Preparation of polydimethylsiloxane thin films containing immobilized CdSeTe/ZnS quantum dots for water sensing applications

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ABSTRACT

Pollutants in water systems are a significant environmental problem, as they can have harmful effects on both human health and the ecosystem. Here we developed a robust method for preparing CdSeTe/ZnS core/shell (C/S) quantum dots (QDs) immobilized into polydimethylsiloxane (PDMS) thin films for pollutant sensing applications. Highly fluorescent hydrophobic QDs were first synthesized using the hot-injection organometallic approach with the use of hydrophobic trioctylphosphine oxide and oleic acid ligands as capping agents. The C/S QDs had an average particle diameter of 4.0 nm and had broad absorbance in the ultraviolet-visible region. Their maximum fluorescence was at 594 nm and the photoluminescence quantum yield of the C/S QDs relative to rhodamine 6G was 47%. The C/S QDs were then immobilized into PDMS (to form QD@PDMS) by means of an optimized spin coating procedure onto glass slides at a speed of 500 rpm and acceleration of 300 rpm/s for 10 s, followed by curing at 80 °C for 15 min. This thin film format enabled direct use and analysis of the thin films by submersion into water samples followed by fluorescence spectroscopy. The homogeneity of the QD@PDMS thin films thus produced was excellent, as determined by visual inspection under an ultraviolet lamp and by fluorescence spectroscopy. An excitation wavelength of 400 nm led to the highest fluorescence intensity of the thin films and repeated exposure to this excitation wavelength did not have a major negative impact on the fluorescence emission of the QD@PDMS thin films, as the difference between the maximum and minimum fluorescence emission intensity was 8% over 60 repeated measurements. A mixture of water and ethanol (2:1) had the smallest effect on the fluorescence of the films and was thus the most effective matrix for sensing of organic pollutants. The interaction of the QD@PDMS films with individual organic pollutants (polar atrazine pesticide and non-polar phenanthrene) and with real water samples, resulted in a change in fluorescence of the thin films indicating that they are a promising candidate for sensing pollutants in water. The relative uptake and interaction of organic compounds by the thin films would need to be determined and their selectivity towards target analytes investigated for a particular application, in order to assess the viability of use of the QD@PDMS thin films to screen for the presence of the analytes and to semi-quantify them using fluorescence.

KEYWORDS

Quantum dot; fluorescence sensing; water pollution; polydimethylsiloxane; thin film

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INTRODUCTION

An extremely diverse range of toxic and potentially toxic pollutants have been released into the environment by anthropogenic activities.[1] The quantities and types of pollutants that have been detected in rivers, lakes, and drinking water treatment plants have notably increased[2,3], thus posing a threat to the aquatic ecosystem. Even at low concentrations, some of these pollutants may have biological activity in water, which could cause harm to the environment and human health through toxicity, carcinogenesis, and interference with organism functions.[4,5,6] Furthermore, when organic pollutants are present in water, they may produce toxic by-products when they undergo degradation or humification reactions.[1]

Monitoring of environmental pollutants is required to determine the potential threat that they may pose.[7] Water pollutants can be detected quantitatively with conventional analytical methods, like chromatography-mass spectrometry or inductively coupled plasma-mass spectrometry. For routine analysis, however, this entails very high instrumentation costs, and thus reliable, robust, portable, cheap, and easy-to-use sensors, which do not require extensive sample preparation need to be developed to detect the presence of pollutants in the environment. Spectrofluorimetric methods, where nanoparticles such as quantum dots (QDs) are used, have gained interest in analytical chemistry for being simple and sensitive sensor-based systems.[8,9] Novel fluorescence sensors have the potential to allow for portable, low-cost, qualitative screening for pollutants, before the samples giving a positive response are quantitatively analyzed with conventional methods.

