

# Quantum dots as self-referenced optical fibre temperature probes for luminescent chemical sensors

P A S Jorge<sup>1,2,3</sup>, M Mayeh<sup>1</sup>, R Benrashid<sup>1</sup>, P Caldas<sup>2,4</sup>,  
J L Santos<sup>2,3</sup> and F Farahi<sup>1</sup>

<sup>1</sup> Department of Physics and Optical Science, University of North Carolina at Charlotte, Charlotte, NC 28223, USA

<sup>2</sup> Unidade de Optoelectrónica e Sistemas Electrónicos, INESC Porto, Rua do Campo Alegre, 687, 4169 007 Porto, Portugal

<sup>3</sup> Departamento de Física da Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 687, 4169 007 Porto, Portugal

<sup>4</sup> Escola Superior de Tecnologia e Gestão—Instituto Politécnico de Viana do Castelo, Av. do Atlântico, Apartado 574, 4901-908 Viana do Castelo, Portugal

E-mail: [pjorge@inescporto.pt](mailto:pjorge@inescporto.pt)

Received 18 July 2005, in final form 26 September 2005

Published 7 April 2006

Online at [stacks.iop.org/MST/17/1032](http://stacks.iop.org/MST/17/1032)

## Abstract

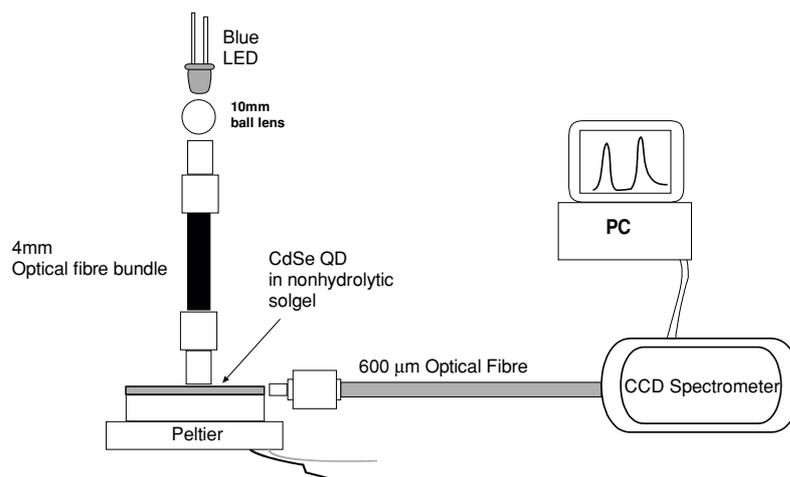
The use of semiconductor nano-particles as temperature probes in luminescence chemical sensing applications is addressed. Temperature changes the intensity, the peak wavelength and the spectral width of the quantum dots luminescent emission in a linear and reversible way. Results are presented that show the feasibility of implementing a self-referenced intensity-based sensor to perform temperature measurements independent of the optical power level in the sensing system. A resolution of 0.3 °C was achieved. In addition, it is demonstrated that self-referenced temperature measurements at multiple points could be performed using reflection or transmission based optical fibre configurations.

**Keywords:** quantum dots, luminescence, optical chemical sensors, temperature

## 1. Introduction

The use of optical techniques to monitor biochemical parameters is an expanding area of research of increasing importance, particularly in environmental and biomedical applications [1, 2]. Luminescence based sensors are specially sensitive and selective [3]. Remote detection and miniaturization can be achieved when luminescent techniques are combined with integrated optics and optical fibre technologies [4]. As a result of a strong research effort in recent years, some examples of optical fibre analytical instruments for the determination of biochemical parameters by luminescent methods are already commercially available (e.g. oxygen and pH). However, in spite of great advances, these sensors suffer from some limitations. Leaching and

photo-bleaching of the sensing dyes usually are important problems [5, 6]. In addition, in the majority of luminescence based sensors, both the luminescence intensity and the excited state lifetime of the sensing dyes are strongly temperature dependent. To minimize the dependence on the optical power level, frequency domain fluorometry is often used [7]. With this technique a phase shift can be measured that depends on the excited state lifetime. It is proportional to the analyte concentration and is independent of the optical power level. However, the phase response is also strongly temperature dependent. In this way, the correct determination of the analyte is only achieved if a temperature measurement is performed in parallel. Some schemes for the simultaneous determination of temperature and a chemical parameter have already been proposed. For example, it has been proposed to use an



**Figure 1.** Experimental set-up used to characterize the temperature behaviour of the luminescent emission of the quantum dots.

alexandrite crystal in combination with platinum complex to detect, with the same fibre probe, oxygen and temperature [8, 9]. However, commercial sensors still rely on conventional technologies for temperature measurement.

