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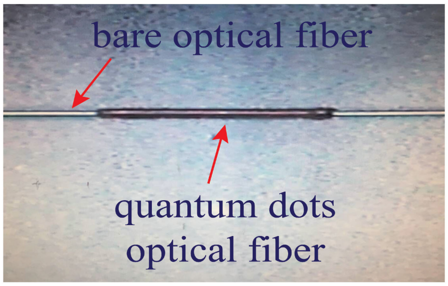

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A Low Loss Quantum-Dot-Doped Optical Fiber Temperature Sensor Based on Flexible Print Technology

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Abstract: A quantum dots optical fiber (QDOF) sensor is proposed for temperature sensing in this paper. The sensor is fabricated by the drop-on-demand inkjet printing technology. By controlling the diameter of droplet, the spacing between droplets and the number of printed layers, the QDOF is printed on the polymer substrate. The loss of QDOF is less than 0.35 dB·mm^{-1} at the fluorescence wavelength. The experimental results show that the temperature sensitivity of sensor is 109 pm/ °C. As far as we know, this is the first time that a QDOF sensor is manufactured by the inkjet printing technology to realize the temperature measurement.

Index Terms: Temperature sensor, quantum dots fiber, inkjet printing.

1. Introduction

In recent decades, quantum dots, a kind of low-dimensional semiconductor material, have been attracting tremendous interest in both theoretical research and technological applications for their unique optical and electronic properties [1]–[3]. Because of the exciton-phonon coupling action and high surface-to-volume ratios, they are highly sensitive to various physical parameters such as temperature and humidity. The optical sensors by using quantum dots materials have become one of the most popular research fields [4]–[10].

Now many optical sensors which are based on quantum dots have been successfully developed [11]–[13]. In 2011, Chao Meng *et al.* utilized the polymer nanofibers which were doped with CdSe/ZnS quantum dots and synthetized by physically drawing solvated polymers for optical sensing [14]. Because the diameter of the polymer nanofibers can’t be controlled by this method, the repeatability is a problem and which will limit the further application of nanofibers. In 2012, A.Bhardwaj *et al.* fabricated the polymer optical fiber preforms doped with quantum dots [15]. However, high temperature is involved in both the fabrication of the preform and the subsequent fiber drawing process, which inevitably affects the fluorescence characteristics of the quantum dots. In 2015, Xiaojin Yin *et al.* proposed a luminescence temperature sensor by employing quantum

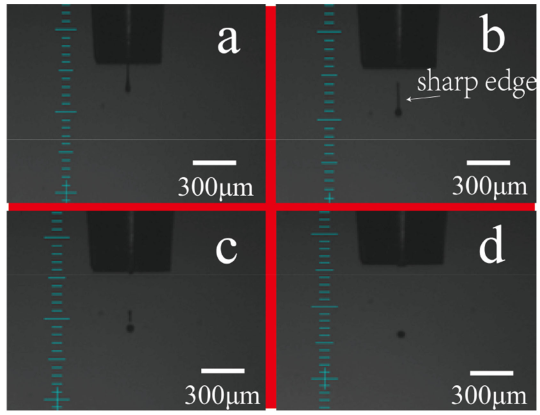

Fig. 1. Droplet ejection sequence in the process of inkjet printing.

dots aqueous solution encapsulated in a segment of photonic crystal fiber [16], [17]. Because it's difficult to fill the quantum dots solution into photonic crystals fiber, the length of the sensor fiber is hard to control.

In this paper, a method to fabricate the QDOF sensor based on drop-on-demand inkjet printing technology is proposed. Since the size of the sensing fiber is determined by the diameter of the nozzle and the number of printed layers, we can precisely fabricate the quantum dots sensing fiber which has the cross sections similar to the commercial fiber by optimizing the inkjet printing program. That not only improves the coupling efficiency between the two different fibers and reduces the transmission loss, but also the fabrication of QDOF sensor has the excellent repeatability and consistency. Meanwhile, this technology can fabricate a more compact and sensitive fiber temperature sensor than that using the fiber Bragg grating (FBG) and the Mach-Zehnder(MZ) interferometer [18]–[20].