Quantum dots are semiconductor crystalline nanomaterials with electronic and optical properties that are unique and attractive for analytical sensor applications.[10] They have good photostability, broad excitation spectra, high quantum yields, long fluorescence lifetimes, and bright photoluminescence.[11] The surface of QDs can be modified and tailored for desired functionalities to enhance the binding of analytes and decrease surface defects. However, QDs are extremely sensitive to processes like surface ligand removal or exchange which can either enhance or quench the fluorescence of the QDs.[12] Surface defects have a negative impact on the fluorescence quantum yield, and lead to luminescence decay and spectral shifts, with the appearance of undesirable band states.[13,14] When coordinated to selected ligands, exposure to surroundings could influence the properties of the QDs.[15] Ligand exchange on the surface of QDs may help with dispersion of the QDs in different media, including polymers, to form hybrid composite materials.

The development of fluorescence sensors that are capable of detecting water pollutants, particularly at low environmentally relevant concentrations, is challenging due to the inherent complexity of the fluorescence emission process. Fluorescence emission of QDs is dependent on many factors as fluorescence properties are variable and sensitive to surface molecules[16], local environments[17] and light illumination[18] owing to their high surface-to-volume ratio. Despite these challenges, QD-based sensors are worth exploring as

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alternative analytical methods due to their promising advantages over conventional methods.

Developing QD fluorescence sensors involves the optimization of several parameters to obtain maximal response and therefore optimal sensitivity. In the case of QDs immobilized in thin films, homogeneous dispersion of QDs within the polymer is needed to ensure optical transparency and long-term stability of the nanocomposites,[19] in addition to reproducible sensing results. Polydimethylsiloxane (PDMS) is a silicone elastomer with numerous properties which make it ideal for immobilizing QDs. It is chemically inert, thermally stable, flexible, permeable to gasses, easy to manipulate and handle, non-toxic and of low cost. It is also transparent and non-fluorescent which in turn improves the optical transparency of the nanocomposites, allowing for light to pass through the material without appreciable scattering.[19] The PDMS is also able to absorb organic nonpolar analytes, allowing for their extraction and pre-concentration from water samples.[20] A QD@PDMS sensor material will therefore have the combined advantages of QDs together with the inertness, flexibility and the ability to pre-concentrate pollutant analytes provided by the PDMS, which is often applied in its pristine form as a sorbent for environmental sampling of polycyclic aromatic hydrocarbons (PAHs) due to these attractive properties.[21,22,23]

The development of fluorescence QD sensors which can be used in solution to detect PAHs has previously been achieved by our group.[24,25,26] Here we develop a method to immobilize hydrophobic QDs into non-polar PDMS by a reproducible spin coating method to provide a functional material for use as a sensor to detect pollutants in water for screening purposes. QD nanoparticles were immobilized into a PDMS polymer matrix on a glass support to provide a robust portable sensor system, enabling *in-situ* measurements of water directly in the field, whilst the PDMS may also reduce the possibility of leaching of the cadmium-based QDs in use.

MATERIALS AND METHODS

Chemicals

Trioctylphosphine oxide (TOPO), 1-octadecene (ODE), oleic acid (OA), cadmium oxide, tellurium, zinc oxide, sulfur powder, rhodamine 6G, and phenanthrene were purchased from Sigma Aldrich (St. Louis, USA). Methanol, chloroform, acetone, ethylenediaminetetraacetic acid (EDTA) and selenium powder were purchased from Merck (Darmstadt, Germany). Isopropanol was purchased from VWR Chemicals (Darmstadt, Germany). An ultrapure Milli-Q Water System (Millipore, Bedford, USA) was used as a water source (18.0 MΩ·cm at 25 °C). A Sylgard 184 silicone elastomer kit was purchased from Dow Corning (Michigan, USA), which included a silicone elastomer base and curing agent. All chemical reagents were used as received from the suppliers without any pre-treatment.

