

# The use of nanotechnology in the development of a distributed fibre-optic temperature sensor for subsea applications

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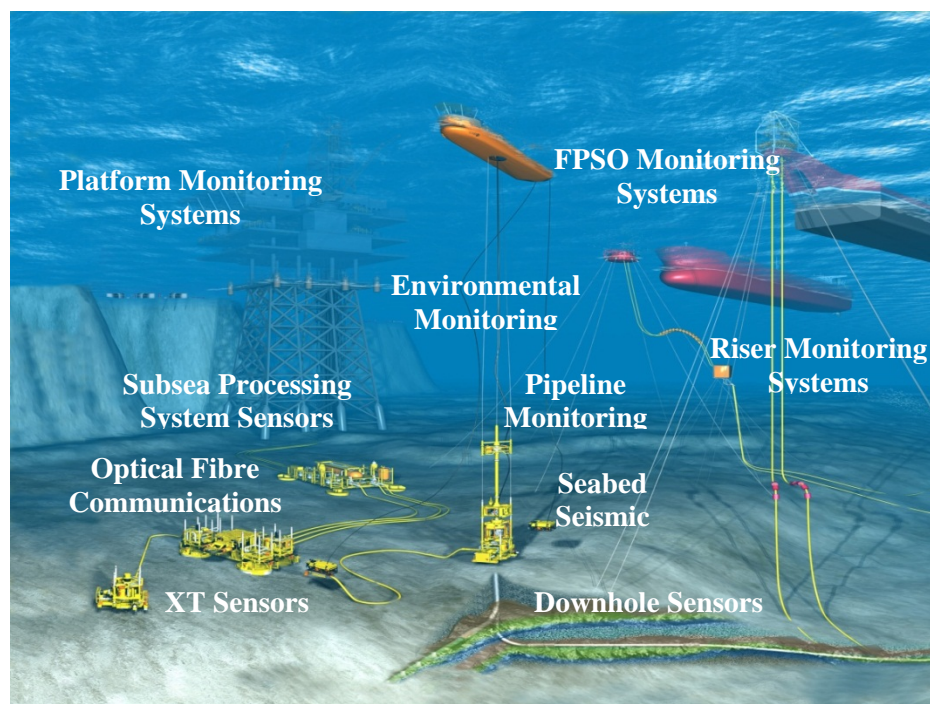
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**Abstract.** Monitoring temperature in subsea pipelines and processing plants is paramount to ensuring the efficient extraction of oil and gas. Preliminary results from studies of an alternative optical temperature sensing methodology based on the fluorescence spectroscopy of quantum dots (QDs) immobilised in a sol-gel thin film are presented. A discussion of the potential for this approach to oil and gas industry applications is given.

## 1. Introduction

The increasing global demand for oil and gas combined with the decrease in the availability of “easy oil” (e.g. large reserves located on-shore) have forced the industry to seek to exploit more remote and difficult to access resources. A key component of this activity is the exploitation of offshore oil and gas reserves. In parallel the industry is investing in new technologies for increased oil recovery (IOR), improved production efficiency along with reduced costs and risk. Increasingly the industry is seeking to reconfigure offshore production such that more of the process is carried out subsea. This possesses a range of challenges and is driving new technological developments within the industry. The future subsea production system is illustrated in figure 1. Typically such a subsea production facility will be a complex array of specialised equipment that may include trees, subsea processing systems, pipelines and risers. This increase in complexity of the subsea system will require a great increase in the degree of instrumentation on the subsea equipment to allow effective monitoring and control. Optical fibre sensing and communications are one of the technologies that the industry is looking at to provide components of the increased monitoring. Optical fibres have a number of advantages over existing electronic systems for subsea oil and gas applications, which include being more reliable in hostile environments, flexible, immune from electromagnetic interference and the variety of sensing formats. These include the ability of a single optical fibre to be made into a distributed sensor or to support a multitude of discrete sensors.





**Figure 1.** Subsea production system

Temperature measurement is a critical parameter for a range of oil and gas production processes as well as being an important tool in integrity monitoring. For example, knowledge of the temperature is of importance in oil and gas pipelines as the parameter can be used to monitor the formation of hydrates. Hydrates or more specifically gas (clathrate) hydrates are crystalline water based solids that resemble ice, which can have detrimental effects within an oil flow line, as the hydrates can restrict or completely block the flow. This occurs due to low temperatures in the subsea environment and high pressures [1]. There is thus considerable interest in new and improved temperature sensing schemes that will lend themselves to use in subsea oil and gas production systems.