2. The Fabrication of Quantum Dots Fiber Sensor

The inkjet printer used in the experiment is the Jetlab II. The printing ink is mixed by ourselves, which is composed of CdSe/ZnS quantum dots and ultraviolet glue. The quantum dots concentration of the printing ink is 5 mg/ml. Owing to the controllable droplet diameter, distance between droplets and number of printed layers, the printer can print various structures with different sizes. When the nozzle with 60 μm diameter is used, the QDOF with the cross sections similar to those of multimode fibers can be fabricated by controlling the printing program, which makes the alignment between them easier.

The drop-on-demand inkjet printing systems produce a droplet when desired, so it can ensure an accurate printing. The droplet (diameter = 63.3 μm) ejection sequence in the process of inkjet printing is shown in Fig. 1. The inkjet printing sequence is from a to d. The sharp edge of the droplet is caused by highly repetitive stroboscopic photography. When stable droplets are formed, we can adjust the spacing between the adjacent droplets to print the ideal optical waveguide. As shown in Fig. 2, when the spacing "d" between the droplets is reduced from 0.12 mm to 0.06 mm, discrete single points gradually form a linear waveguide on the substrate. The smoothness of the waveguide sidewall is highest when the spacing is set as 0.08 mm. If the spacing is decreased continuously, the width of the waveguide will widen, and the sidewall will become unsmooth.

As the thickness of waveguide formed by single printing is too thin to form the cylindrical structure, the method that printing layer by layer is adopted. In addition, every layer is UV cured before each superimposing. By controlling the number of printing layers, the QDOF with the circular cross section which is similar to the traditional fiber can be precisely fabricated. Fig. 3 presents the

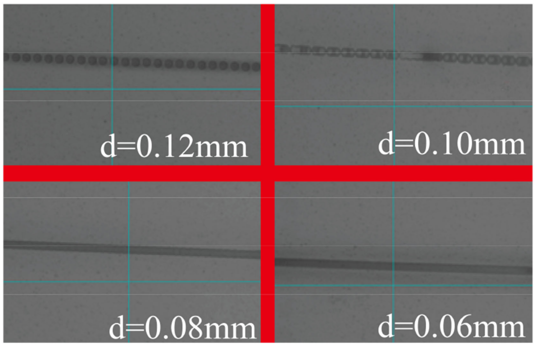

Fig. 2. The printed waveguides when different spacing is set.

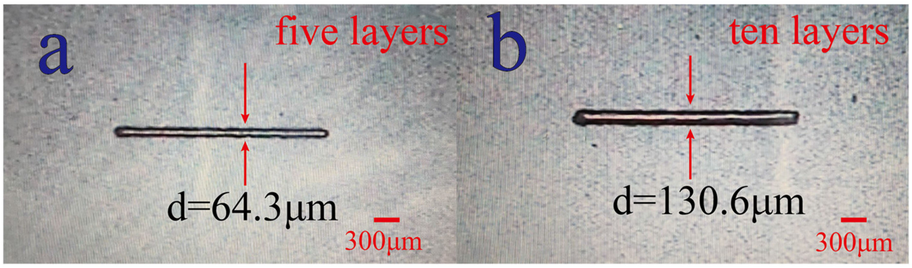

Fig. 3. The images of QDOF with different printing layers by metallographic microscope.