Synthesis of CdSeTe/ZnS QDs

CdSeTe/ZnS QDs were synthesized by following a method previously developed in our research group, as shown schematically in Figure 1 and reported in Nsibande and Forbes.[27] CdO was used to which different precursors were added and reacted in a stepwise process at controlled high temperatures. Each precursor was separately prepared by dissolution in the organic solvents TOPO and ODE, whilst stirring vigorously at a temperature of 40 °C for 4 hours using a hot plate and a magnetic stirrer to ensure homogeneity. The TOPO and ODE served both as reaction solvents and surfactants to stabilize the QD nanocrystals after nucleation. To form the precursors, TOPO was added to ODE first and heated at 80 °C, until it dissolved, and then Te and Se were added to form the precursors. The tellurium precursor (TOP-Te) was prepared by adding 0.16 g Te to 0.68 g TOPO in 8.3 mL ODE and the selenium precursor (TOP-Se) was prepared by adding 0.30 g Se to 1.95 g TOPO in 25 mL ODE. The ZnO and S precursors were prepared separately by adding 0.14 g ZnO and 0.07 g S to both 6.6 mL OA and 10 mL ODE.

To 1.30 g CdO powder, 50 mL ODE and 30 mL OA were added giving a dark brown mixture which was stirred vigorously at a temperature of ~260-290 °C until the solution turned clear. Thereafter, 5 mL of the TOP-Te precursor was added to the TOP-Se precursor solution while continuously purging it with argon. Then, 25 mL of this TOP-Se-Te precursor mixed solution was added to the clear CdO solution which immediately turned orange indicating the initiation of the formation of the CdSeTe core through nucleation.

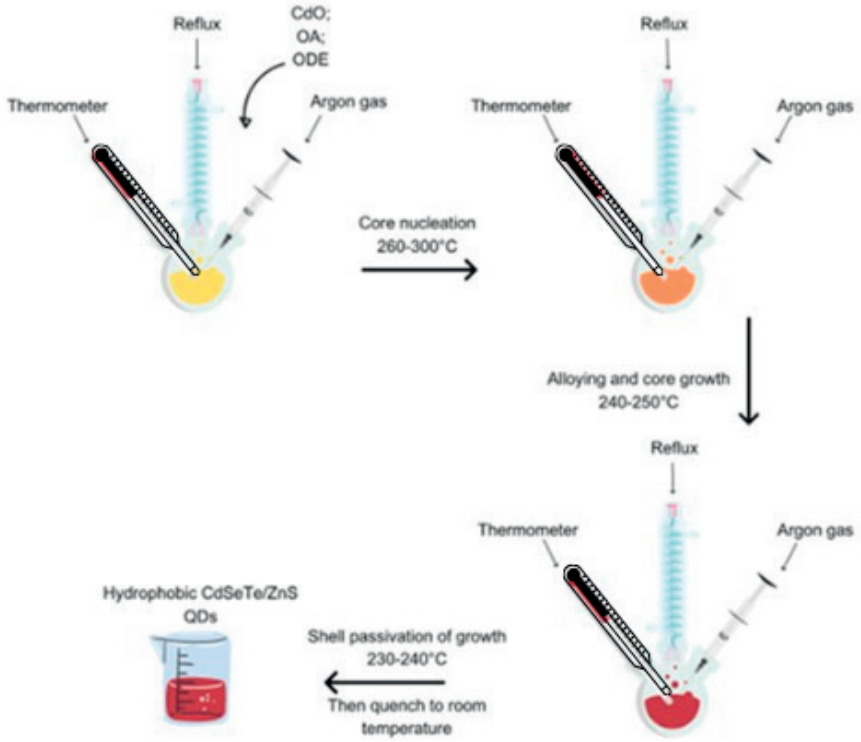

Figure 1: Schematic of the stepwise hot injection of organometallic precursors to synthesize CdSeTe/ZnS QDs (adapted from Nsibande and Forbes[27]).

During synthesis, the fluorescence of the core QDs and core/shell (C/S) QDs were measured to indicate the growth thereof as indicated by changes in the measured emission wavelength. The core QDs were allowed to grow and the fluorescence thereof (dispersed in chloroform) was measured after 20, 40 and 60 s and at 3, 5 and 10 min of growth. After 10 min, about 20 mL of the core QD solution was set aside and cooled to room temperature to quench the growth of the QDs.