The recent developments in nano-materials have provided new possibilities in the area of chemical and biological sensors [10, 11]. Luminescent semiconductor nanocrystals, or quantum dots (QDs), are especially attractive in this area. QDs are nanometre scale particles of semiconductor material [12–14]. Because of their small size they are subject to the quantum confinement effect, meaning that the electronic energy distribution of these particles will be determined by their physical size. This gives them unique optical properties that are highly favourable when compared to traditional fluorophores, and can be used with great advantage in a large number of bioassays and chemical sensing techniques [15–17]. When compared with traditional luminescent dyes, QDs have a narrow emission spectrum, and they are bright and can be excited by any wavelength lower than their emission peaks. They provide outstanding photostability and the ability to tune their optical properties by simply changing the nanocrystal size or the semiconductor material. At present, they are available in a variety of emission wavelengths (from 350 to 2000 nm), and can be provided in the form of colloidal suspensions suitable to be immobilized in polymers or sol–gel-based materials. This combination of properties gives QDs great potential for multiplexing applications [18].

The behaviour of the luminescent properties of QDs with temperature has recently been reported to have suitable characteristics for application as temperature probes [19–22]. In this paper, we propose to use QDs to develop self-referenced intensity-based sensors and to perform temperature measurements independent of the system optical power level. In addition, the possibility of multiplexing fibre optic temperature sensors using QDs is addressed in both reflection and transmission configurations. The results obtained have great potential for applications where the simultaneous determination of temperature and a chemical parameter is needed.

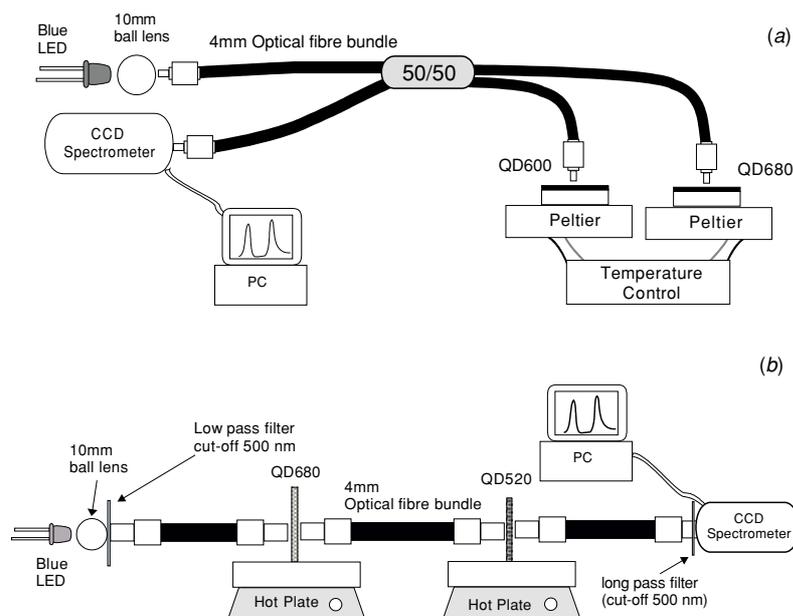
## 2. Experimental details

### 2.1. Preparation of samples

To implement the temperature sensors using QDs, different nanocrystals were acquired from *Nanoco* and *Evident Technologies*. Several samples of cadmium selenide and cadmium tellurium core-shell QDs, emitting from 520 nm to 680 nm, were available. Core-shell QDs were chosen because they have a semiconductor material core, e.g. CdSe or CdTe, coated with a passivating layer of ZnS, which ensures higher stability of their luminescent properties. The nanocrystals were used to dope different solutions of a non-hydrolytic sol-gel with a concentration of 5 mg ml<sup>-1</sup>. After stirring for 6–8 h, to obtain a homogeneous mixture, the solutions were filtered through a 0.1 µm filter. Thin films and bulk samples with different characteristics were made by spin coating (1500 rpm) or moulding in silicone. All the samples were subjected to temperature treatments under a nitrogen flux. The exact baking times and temperatures (ranging from 100 °C to 200 °C) depended on the sample thickness. After the thermal treatment, a dense glass material was formed that protected the nanoparticles from oxidation and contact with other impurities.

### 2.2. Self-referenced intensity-based temperature measurement

The characterization of the behaviour of the luminescent emission of the different samples was performed using the experimental set-up in figure 1. The samples were placed in thermal contact with a Peltier device that controlled their temperature. Due to their broad absorption spectra all the nanocrystals could be excited using a blue LED (470 nm from Nichia). Optical fibre bundles with 4 mm diameter were used to lead the excitation radiation to the QDs. A 600 µm multimode fibre cable, oriented at 90° relative to the excitation fibre, was used to collect the luminescence signals. The spectral response of the QDs to temperature was recorded using a dual channel CCD spectrometer and a PC with adequate software. The spectrometer was an Ocean Optics S2000, with channel 1 ranging from 282 nm to 607 nm,



**Figure 2.** Experimental set-ups for simultaneous interrogation of two QD samples: (a) parallel topology, (b) series topology.

with no filter, and channel 2 ranging from 575 nm to 835 nm, with a built-in long pass filter with cut-off wavelength at 550 nm.

