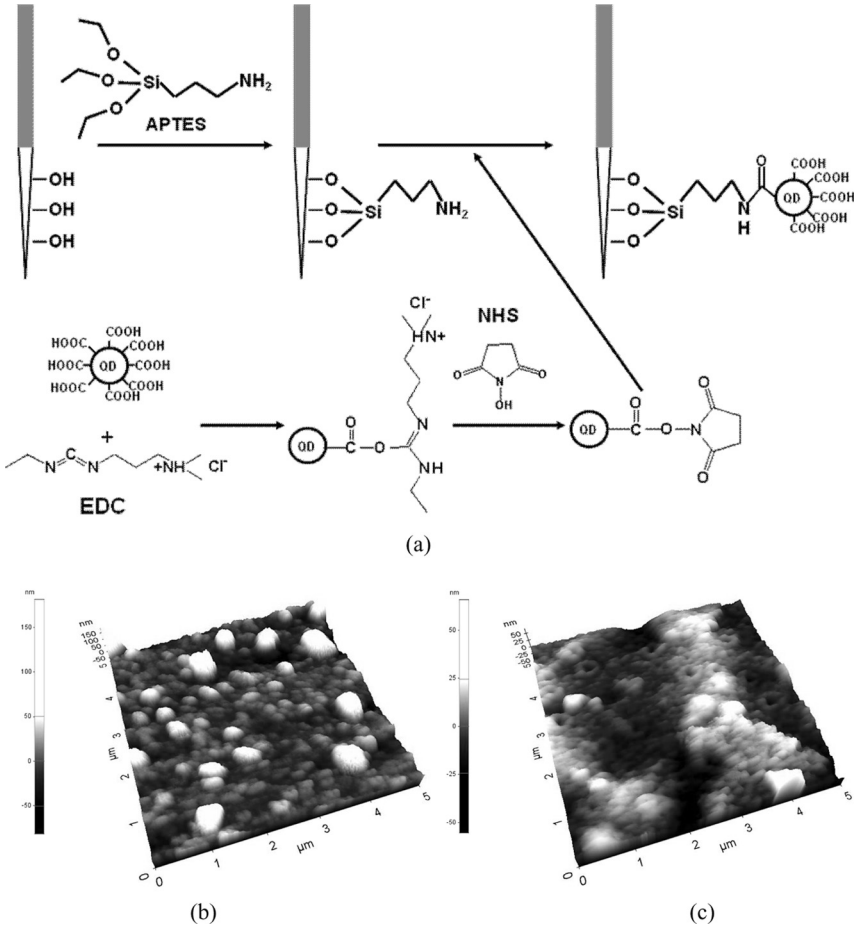

Figure 3. (a) The surface treatment of optical fiber by silanization and the reaction scheme of EDC/NHS coupling for immobilization of QDs. The AFM images of optical fiber surface before (b) and after (c) QDs attachment.

coupling agent, EDC and NHS [9]. The morphology of the QD-modified fibers was investigated using AFM. Figure 3(b) and (c) show AFM images of the surface of optical fibers before and after immobilization of QDs. The figure shows that the roughness of the fiber was significantly reduced by the immobilization of the QDs. Quantitative measurements obtained from images of 5 μm × 5 μm size scales showed