Then 15 mL of both the ZnO and S precursors were combined, purged with argon and poured into the remaining core QD solution. The temperature was reduced to ~240 °C to allow for the formation of a ZnS shell over the CdSeTe core. Fluorescence of the C/S QDs was measured at 5, 10, 20 and 40 min. When the growth slowed down and no significant additional red shifting of the fluorescence emission peak occurred, the reaction was stopped by cooling to room temperature.

To purify the obtained QDs, the core and C/S QDs were then transferred to centrifuge tubes wherein they were washed with acetone, chloroform and methanol to remove any unreacted precursors. Chloroform was added to disperse the QDs into solution. They were then sonicated and vortexed to ensure good mixing, and the rest of the centrifuge tube was filled with a mixture of acetone and methanol to form a 1:1:1 ratio. The QDs were centrifuged and washed at 6000 rpm for 5 min and the supernatant was separated from solid QDs. This process was repeated several times until the QDs had the appearance of dispersed particles in solution, which readily settled.

Characterization of synthesized QDs

Fluorescence spectra were measured using a Horiba Jobin Yvon FluoroMax-4 Spectrofluorometer (Horiba Scientific, New Jersey, USA). The fluorescence of QDs dissolved in chloroform was measured using an excitation wavelength of 470 nm, with a recorded emission wavelength range of 480-800 nm and slit widths of 5 nm.

Ultraviolet-visible (UV-Vis) spectra of dispersed QDs were recorded using a Cary Eclipse spectrophotometer (Varian, Victoria, Australia). Chloroform was used as a blank and all QDs were dispersed in this solvent. In order to measure photoluminescence quantum yield (PLQY), the absorbance of the QDs was adjusted by dilution to within the range of 0.02-0.05.[28] This prevents the inner filter effect and reabsorption of emitted fluorescence.

The relative PLQY of the C/S QDs was calculated using a standard sample (rhodamine 6G) which has a fixed and known fluorescence quantum yield value of $\Phi_{ST} = 0.95$[29], and was used to determine the unknown fluorescence quantum yield of the QDs (Φ_X) according to Equation 1. The PLQY determination was conducted in a chloroform solvent with a refractive index of $\eta_X = 1.44$. Additionally, the rhodamine 6G standard used for comparison was dissolved in ethanol with a refractive index of $\eta_{ST} = 1.36$. The calculation also considered the relative emission intensity gradients of both solvents.[30,31]

$$\phi_X = \phi_{ST}\left(\frac{Grad_X}{Grad_{ST}}\right)\left(\frac{\eta^2_X}{\eta^2_{ST}}\right) \quad (1)$$

High resolution transmission electron microscopy (HRTEM) analysis was employed to determine the size and morphology of the synthesized core and C/S QDs dispersed in chloroform (QD@chloroform) (JEOL JEM 2100F TEM, Tokyo, Japan) operated at 200 kV. ImageJ software was used to estimate the particle size distribution from the HRTEM micrographs.[32]

Manufacture of QD@PDMS thin films

The manufacture of thin films containing the synthesized CdSeTe/ZnS quantum dots immobilized in PDMS (QD@PDMS) was optimized by testing different parameters namely: spin speed (100, 300, 400, 500, 800 and 1000 rpm), acceleration (100, 200, 300, 400 and 500 rpm/s), spin time (10, 15 and 60 s), curing temperature (80, 100, 130, 150 and 170 °C) and curing time (4 and 6 min). The substrate type (silicon wafer versus a glass slide both with and without a sacrificial polyacrylic acid layer) and size were also optimized for easy handling and application of the sensor.