After completing the characterization of several samples, the possibility of performing temperature measurements independent of the optical power level in the system was tested. Since shift in the central wavelength of the luminescent emission from QDs depends on temperature we developed a simple detection scheme in order to obtain self-referenced temperature measurements. Two signals,  $S_1$  and  $S_2$ , corresponding to two narrow spectral windows on opposite sides of the emission spectrum of the QD were normalized according to  $(S_1 - S_2)/(S_1 + S_2)$ , and it was realized that the resulting normalized output is proportional to temperature and is independent of the optical power level in the system.

### 2.3. Multiplexing configurations

In order to demonstrate the possibility of simultaneous interrogation of several QDs with the same fibre system, two different topologies were implemented: a parallel configuration for simultaneous interrogation of two QDs where the system worked in reflection, and a series configuration for interrogation of two different samples where the system worked in transmission. The corresponding experimental set-ups can be seen in figures 2(a) and (b), respectively. The same excitation source and detection instrumentation that were used in the set-up of figure 1 were also used in both multiplexing configurations. Optical fibre bundles with 4 mm diameter were used for both excitation and detection.

In the transmission setup the QD with higher emission wavelength was placed first in the series. If the sensor with the QDs of lower emission was placed first, its emission signal would have been absorbed by the QDs of the second sensor. In this particular topology the level of excitation optical power reaching the CCD is much higher than in a reflection configuration. In this way, additional optical

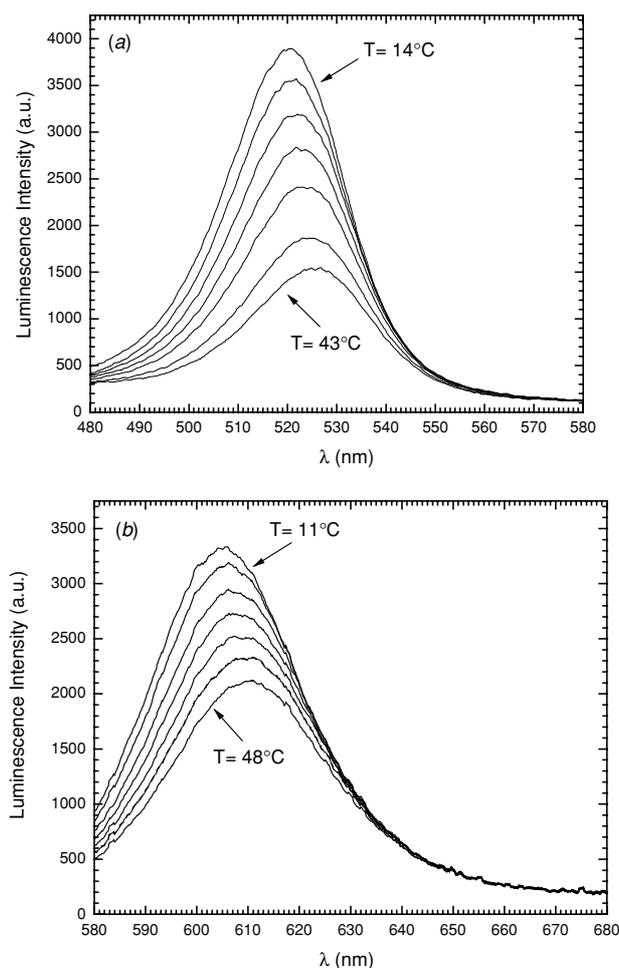
filtering was necessary to achieve increased noise rejection. A short pass filter (cut-off wavelength at 500 nm) was placed at the fibre input and a long pass filter (cut-off wavelength at 500 nm) was placed at the fibre output. In addition, in this configuration hot plates were used to control the QDs temperature. In both configurations the temperature of each sensor was independently varied and simultaneous interrogation of two sensors was evaluated.

## 3. Results and discussion

### 3.1. Self-referenced intensity-based temperature measurement

All sensors were made from sol-gel doped with QDs and the results of many tests showed that they have similar behaviour. All samples were strongly luminescent when excited by the blue radiation, presenting a nearly symmetrical emission spectrum with FWHM of approximately 30 nm. This is in agreement with the 5% variation in the QDs size distribution stated by the manufacturer and demonstrates that the nanocrystals luminescent properties were maintained upon the sol-gel immobilization procedures.