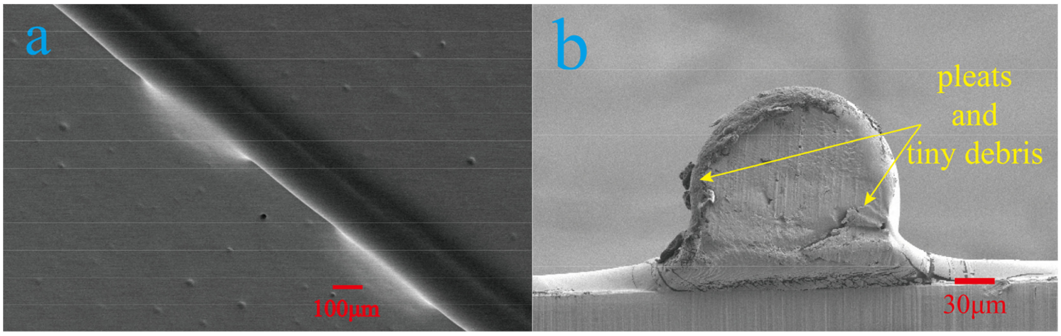

Fig. 4. The image of QDOF by scanning electron microscopy a) the side views of QDOF b) the cross section image of QDOF.

printing results when the printing layers are five and ten. The image is obtained by metallographic microscope. It can be found that the width of QDOFs is 64.3 μm and 130.6 µm, respectively.

Since the images observed by the metallographic microscope are not clear enough, we use the scanning electron microscope (SEM) to obtain the high-resolution pictures. The picture of 130.6-μm-width QDOF observed by the SEM is shown in Fig. 4. The QDOF is close to the cylindrical structure and can be regard as the optical fiber. As shown in Fig. 4a, the fiber has uniform diameter and smooth sidewall, which is necessary for low-loss optical waveguide. Fig. 4b shows that the cross section of QDOF is close to circle, so the connection loss between traditional optical fiber and QDOF can be low.

The pleats and tiny debris on the cross section are caused by the cleaving. When the 475 nm light is used as excitation light and coupled into the QDOF from the multimode fiber, the QDOF

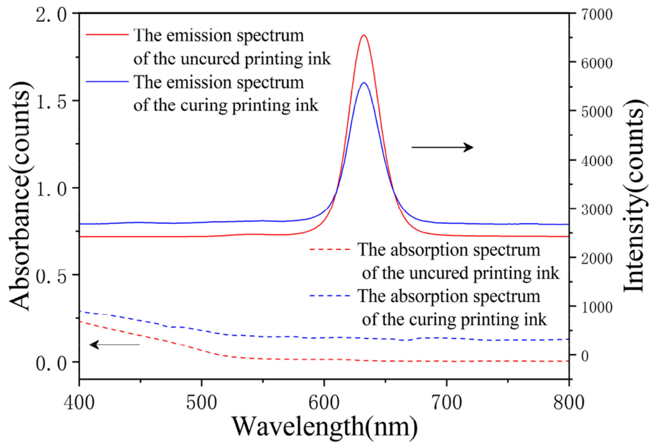

Fig. 5. The effect of UV curing on the absorption and emission spectrum of printing ink.

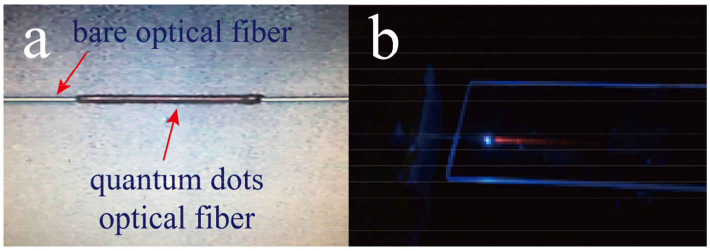

Fig. 6. a) The quantum dots optical fiber sensor b) The luminescence characterization of QDOF.

demonstrates excellent waveguide properties with a bright output at the other end. The fluorescence wavelength is at 631 nm. In order to study the transmission loss of QDOF, we measured the output power when the 631 nm laser propagated different length of QDOF. The transmission loss coeff α is given by

$$\alpha = \frac{10}{L_2 - L_1} lg \frac{P_2}{P_1} \text{(dB/mm)} \quad (1)$$

Where L_1, L_2 is the length of the QDOF and P_1, P_2 is the output power of laser after propagating the QDOF, respectively. The transmission loss of QDOF is less than 0.35 dB·mm^{-1} at room temperature, which is low and in the same order compared with the results in Ref. [14].