In this paper we report results from preliminary studies into the potential of employing semiconductor Quantum Dot (QD) nanoparticles as the basis of a distributed array optical fibre temperature sensor scheme. Although still at a relatively early stage QD technology is an expanding area of interest, particularly in environmental and biomedical applications [2], with a number of the initial QD materials possessing properties that make them potentially suitable for temperature sensing applications. The QD materials are nanometer scale particles which follow the quantum confinement effect [3]. This means that the energy level of a QD is dependent on its size. Therefore, the smaller the QD the larger the band gap (the greater the difference in energy between the highest valence band and the lowest conduction band) resulting in more energy being required to excite a QD. This gives QDs unique optical properties which provide outstanding photostability, relatively high quantum yields (>50%) and with comparison to other luminescent dyes, have a narrow emission spectrum, are bright and can be detected through visible excitation.

Recently, it has been demonstrated that temperature has an effect on QDs luminescence, opening the field for thermometry applications. QDs have been shown to shift in wavelength with the increase of temperature, in studies ranging from room temperature to 100 °C and 200 °C respectively [4-5]. The highest reported temperature range using QDs was carried out by Pugh-Thomas et al [6] who carried out temperature studies of a QD encased in a sol-gel environment ranging from 22-252 °C resulting in a linear red wavelength shift and a linear decrease in luminescence intensity. A reversible wavelength shift is observed due to heat expanding the size of the QD, decreasing the band gap energy, hence less energy is required to excite the QD [6].

## 2. Experimental

### 2.1 General

The QD (CdSe/ZnS) nanopowders were supplied by Ocean NanoTech (USA). The Cadmium selenide (CdSe) core shell QDs is coated with a passivating layer of zinc sulphide (ZnS) to yield stable and highly emissive QDs. The quantum yield (>50%) of the QDs was determined by the manufacturer using the integrating sphere. All solvents were purchased from Sigma Aldrich UK (>99% purity) and were used as received. QD thin films were prepared on a glass substrate and the temperature response characterised using fluorescence spectroscopy.

### 2.2 Sensor preparation

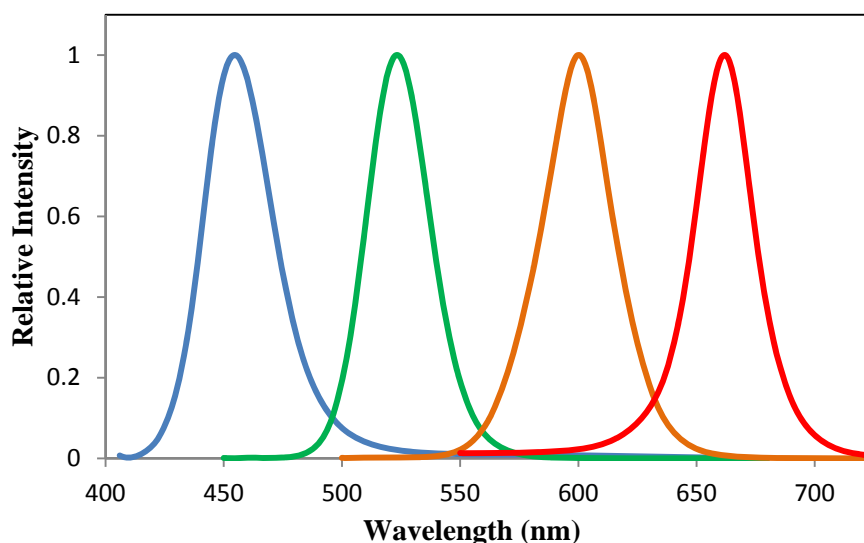
A sol solution was prepared by mixing 3ml of tetraethyl orthosilicate (TEOS) with 3ml of ethanol, in which 1ml of deionised water was added dropwise. 150 $\mu$ l of 0.01M HCl was added to catalyse the polymerisation of the slightly acidified sol-gel precursor, avoiding too strong an acidic solution to prevent degradation of the QD nanoparticles. The sol precursor was mixed uncovered for 45 minutes using a magnetic stirrer and flee. After, the vial was sealed with parafilm and placed in an oven at 60°C for 4 hours. 2mg of each QD powder was mixed with 500 $\mu$ l of the sol-gel precursor using an ultrasonic bath for 2 minutes. The QD/sol mixture was then mixed for 30 minutes before being placed onto clean glass substrate. The QD films were then left to dry for 48 hours and then placed within an oven at 100°C, producing QD glass films. All films were kept in the dark until used.