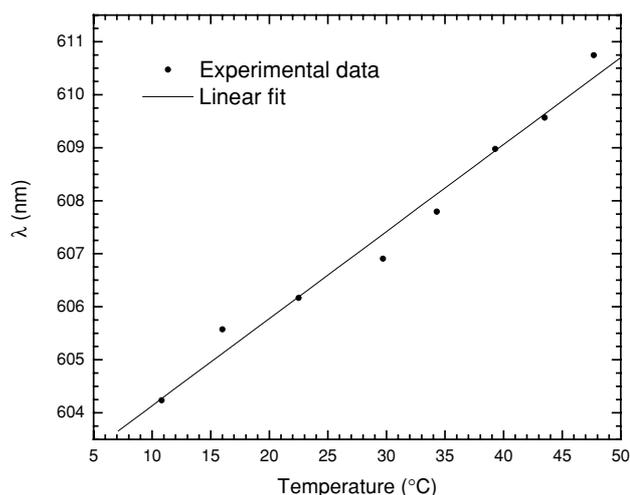
As the temperature of the sensing samples was increased, the luminescence intensity decreased, the peak wavelength shifted towards the red and the spectral width increased. These changes were linear and reversible with temperature. In figure 3(a), the spectral response of a 1 cm<sup>2</sup> ( $\approx 1$  mm thick) bulk glass doped with CdSe-ZnS QDs with emission peak at 520 nm (QD<sub>520</sub>) is presented. The temperature of the sample was increased from 14 °C to 43 °C. From these data it can be estimated that the luminescence intensity was decreased, as temperature increased, with a rate of  $-1.6\% \text{ }^\circ\text{C}^{-1}$ . In figure 3(b), similar behaviour was obtained with a thin film ( $\approx 5 \mu\text{m}$ ) doped with a CdSe-ZnS QD with emission peak at 600 nm (QD<sub>600</sub>). For this sample an intensity decrease of approximately  $-0.7\% \text{ }^\circ\text{C}^{-1}$  was estimated as temperature increased. Rates between  $-0.7\% \text{ }^\circ\text{C}^{-1}$  and  $-1.6\% \text{ }^\circ\text{C}^{-1}$  were



**Figure 3.** Behaviour of the luminescent emission of QDs with temperature: (a) response of a QD<sub>520</sub> bulk sample, (b) response of a QD<sub>600</sub> thin film.

found in other samples. It can also be observed, in both samples, that the peak wavelength,  $\lambda_{\text{peak}}$ , increased in a linear fashion as temperature was increased. This can be seen in more detail in figure 4, where the peak wavelength of the luminescent emission of a sample doped with QD<sub>600</sub> is plotted as a function of temperature. Although linear behaviour is apparent, relatively high data dispersion can be observed. This happened because the emission peak was relatively broad and the determination of  $\lambda_{\text{peak}}$  was not straightforward. Comparing the behaviour of this parameter in different samples it was concluded that the rate of change of  $\lambda_{\text{peak}}$ , towards longer wavelengths, as the temperature increased was, in all cases, approximately  $0.2 \text{ nm } ^\circ\text{C}^{-1}$ . This may indicate that the differences in sensitivity shown in the intensity response could be due to different immobilization environments, distinct film thickness, etc. On the other hand, considering the similar wavelength shift response, it is reasonable to conclude that the intrinsic response to temperature of all samples was identical.

Either the luminescence intensity variation or the shift in  $\lambda_{\text{peak}}$  can be used to obtain temperature information. However, simple intensity measurements are prone to error due to optical power source fluctuations, changing under the coupling conditions, etc. In order to evaluate the system susceptibility

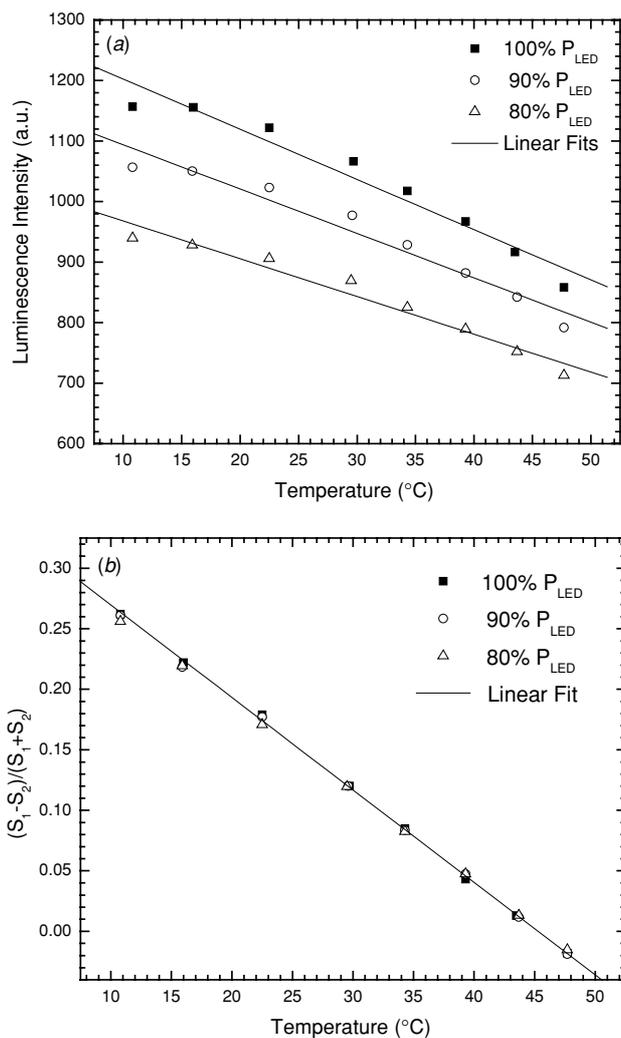


**Figure 4.** Position of  $\lambda_{\text{peak}}$  as a function of temperature, for a QD<sub>600</sub> thin film.

to optical power changes the luminescent intensity response of QD<sub>600</sub> to temperature was recorded for three different levels of LED output power (100%, 90% and 80%). In figure 5(a), it is clearly shown that the luminescence intensity response depends strongly on the LED output. In addition, in each individual curve, a nonlinearity can be observed at lower temperatures, which was due to condensation of water on the surface of the sample that consequently changed the coupling conditions.