Because the printing process does not affect the optical properties of the printing ink, the effect of UV curing on the absorption and emission spectrum of printing ink is studied. The results are shown in Fig. 5. Due to little change about absorption and emission spectrum and the unchanged peak of emission, we believe that the UV curing does not affect the photoluminescence (PL) characteristic of quantum dots. Then the printed QDOF is used in the sensing experiment. Due to fluorescence quenching and transmission loss, In the case of constant excitation power, when the length of the QDOF is less than 3 mm, the fluorescence intensity increases sharply with the increase of the length. When the length of the QDOF is more than 3 mm, the fluorescence intensity decreases about 7% with each 1mm increase. Therefore, the length of QDOF used in the experiment is 3 mm. The optical alignment system is used to achieve the connection of the multimode fiber (MMF) and the QDOF sensor. For robustness, the low-index UV-cured adhesive was used as binders at the connection region between the QDOF and MMF. Finally, the QDOF sensor is shown in Fig. 6(a). And the luminescence characterization of QDOF is shown in Fig. 6(b).

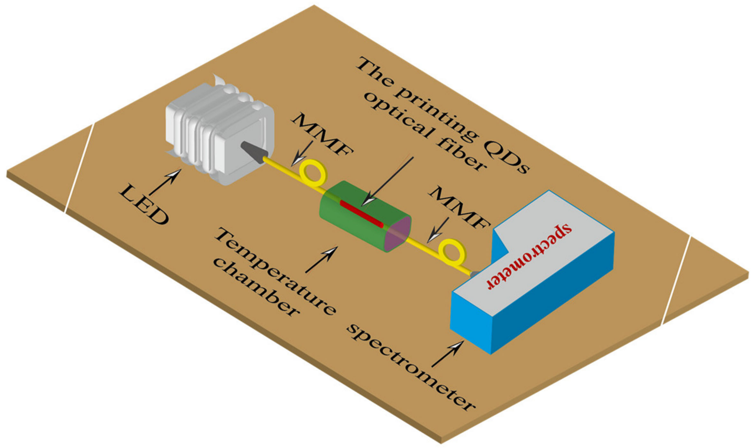

Fig. 7. Experimental setup of the QDOF temperature sensor.

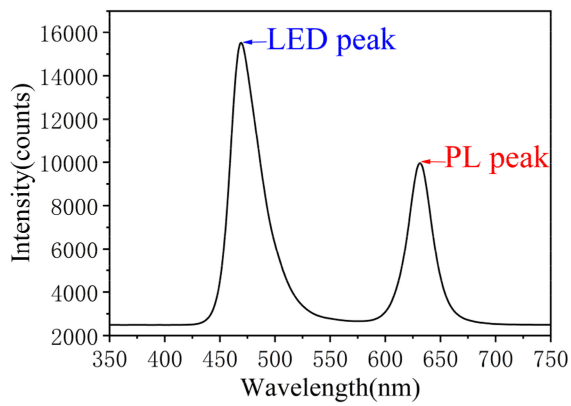

Fig. 8. The excited spectrum of the QDOF sensor.

3. The Temperature Sensing Experimental Setups

The experimental setup is shown as Fig. 7. A semiconductor light-emitting diode (LED, $\lambda_{\rm LED} =$ 475 nm) is used as an excitation source for QDOF sensor, and the fluorescence ($\lambda_{\rm QDOF} = 631$ nm) of the QDOF is detected by the spectrometer. The experiment result is shown in Fig. 8, and the spectra of excitation and emission can both be observed. As far as we know, this is the first time that luminescence peak is detected through the QDOF sensor which is manufactured by inkjet printing technology.

We studied the response of QDOF's fluorescence to temperature and strain, respectively. In order to study the response of QDOF's fluorescence to strain, the multimode fibers which connects the two ends of the quantum-dot fiber was clamped on two displacement platform. One platform was fixed, and the other one was driven by a motor to stretch the QDOF. Due to deformation which is caused by stretch, the light leakage of QDOF increases. Therefore, the loss increases. The effect of strain on PL characteristic of QDOF sensor is shown in Fig. 9. With the increase of strain, the PL peak and the full width at half maxima (FWHM) of QDOF sensor demonstrate excellent stability, but the PL intensity of sensor decreases.