### 2.3 Sensor characterisation

Absorption spectrometry of the QDs in solvent was performed using a Perkin Elmer Lambda 2 dual beam UV-Vis spectrometer. Luminescence spectrometry was carried out using a FluoroMax-3 Spectrometer (HORIBA Jobin Yvon Ltd). In order to characterise the emission of the QDs with temperature, the sensors were placed into a thermally controlled oven with an entry port, capable of supporting a high temperature resistive bifurcated fibre-optic bundle that was connected to a holder within the spectrometer. Excitation of the QD films was performed using a 405nm laser diode with an operating output power of 30mW. A 455nm cut-on long pass wavelength filter (Schott GG455) was placed in front of the emission monochromator, to exclude excitation light.

## 3. Experimental results

General characterisation of the QDs was performed by dissolving 1mg of each QD powder in dichloromethane (DCM). Absorbance and emission spectra were obtained for all QD nanoparticles.



**Figure 2.** Luminescence emission spectra of the QD nanoparticles in DCM,  $\lambda_{\text{ex}} = 405$  nm

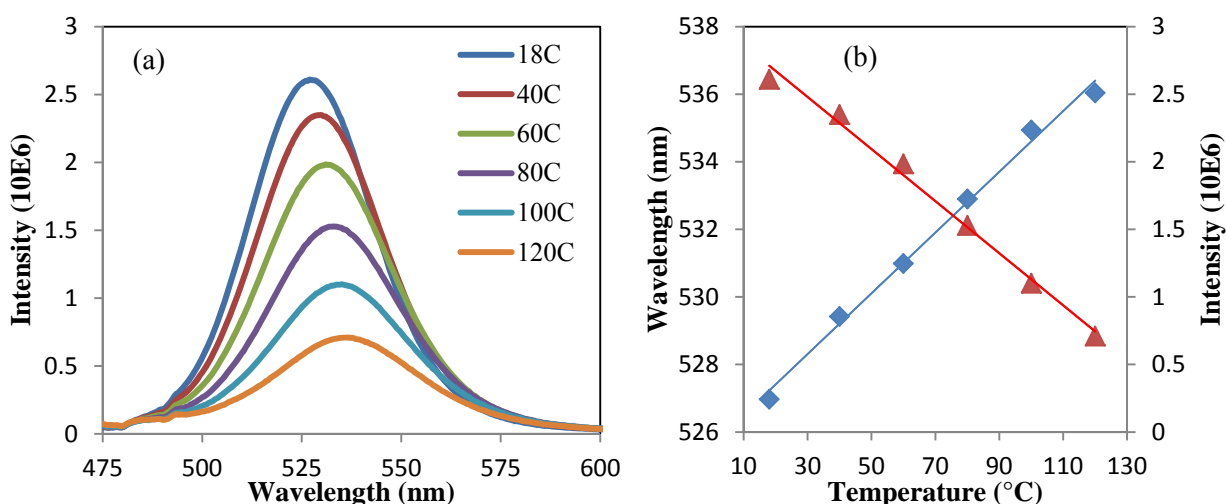
Figure 2 shows the luminescence spectrum of each of the QDs, highlighting that each signal can be easily distinguished from one another. Each QD has a specific absorption peak (table 1) overlaid on a broad absorption band allowing each QD to be excited using the same excitation wavelength (405nm). This is beneficial in the development of a distributed system, as the instrument development will be simplified by the use of one commercially available light source. Table 1 provides the corresponding data, with reference to the manufacturer's specifications.

**Table 1.** Specifications of the QD nanoparticle powders

QD powder (nm)	Manufacturer's Values		Measured Values	
	Absorbance (nm)	Emission (nm)	Absorbance (nm)	Emission (nm)
450	431	453	430	454
525	509	523	506	526
600	584	602	584	600
665	650	663	653	662

It is evident from table 1 that the optical properties meet the specifications outlined by the manufacturer, as the tolerance peak wavelength for each QD is  $\pm 5$  nm. All Full Width Half Maximum (FWHM) were less than 35 nm.