A simple detection scheme can be implemented in order to take self-referenced temperature measurements. If two signals,  $S_1$  and  $S_2$ , corresponding to two narrow spectral windows on opposite sides of the spectrum, are normalized according to  $(S_1 - S_2)/(S_1 + S_2)$ , the resulting output will be proportional to temperature and independent of the optical power level in the system. This procedure was implemented using a QD<sub>600</sub> thin film. With software controlling the CCD spectrometer it was possible to obtain signals  $S_1$  and  $S_2$  corresponding to the spectral windows 595–600 nm and 620–625 nm, respectively. The normalization scheme was applied to the curves in figure 5(a). The resulting plots, given in figure 5(b), show that the normalized output has a linear dependence with temperature and is independent of the changes in the system optical power level (data dispersion was within the noise level). An accuracy of approximately  $0.3 \text{ } ^\circ\text{C}$  was obtained. This demonstrates that, with this detection scheme, QDs can be used as self-referenced temperature probes suitable for chemical sensing applications. QDs can be used in combination with a sensing dye, allowing us to simultaneously obtain information about a chemical parameter and the temperature information. Due to the ability to tune their optical properties, a QD with no spectral overlap with a particular sensing dye can easily be chosen.

The samples were tested in a temperature range near ambient conditions (approximately  $10 \text{ } ^\circ\text{C}$  to  $50 \text{ } ^\circ\text{C}$ ), which is fine for most chemical and biosensing applications. However, applications in more extreme situations are also possible. It has been reported in the literature that the temperature response of Cd–Se QDs is reversible in a temperature range from 100 K to 315 K (although it is not linear in the full range). Also, the

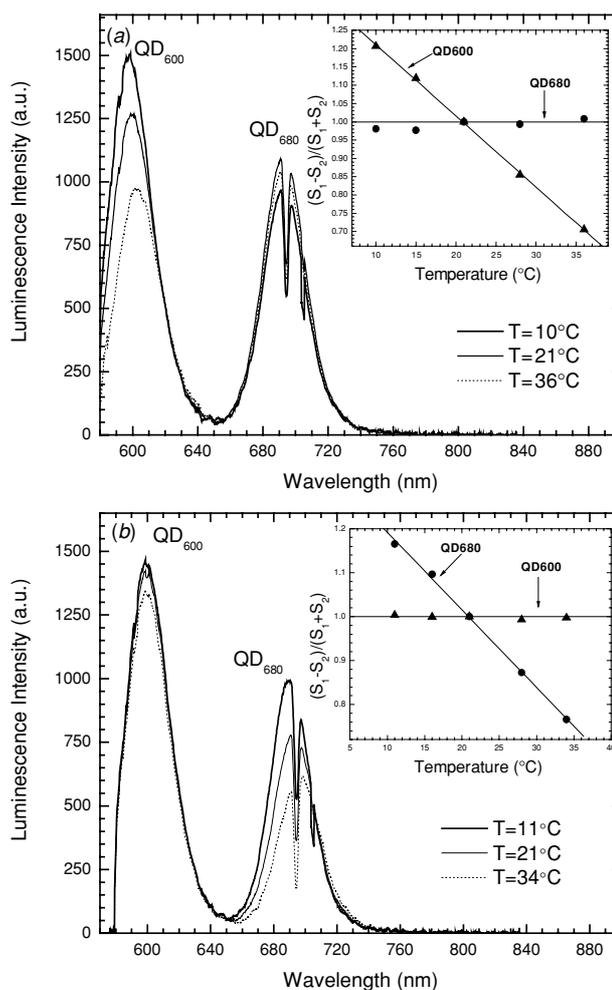


**Figure 5.** (a) Luminescent intensity of QD<sub>600</sub> as a function of temperature for three levels of LED optical power (100%, 90% and 80%); (b) normalized output for the same three levels of LED optical power.

sol-gel samples were cured at 200 °C without damaging the QDs, indicating that, as long as the emission is not completely quenched, temperature measurements could be made in this range.

Blinking of the luminescence of single quantum dots has been reported [23]. However, when using bulk samples doped with nanocrystals, the average luminescent output observed is stable. Throughout all the tests performed, outstanding photostability was observed in the majority of the samples. This was further tested by irradiating a 1 mm thick bulk sample of QD<sub>520</sub> with a blue LED. The sample was irradiated for 16 h with approximately 20 mW cm<sup>-2</sup>, showing no sign of photodegradation. However, for this to be achieved core shell QDs must be used. In addition, the curing of the sol-gel material must be performed under nitrogen to prevent oxidation.