In order to test the temperature sensitivity of the QDOF sensor, the QDOF sensor is placed in a temperature-controlled chamber. the length of QDOF has a very little change and the width of the QDOF increase about 8% when the temperatures from 20 $^{\circ}$C to 70 $^{\circ}$C. The optical response of the

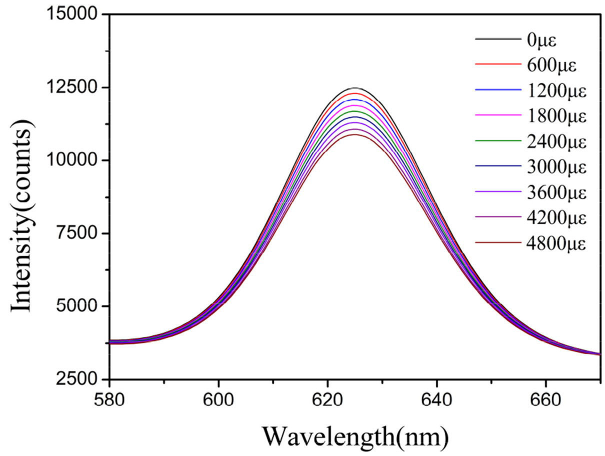

Fig. 9. The luminescence spectra of QDOF sensor at different strains.

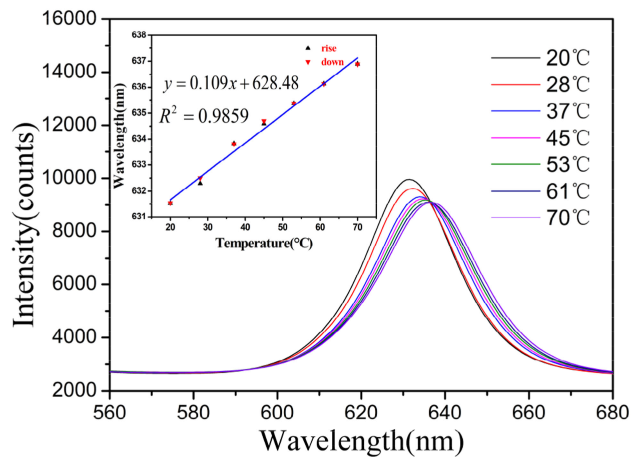

Fig. 10. The luminescence spectra of the QDOF temperature sensor at different temperatures.

QDOF sensor is shown in Fig. 10. As expected, with increases of temperature, not only the PL peak shows red shifts, but also the intensity of the PL decreases. The experimental results agree well with the theoretical analysis, that is, with the temperature increasing, the temperature-dependent band-gap will shrink, some nonradiative process will be activated, at the same time the exciton-LO phonon scattering will enhance. These changes that lead to the PL peak red shift, the PL intensity decrease and the PL bandwidth broaden, respectively [21], [22].

4. Results and Discussion

According to the above experiments, it can be found that strain and temperature change can both affect the PL intensity and may result in the cross sensitivity. Therefore, the PL intensity is not suitable for temperature measurement. The shifts of the PL peak and the width of PL FWHM are used to measure the temperature changes in the next experiment. As shown in Fig. 10, the PL peak wavelength of QDOF sensor owns good linear response to the change of temperature. The correlation coefficient square (R^2) is close to 1, and the temperature sensitivity of the sensor is about 109 pm/ °C. And it can be seen that the temperature response of the QDOF sensor has excellent reversibility. We also research the relationship of FWHM with the different temperatures,