The films were prepared using the optimized method shown in Figure 2 by weighing QDs and dispersing them in chloroform to form a QD@chloroform solution with concentrations of 0.004 g/mL for low concentration quantum dot (LQD) and 0.008 g/mL for high

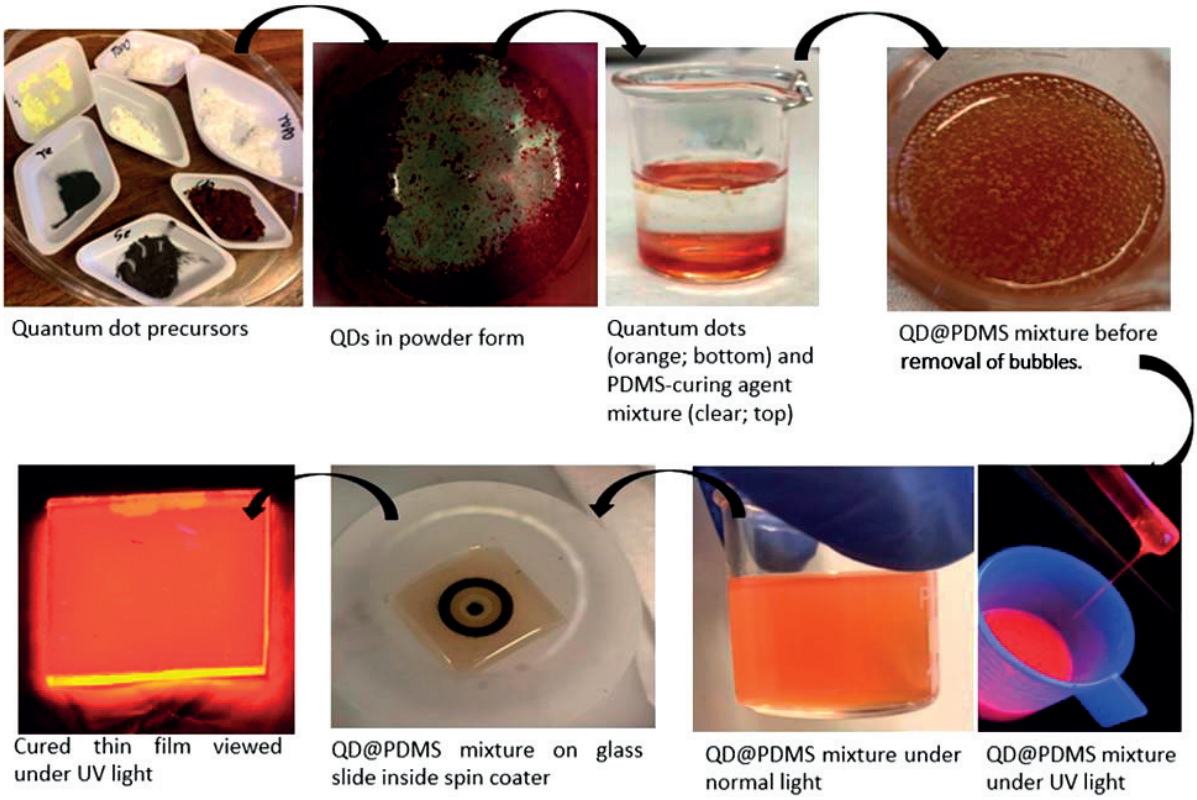

Figure 2: Schematic illustration of the protocol that was followed for the preparation of QD@PDMS thin films.

concentration quantum dot (HQD) films, respectively. These were sonicated for 30 min to ensure a homogenous dispersion. To 1 mL of each of the QD@chloroform solutions, curing agent and PDMS were added using a ratio of 1 g curing agent: 10 g PDMS. The resulting mixture was mixed thoroughly and was placed under vacuum for ~30 min to remove air bubbles that formed. A clean glass slide (20 mm × 20 mm × 2 mm) was placed in the centre of the spin coater and 0.5 mL of the degassed mixture was placed in the centre of the glass slide.