All the tests were performed using low excitation power densities varying from 2 to 40 mW cm<sup>-2</sup>. In this range the luminescence intensity depends linearly on the excitation optical power. Linear behaviour is expected for power

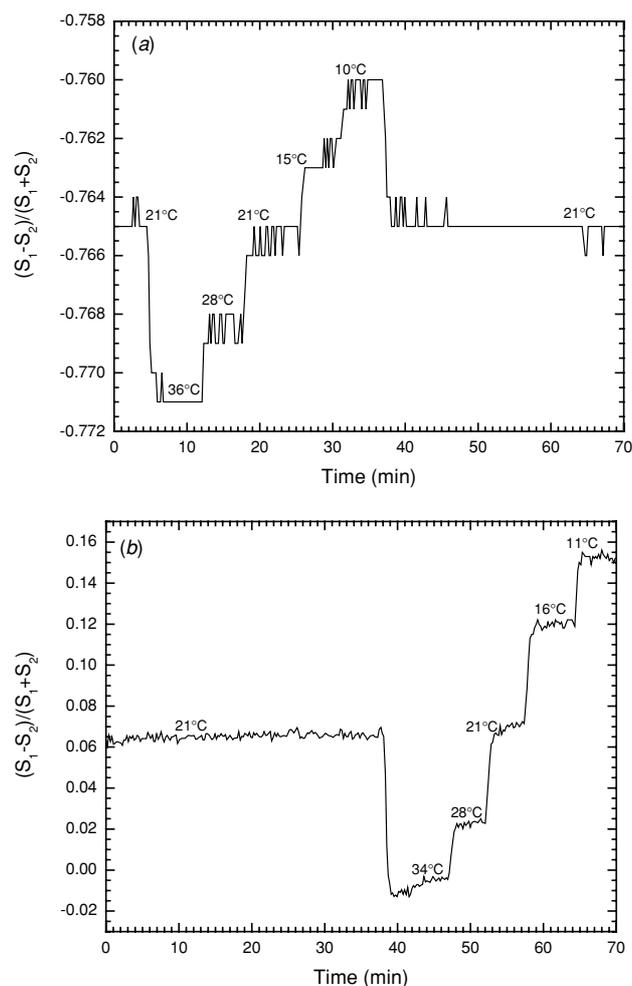


**Figure 6.** Spectral response of two QD samples, in a reflection configuration, to temperature variations (inset: normalized outputs): (a) QD<sub>600</sub> temperature was changed and QD<sub>680</sub> temperature was kept constant; (b) QD<sub>680</sub> temperature was changed and QD<sub>600</sub> temperature was kept constant.

densities up to about 400 W cm<sup>-2</sup>, while saturation behaviour could be observed at higher powers (above 100 kW cm<sup>-2</sup>) [24]. In the presented system, where large diameter optical fibre bundles are used, these limits would correspond to very high optical power levels not likely to be reached in a practical situation. However, when using standard single mode optical fibres in combination with laser sources, very high energy densities can be attained. Because this can compromise the proposed reference scheme, it should be taken into consideration when designing a practical system.

### 3.2. Multiplexing configurations

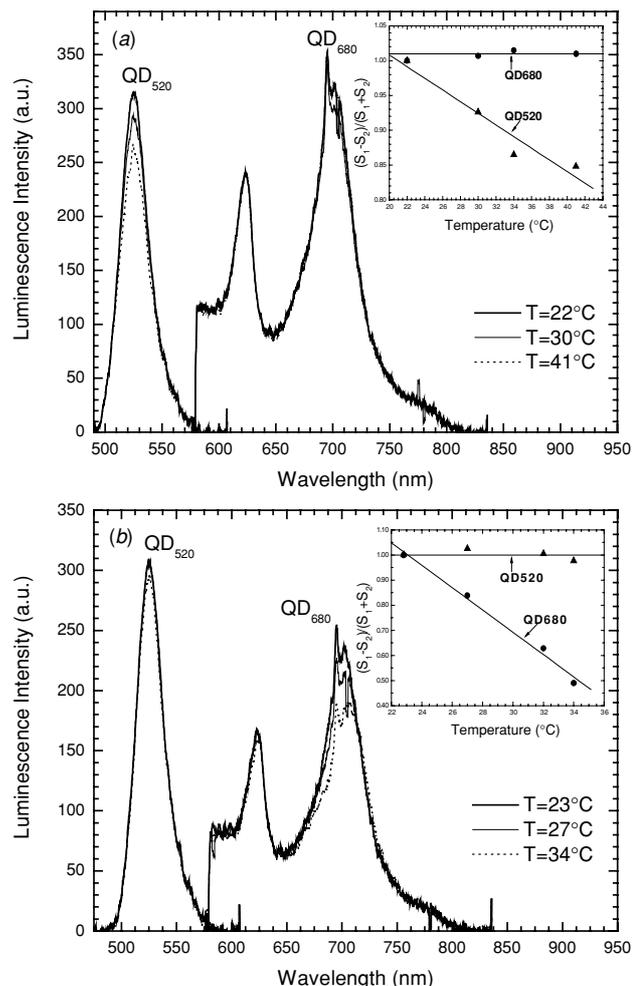
The possibility of self-referenced intensity-based multiplexed temperature measurements with QDs was tested in a reflection configuration using the set-up of figure 2(a) to interrogate two samples: a thin film of QD<sub>600</sub> and a thick film doped with CdTe-ZnS QDs with emission peak at 680 nm (QD<sub>680</sub>). The temperature of each sample was changed independently. The spectral response of both samples (after subtracting the dark spectrum) can be seen for two different cases. In figure 6(a),