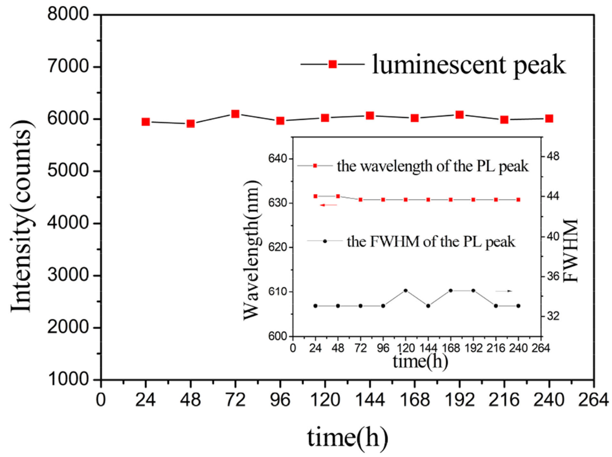

Fig. 11. The long-term luminescence stability of QDOF sensor within 240 h at the 30 °C.

and the sensitivity is 90 pm/ °C, the correlation coefficient square (R^2) is 0.968. Due to the higher sensitivity, we use the wavelength of PL peak as the temperature indicator in this paper. The measurement range can be expanded by optimizing the fabrication technology of the quantum dots.

The long-term stability of luminescence is more important to a quantum dots sensor. We put a 3 mm-length QDOF sensor in a thermostat. The Fig. 11 shows the luminescence stability of the QDOF sensor within 240 h at the 30 °C. The change of the PL peaks is very small. The fluctuation of luminescence intensity is no more than 1.4%, and the broadening of PL FWHM is no more than 4.6%, respectively. Therefore, the QDOF temperature sensors demonstrate good prospects for application.

5. Conclusion

In conclusion, a quantum dots optical fiber temperature sensor based on the drop-on-demand inkjet printing technology is presented in this paper. We can fabricate the different sizes of QDOF by precise control of printing process. The experimental results show that the QDOF owns strong and stable PL intensity, low transmission loss and easier coupling with multimode fibers. When the QDOF is used in the temperature measurement, the QDOF sensor demonstrated high temperature sensitivity about 109pm/ °C and excellent reversibility. Considering the flexibility, controllability and repeatability, the printing method may be a good candidate for fabricating optical fiber and other optical elements with arbitrary structure, such as optical microcavity. Using the change of PL intensity, QDOF sensor will realize the simultaneous measurement of temperature and strain in the future.

References

[1] J. Wu, S. M. Chen, A. Seeds, and H. Y. Liu, “Quantum dot optoelectronic devices: Lasers, photodetectors and solar cells,” *J. Phys. D Appl. Phys.*, vol. 48, no. 36, 2015, Art. no. 363001.
[2] U. Resch-Genger, M. Grabolle, S. Cavaliere-Jaricot, R. Nitschke, and T. Nann, “Quantum dots versus organic dyes as fluorescent labels,” *Nat. Methods*, vol. 5, no. 9, pp. 763–775, 2008.
[3] P. A. S. Jorge, M. A. Martins, T. Trindade, J. L. Santos, F. Farahi, “Optical fiber sensing using quantum dots,” *Sensors-Basel*, vol. 7, no. 12, pp. 3489–3534, 2007.
[4] X. Li, J. Qian, J. LI, and S. L. He, “Fluorescence quenching of quantum dots by gold nanorods and its application to DNA detection,” *Appl. Phys. Lett.*, vol. 94, no. 6, 2009, Art. no. 063111.
[5] G. Shambat *et al.*, “A photonic crystal cavity-optical fiber tip nanoparticle sensor for biomedical applications,” *Appl. Phys. Lett.*, vol. 100, no. 21, 2012, Art. no.213702.