This was spin coated (Laurell Technologies, North Whales, USA) at a speed of 500 rpm (300 rpm/s) for 10 s to distribute the QD@PDMS solution over the glass surface. The glass slide with the QD@PDMS film was then removed from the spin coater and cured on a hot plate at 80 °C for 15 min. The same protocol was followed for the preparation of HQD films. The fluorescence of the QD@PDMS films was measured at nine spatially resolved spots over the film surface (Figure 3). The statistical significance of differences between fluorescence intensity measurements was evaluated by t-tests using a 95% confidence interval.

Characterization of the thin films

Fluorescence spectra of the QD@PDMS thin films were measured using a Horiba Jobin Yvon FluoroMax-4 Spectrofluorometer (Horiba Scientific, New Jersey, USA). An excitation wavelength of 400 nm and an emission wavelength range of 410-700 nm were employed. Narrow slit widths of 2 nm were used due to the high fluorescence intensity of these films.

The thickness of the QD@PDMS thin films prepared on the glass slides was determined by high resolution scanning electron microscopy (HRSEM) analysis (Zeiss Ultra PLUS FEG SEM, Jena, Germany) after the QD@PDMS films were cut using a diamond blade and etching pen to score the glass. The films were then placed under liquid nitrogen to enable breakage along a line of structural weakness carved into the glass with the diamond blade and etching pen.

Fluorescence sensing using the QD@PDMS thin films

In order to determine which solvent was best for sensing applications, three films of LQD and HQD were each immersed in 4 mL solvents, namely 100% deionized water, 100% ethanol, and a mixture of H_2O:ethanol (2:1), for 24 hours to determine the effect thereof on the fluorescence emission.

Standard solutions of a polar (atrazine) and a non-polar (phenanthrene) organic water pollutant, respectively were used for preliminary testing of the QD@PDMS sensors. Firstly, nine films of both LQD and HQD respectively were interacted with atrazine concentrations of 2, 8 and 12 × 10^{-7} M (N= 3), by placing 400 µL of the atrazine solution on the film surface for 1 min. This interaction time had been previously found to be suitable for interaction of atrazine and these QDs dispersed in chloroform. Subsequently, optimized films of LQD and HQD were immersed in 4 mL phenanthrene solutions in H_2O:ethanol (2:1) solvent, with respective phenanthrene concentrations of 0; 5.61 × 10^{-6} and 5.61 × 10^{-5} M (N= 3) for 24 hours. While these concentrations are orders of magnitude higher than typical levels of phenanthrene found in local water systems[33], these were chosen as part of preliminary testing of the films. The fluorescence of the films was measured before and after the interaction.

Water samples were obtained from the inlet to a water treatment plant. LQD and HQD films were immersed in the filtered (22 µm nylon syringe filter), unconcentrated water sample for 1 min, 1 h and 24 hours. A 400 mL aliquot of the water sample was also pre-treated by solid phase extraction (SPE) using a Waters Oasis HLB cartridge (6 mL, 200 mg) after 0.2% (w/v) of EDTA had been added to the sample to chelate any residual free metal ions. Analytes were eluted with 6 mL ethanol which was subsequently blown off under vacuum at 30 °C. The dried sample was reconstituted in H_2O:ethanol (2:1) to a final volume of 3 mL. Different films were then consecutively interacted with this sample extract starting with a LQD and thereafter a HQD film for 24 hours each.

RESULTS

Hydrophobic QD synthesis and characterization

Hydrophobic QDs were successfully synthesized by the organometallic hot injection method. The hydrophobic nature of the QDs, provided by the ligands (trioctylphosphine oxide and oleic acid) attached to the QDs was maintained to facilitate their optimal interaction with the non-polar PDMS. The maximum emission wavelength peak of the core QDs was 588 nm and upon the addition of the shell, this red-shifted to 594 nm after 60 min of the reaction due to their increase in size (Figure 4).

It is shown from the UV-Vis spectra in Figure 5, that the absorbance spectra of the CdSeTe QDs and CdSeTe/ZnS QDs in chloroform solution were broad, which indicated that a wide range of excitation wavelengths could be employed when using these materials as fluorescence sensors.