**Figure 7.** Simultaneous temporal responses of both samples subjected to independent temperature changes: (a) QD<sub>680</sub>, (b) QD<sub>600</sub>.

the temperature of QD<sub>600</sub> was changed from 10 °C to 36 °C, and the temperature of QD<sub>680</sub> was kept constant (at 21 °C). In figure 6(b), the temperature of QD<sub>680</sub> was changed from 11 °C to 34 °C, and the temperature of QD<sub>600</sub> was kept constant (at 21 °C). The corresponding normalized outputs are inserted in the respective figures.

Clearly the intensity and the peak wavelength of the QDs luminescent emission change with the variation in temperature. However, due to a low signal-to-noise ratio, intensity fluctuations are noticeable in the QDs with constant temperature. This error is mostly corrected for by normalizing the signal as discussed earlier (see insets in figure 6) and, as a result, an output signal proportional to the wavelength shift could be obtained. To assess the validity of this statement the normalized responses of both QDs were recorded in real time as their temperatures were changed alternately. Figures 7(a) and (b) show the responses of QD<sub>680</sub> and QD<sub>600</sub>, respectively. The normalized signals clearly follow the temperature variations and do not suffer from the effect of intensity fluctuations. Furthermore, it can be observed that the change in the temperature of one of the samples had no effect on the other sample output. This clearly demonstrates the possibility of implementing self-referenced wavelength



**Figure 8.** Spectral response of two QD samples, in a transmission configuration, to temperature changes (inset: normalized outputs): (a) QD<sub>520</sub> temperature was changed and QD<sub>680</sub> was kept constant. (b) QD<sub>680</sub> temperature was changed and QD<sub>520</sub> was kept constant.

multiplexed temperature sensing systems using semiconductor nanocrystals.

The same principle was tested in a transmission configuration (figure 2(b)) using two thick films doped respectively with QD<sub>520</sub> and QD<sub>680</sub>. Because QDs absorb at any wavelength lower than their emission peak, in a transmission configuration the samples must be placed in an ordered sequence (higher wavelengths first), to avoid mutual absorption. In this way, in this particular test, QD<sub>680</sub> was placed first in series. The temperature of each sample was changed alternately, using hotplates, while their spectral response was recorded. The spectra of each sample can be observed in two different situations. In figure 8(a), the temperature of QD<sub>520</sub> was changed, while the temperature of QD<sub>680</sub> was kept constant (21 °C). In figure 8(b), the temperature of QD<sub>680</sub> was changed while the temperature of QD<sub>520</sub> was kept constant (21 °C). The normalized output responses are inserted in their respective figures.

This configuration is intrinsically more affected by noise from the excitation source. In spite of double optical filtering and subtraction of the dark spectrum a strong background signal was observed, particularly in the QD<sub>680</sub> output (the

grating in channel 2 from the CCD was optimized for the spectral range 575 nm to 835 nm). In addition, because the curing process of the sample doped with QD<sub>680</sub> was not complete, this sample was suffering from photobleaching, which caused a gradual decrease in its luminescent emission. This particular QD was obtained in the form of a suspension in a liquid solvent (toluene), while all the other samples were acquired as a solid powder. In this way, in spite of the solvent being evaporated prior to the sol-gel immobilization of QD<sub>680</sub>, it may have interfered with the curing process. Nevertheless, the normalized outputs clearly show temperature measurements that are mutually independent and insensitive to intensity changes.

Some design considerations are being investigated to improve the performance of this series configuration, in particular the implementation of evanescent excitation/detection geometries that could allow for increased numbers of sensing points.

#### 4. Conclusion

A new fibre optic intensity based temperature sensor using quantum dot nanoparticles was presented. It was shown that temperature measurements are independent of optical power fluctuations. The feasibility of wavelength multiplexing of multiple point sensors in reflection and transmission configurations was investigated. These results establish that quantum dot based sensors are excellent self-referenced temperature probes for a wide range of applications. In particular, biochemical sensing applications can greatly benefit from such luminescent temperature probes with great versatility both in their chemical and optical properties.