[6] B. W. Wang *et al.*, "Photonic crystal cavity on optical fiber facet for refractive index sensing," *Opt. Lett.*, vol. 37, no. 5, pp. 833–835, 2012.
[7] A. Hreibi, F. Gerome, J. L. Auguste, Y. Zhang, W. W. Yu, and J. M. Blondy, "Semiconductor-doped liquid-core optical fiber," *Opt. Lett.*, vol. 36, no. 9, pp. 1695–1697, 2011.
[8] J. H. Wang *et al.*, "Modification of CdTe quantum dots as temperature-insensitive bioprobes," *Talanta*, vol. 74, no. 4, pp. 724–729, 2008.
[9] G. de Bastida, FJ. Arregui, J. Goicoechea, and I. R. Matias, "Quantum dots-based optical fiber temperature sensors fabricated by layer-by-layer," *IEEE Sens. J.*, vol. 6, no. 6, pp. 1378–1379, Dec. 2006.
[10] N. Irawati, S. W. Harun, H. A. Rahman, S. S. Chong, N. A. Hamizi, and H. Ahmad, "Temperature sensing using CdSe quantum dot doped poly(methyl methacrylate) microfiber," *Appl. Opt.*, vol. 56, no. 16, pp. 4675–4679, 2017.
[11] P. A. S. Jorge, M. Mayeh, R. Benrashid, P. Caldas, J. L. Santos, and F. Farahi, "Quantum dots as self-referenced optical fibre temperature probes for luminescent chemical sensors," *Meas. Sci. Technol.*, vol. 17, no. 5, pp. 1032–1038, 2006.
[12] C. S. Chu and C. J. Su, "Fluorescence ratiometric optical broad range pH sensor based on CdSe/ZnS quantum dots and O170 embedded in ethyl cellulose matrix," *J. Lightw. Technol.*, vol. 36, no. 4, pp. 857–862, Feb. 2018.
[13] L. Y. Ding *et al.*, "Nitric oxide optical fiber sensor based on exposed core fibers and CdTe/CdS quantum dots," *Sensor Actuat B-Chem.*, vol. 273, pp. 9–17, 2018.
[14] M. Chao, X. Yao, W. Pan, L. Zhang, Y. X. Liu, and L. M. Tong, "Quantum-dot-doped polymer nanofibers for optical sensing," *Adv. Mater*, vol. 23, no. 33, pp. 3770–3774, 2011.
[15] A. Bhardwaj *et al.*, "PbS quantum dots doped glass fibers for optical applications," in *Proc. Conf. Lasers Electro-Opt.*, San Jose, CA, 2012, pp. 1–2.
[16] X. J. Yin, W. Y. Wang, Y. Q. Yu, Y. F. Geng, and X. J. Li, "Temperature sensor based on quantum dots solution encapsulated in photonic crystal fiber," *IEEE Sens. J.*, vol. 15, no. 5, pp. 2810–2813, May 2015.
[17] WY. Wang *et al.*, "Quantum dots-based multiplexed fiber-optic temperature sensors," *IEEE. Sens. J.*, vol. 16, no. 8, pp. 2437–2441, Apr. 2016.
[18] H. L. Wang and A. J. Yang, "Temperature sensing property of hollow-core photonic bandgap fiber filled with CdSe/ZnS quantum dots in an UV curing adhesive," *Opt. Fiber Technol.*, vol. 38, pp. 104–107, 2017.
[19] H. Li, H. B. Li, F. Y. Meng, X. P. Lou, and L. Q. Zhu, "All-fiber MZI sensor based on seven-core fiber and fiber ball symmetrical structure," *Opt. Laser Eng.*, vol. 112, no. si, pp. 1–6, 2019.
[20] R. Di Sante and F. Bastianini, "Temperature-compensated fibre Bragg grating-based sensor with variable sensitivity," *Opt. Laser Eng.*, vol. 75, pp. 5–9, 2015.
[21] B. Chon *et al.*, "Unique temperature dependence and blinking behavior of CdTe/CdSe (Core/Shell) Type-II quantum dots," *J. Phys. Chem. C*, vol. 115, no. 2, pp. 436–442, 2011.
[22] P. T. Jing *et al.*, "Temperature-dependent photoluminescence of CdSe-core CdS/CdZnS/ZnS-multishell quantum dots," *J. Phys. Chem. C*, vol. 113, no. 31, pp. 13545–13550, 2009.