The relative photoluminescence quantum yield (PLQY) of the QDs was measured by comparison to rhodamine 6G in ethanol and was calculated to be 47%. The calculated PLQY of the QDs was lower than expected as the fluorescence of the C/S QDs was very bright even when immobilized in the PDMS to produce QD@PDMS thin films, as observed under UV light.

The size of the QDs was determined using transmission electron microscopy (TEM) (Figure 6) in combination with ImageJ software and it was found that core and C/S QDs had average particle diameters

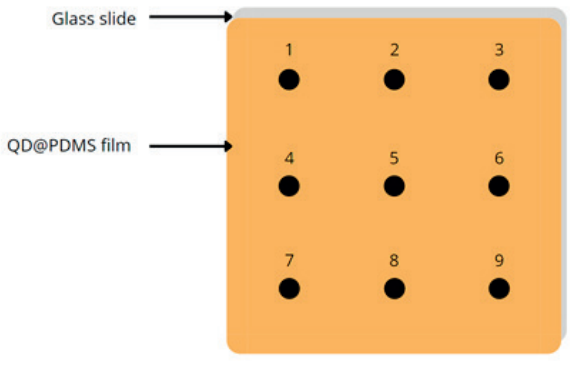

Figure 3: Fluorescence measurement positions over nine spots on the QD@PDMS thin film supported on a glass slide.

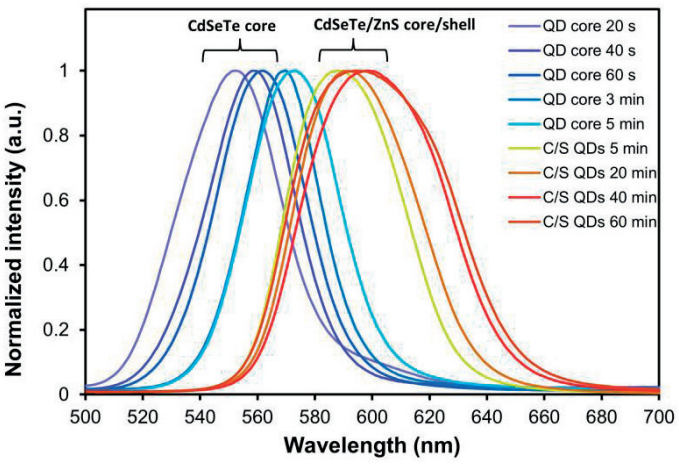

Figure 4: Normalized fluorescence spectra of hydrophobic CdSeTe core QDs and CdSeTe/ZnS core/shell QDs showing the change in fluorescence wavelength upon growth thereof (470 nm excitation wavelength).

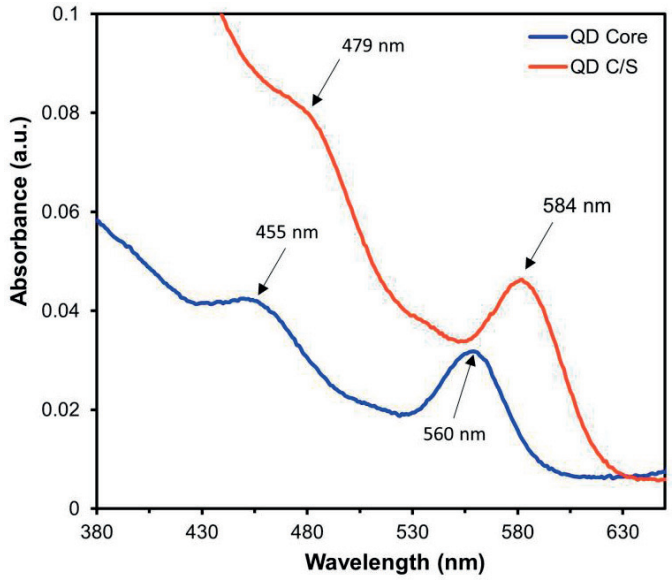

Figure 5: UV-Vis absorbance spectra of the CdSeTe and CdSeTe/ZnS QDs.