#### Acknowledgments

Pedro Jorge would like to acknowledge the financial support of FCT—Fundação para a Ciência e a Tecnologia and of FLAD—Fundação Luso Americana para o Desenvolvimento.

#### References

- [1] Holst G and Mizaikoff B 2002 Fiber optic sensors for environmental applications *Handbook of Optical Fibre Sensing Technology* (New York: Wiley) pp 729–55
- [2] Mehrvar M, Bis C, Scharer J M, Moo-Young M and Luong J H 2000 Fiber-optic biosensors—trends and advances *Anal. Sci.* **16** 677–92
- [3] Orellana G 2004 Luminescent optical sensors *Anal. Bioanal. Chem.* **379** 344–6
- [4] Wolfbeis O S 2002 Fiber optic chemical sensors and biosensors *Anal. Chem.* **72** 81R–89R
- [5] Hartmann P, Leiner M J P and Kohlbacher P 1998 Photobleaching of a ruthenium complex in polymers used for oxygen optodes and its inhibition by singlet oxygen quenchers *Sensors Actuators B* **51** 196–202
- [6] Malins C, Glever H G, Keyes T E, Vos J G, Dressick W J and MacCraith B D 2000 Sol-gel immobilised ruthenium II polypyridyl complexes as chemical transducers for optical pH sensing *Sensors Actuators B* **67** 89–95
- [7] McDonagh C, Kolle C, McEvoy A K, Dowling D L, Cafolla A A, Cullen S J and MacCraith B D 2001 Phase fluorometric dissolved oxygen sensor *Sensors Actuators B* **74** 124–30
- [8] Liao S-C, Xu Z, Izatt J A and Alcalá J R 1997 Real-time frequency domain temperature and oxygen sensor with a single optical fiber *IEEE Trans. Biomed. Eng.* **44** 1114–21
- [9] Klimant I, Kuhl M, Glud R N and Holst G 1997 Optical measurement of oxygen and temperature in microscale: strategies and biological applications *Sensors Actuators B* **38–39** 29–37
- [10] Penn S G, Hey L and Natanz M J 2003 Nanoparticles for bioanalysis *Curr. Opin. Chem. Biol.* **7** 609–15
- [11] Kurner J M, Klimant I, Krause C, Pringsheim E and Wolfbeis O S 2001 A new type of phosphorescent nanospheres for use in advanced time-resolved multiplexed bioassays *Anal. Biochem.* **297** 32–41
- [12] Gaponenko S V 1998 *Optical Properties of Semiconductor Nanocrystals (Cambridge Studies in Modern Optics vol 23)* ed P L Knight and A Miller (Cambridge: Cambridge University Press)
- [13] Klimov V I 2003 Nanocrystal quantum dots *Los Alamos Science* **28** 214–20
- [14] Trindade T, O'Brien P and Pickett N L 2001 Nanocrystalline semiconductors: synthesis, properties, and perspectives *Chem. Mater.* **13** 3843–58
- [15] Murphy C J 2002 Optical sensing with quantum dots *Anal. Chem.* **74** 520A–526A
- [16] Riegler J and Nann T 2004 Application of luminescent nanocrystals as labels for biological molecules *Anal. Bioanal. Chem.* **379** 913–9
- [17] Jaiswal J K and Simon S M 2004 Potentials and pitfalls of fluorescent quantum dots for biological imaging *Trends Cell Biol.* **14** 497–504
- [18] Clapp A R, Medintz I L, Mauro J M, Fisher B R, Bawendi M G and Mattoussi H 2004 Fluorescence resonance energy transfer between quantum dot donors and dye-labeled protein acceptors *J. Am. Chem. Soc.* **126** 301–10
- [19] Wu Y, Arai K and Yao T 1996 Temperature dependence of the photoluminescence of ZnSe/ZnS quantum-dot structures *Phys. Rev. B* **53** R10485–8
- [20] Walker G W, Sundar V C, Rudzinski C M, Wun A W, Bawendi M G and Nocera D G 2003 Quantum-dot optical temperature probes *Appl. Phys. Lett.* **83** 3555–7
- [21] Labeau O, Tamarat P and Lounis B 2003 Temperature dependence of the luminescence lifetime of single CdSe/ZnS quantum dots *Phys. Rev. Lett.* **90** 257404
- [22] Biju V, Makita Y, Sonoda A, Yokoyama H, Baba Y and Ishikawa M 2005 Temperature-sensitive photoluminescence of CdSe quantum dot clusters *J. Phys. Chem. B* **109** 13899–905
- [23] van Sark W G J H M, Frederix P L T M, Bol A A, Gerritsen H C and Meijerink A 2002 Blueing, bleaching, and blinking of single CdSe/ZnS quantum dots *Chemphyschem.* **3** 871–9
- [24] Verma P, Irmer G and Monecke J 2000 Laser power dependence of the photoluminescence from CdS<sub>x</sub>Se<sub>1-x</sub> nanoparticles in glass *J. Phys.: Condens. Matter* **12** 1097–110