Once prepared, the QD sol-gel films were then exposed to temperature measurements in which the QD luminescence peak wavelength and intensity were recorded. QD luminescence spectra of the green (526 nm) QDs and experimental data are seen in figure 2. Each QD showed a linear red wavelength shift as temperature increased (table 2). The green (526 nm) and red (662 nm) QDs showed a similar wavelength shift whereas that observed for the orange (600 nm) QDs was half. The QD luminescence intensity decreased linearly with increasing temperature and the FWHM increased by  $\sim 5$  nm over the temperature range studied. The decrease in luminescence intensity can be attributed to temperature quenching of the luminescence, with the green QD showing the greatest decrease in peak luminescence intensity. Similar observations were reported by Biju et al [7] for QDs in solution.



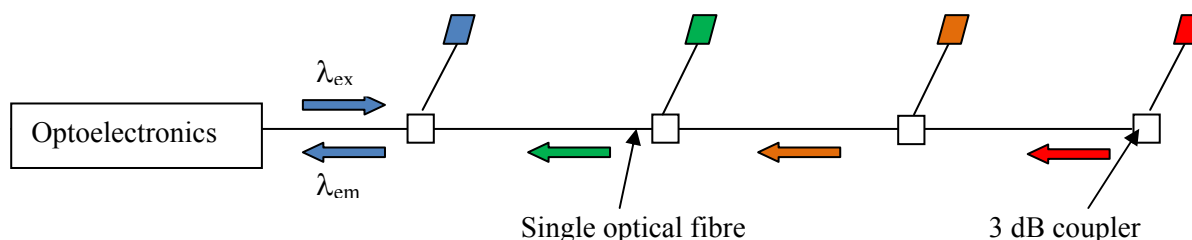
**Figure 1.** QD luminescence spectra of the 526 nm QDs with temperature (a) and corresponding temperature response (b) of luminescence wavelength ( $\diamond$ ) and luminescence intensity ( $\Delta$ ).  $\lambda_{\text{ex}} = 405$  nm

**Table 2.** Temperature response from each of the QD sol-gel films

QD (nm)	Wavelength shift (nm/°C)	Coefficient of variation ( $R^2$ )
525	$0.086 \pm 0.006$	0.996
600	$0.041 \pm 0.004$	0.987
665	$0.098 \pm 0.008$	0.994

The wavelength shift of the QDs observed with temperature introduces the possibility of implementing a distributed array sensor. One excitation source simplifies the build of such a system, in which, a large Stoke's Shift between excitation and luminescence signals, aids in the easy separation of the spectra.

Here the emission spectra of 3 QDs with temperature were measured. The manufacturer currently supplies 9 QD powders (450, 490, 525, 540, 575, 600, 630, 645 and 665 nm), therefore giving the possibility of 9 different QD sensing sites. Assuming that each QD shifts  $\sim 10$  nm over a  $100^\circ\text{C}$  range, then each QD emission spectrum can still be distinguished. This opens up the possibility of a multipoint temperature sensing system for use in subsea applications. Figure 3 shows a schematic representation of how this would be achieved. In this method the QD material would be located at the distal end of a spliced fibre. The excitation light ( $\lambda_{\text{ex}}$ ) would be transmitted down the fibre, in which the 3 dB coupler would split the excitation light and a small percentage would be directed to the QD sensing tip, the rest of the light would continue down the fibre until it gets to the next coupler, and so on. The emission signals ( $\lambda_{\text{em}}$ ) would be coupled back into the fibre and detected by a CCD spectrophotometer. The QD emission spectra can then be separated by their wavelength response.

**Figure 2.** Schematic diagram of a distal end fibre-optic distributed system

#### 4. Conclusions

The use of semiconductor QD nanoparticles in thermometry applications has been addressed. The technology described is beneficial for distributed temperature sensing and could prove useful in the oil and gas industry for subsea applications. Introducing a variety of luminescent QDs within the sensing system opens up the possibility of more temperature sensing points in, for example, an oil flow line. Preliminary results indicate a linear wavelength response from the QD films in going from room temperature to  $120^\circ\text{C}$ . This temperature range would limit the sensors use i.e. it could not be used in down-hole environments, as temperatures here exceed  $120^\circ\text{C}$ . Nevertheless, a luminescence based fibre-optic temperature sensor has been demonstrated with the use of semiconductor QD nanoparticles, which can be used in the application of a distributed sensing methodology.

**References**

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