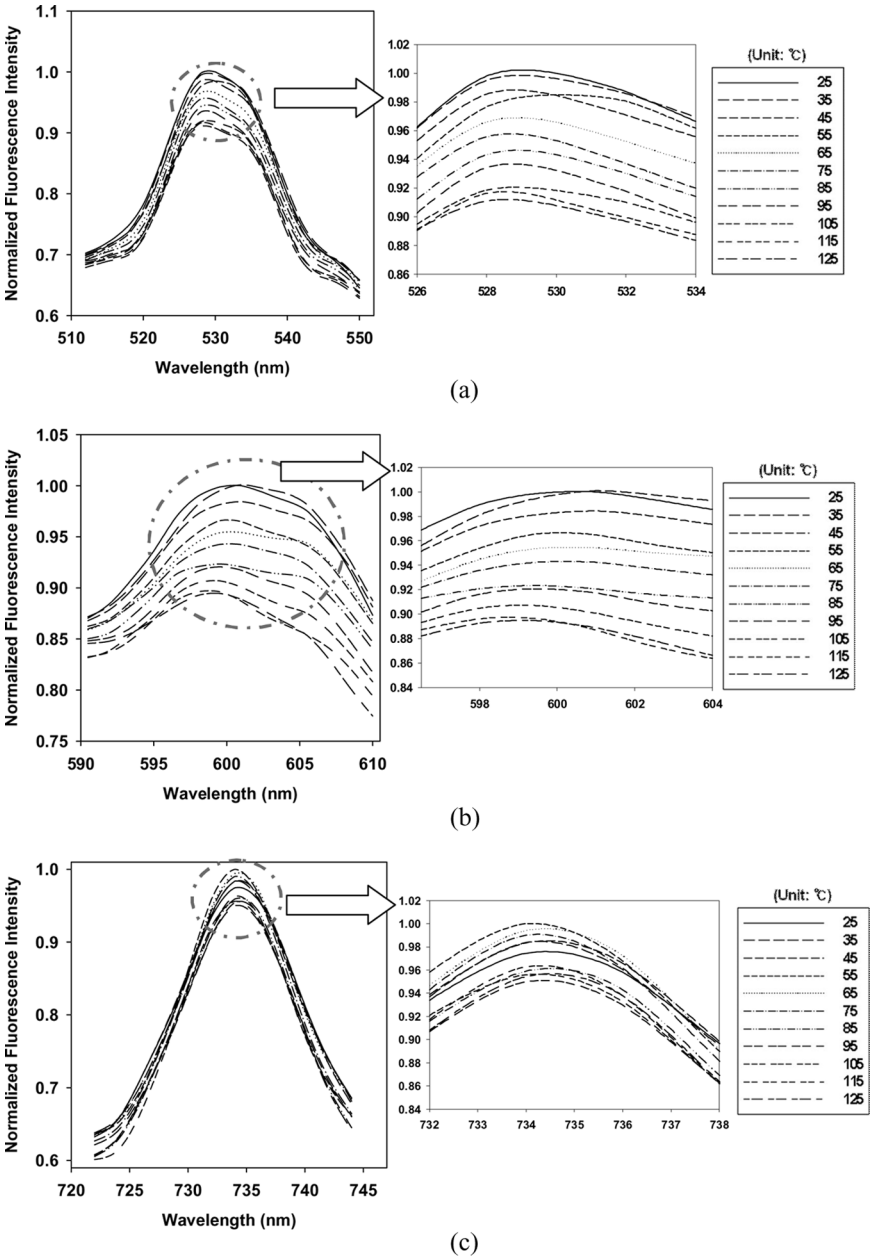

Figure 4. PL spectra of QDs immobilized on optical fiber at different temperatures: (a) green QD at 410 nm, (b) yellow QD at 466 nm, and (c) red QD at 466 nm of excitation wavelength.

that the mean surface roughness decreased from 16.018 nm to 6.729 nm. This suggests that the surface of the optical fiber has been covered by clusters of QDs, which resulted in less roughness value. The immobilized QDs were also identified by emission spectra using photoluminescence spectroscopy.

3.3. *Temperature Dependent Emission Spectra*

Figure 4 shows the PL spectra of QDs immobilized on optical fibers. The temperature was varied from 25 to 120°C, and the emission spectra was measured after 15 min of thermal equilibrium. The excitation wavelength of green QDs was 410 nm, while that of yellow and red QDs was 466 nm. The figure shows that emission intensity of yellow and green QDs was gradually decreased with increase of temperature and emission maxima was red-shifted, which is coincide with the previous reports with QDs clusters in solution [10]. But less change was observed with red QDs, which might be due to larger energy requirements for thermal quenching due to bigger size distribution. Compared to the emission scan from QDs dispersed in solution, the spectral width became much broader. This is due to the cluster formation of QDs on the surface of the optical fiber, which results in not uniform size distribution. Figure 5 shows the normalized PL intensity dependence of QDs on temperature. The normalized intensity decreased linearly with increase of temperature in optical fiber sensors with green and yellow QDs. The thermal quenching of QDs was previously explained to be due to a thermal activation of surface trap states and an increased nonradiative Augur exciton recombination [10]. The figure also shows that steeper slope was observed with yellow QDs, which indicates that sensitivity of QDs temperature sensor depends on the size of QDs. It is not clear at this point why yellow QDs shows steeper slopes than green QDs. But both QDs show a great linearity over quite long range of temperature. This shows that QDs are promising candidate for temperature sensing media, and optical fiber temperature sensor can be fabricated by immobilization of QDs on optical fiber.

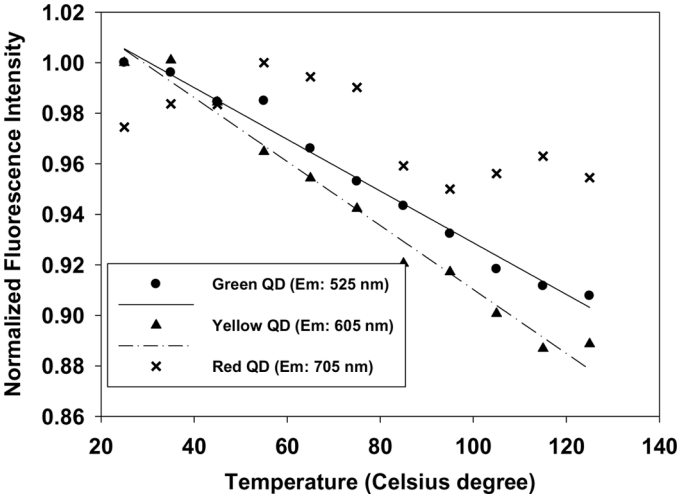

Figure 5. The dependence of PL intensity of QDs attached on optical fiber on ambient temperature.

4. Conclusion

Optical fiber temperature sensor has been fabricated by immobilizing CdSe/ZnS QDs on the surface of tapered optical fiber using EDC/NHS coupling reaction. The fluorescent spectra were red shifted with increase of the size of QDs. The fluorescent intensity was decreased with increase of temperature, and great linearity was observed between temperature and emission intensity of yellow and green QDs. This shows that QDs are promising candidates for temperature sensing media.

Acknowledgements

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