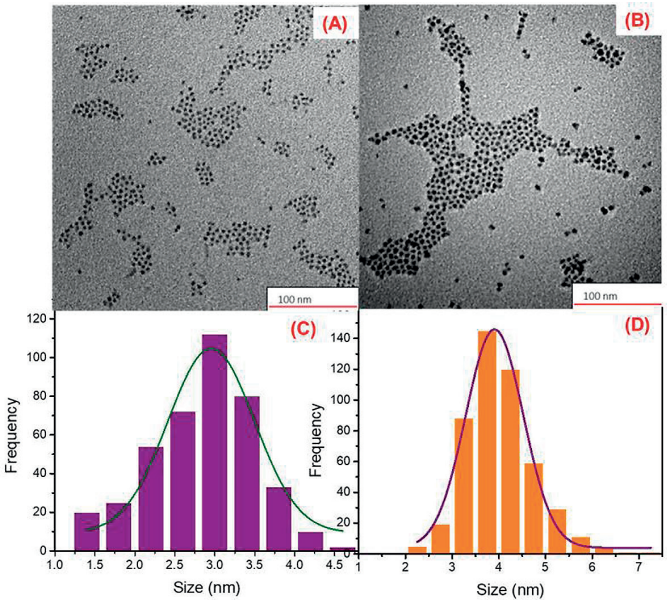

Figure 6: TEM micrographs of the CdSeTe QDs A) and CdSeTe/ZnS QDs (B) examined at a high magnification (~100 000x) with 100 nm scale bars. Average particle size distribution of the CdSeTe QDs (C) and CdSeTe/ZnS QDs (D).

of 3.1 and 4.0 nm, respectively. A size increase was observed as the shell layer had been coated over the QD core, as expected. There was a slightly larger size distribution for the C/S QDs than what was found with the core QDs (Figure 6) with full-width half maximum (FWHM) values of 31 and 49.5 nm, respectively.

Manufacture of QD@PDMS thin films

Initially, the QD@PMDS thin films were prepared on silicon wafers which had been coated with a polyacrylic acid (PAA) sacrificial layer to enable removal of the thin film from the substrate after curing. It was found that it was difficult to remove the thin films from the wafer and then handle them without a support present. On the other hand, it was not possible to utilize the thin films directly on the wafers for immersion in water samples and also for insertion into the fluorescence spectrophotometer due to the size of the wafers. The resulting thin films were thus difficult to work with, which made them unsuitable for sensing applications. Glass slides were thus cut to size such that they could be inserted directly into the solid sample holder of the fluorescence spectrophotometer. Thin films prepared onto these

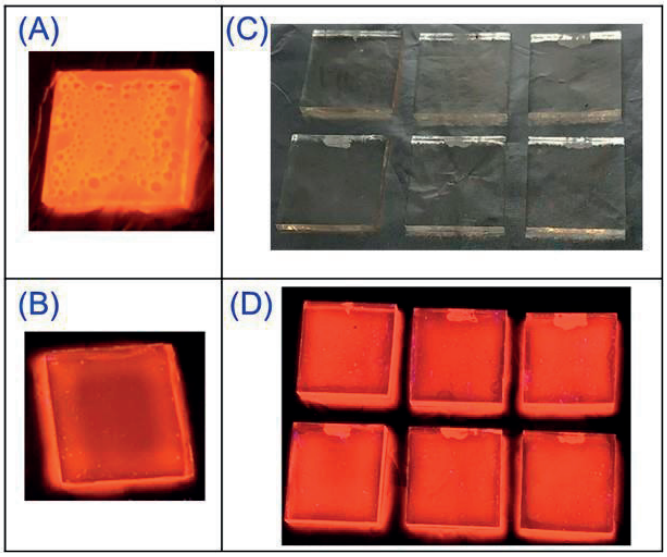

Figure 7: Unoptimised QD@PDMS thin films under UV light showing: entrained bubbles (A) and inconsistent dispersion of QDs within the QD@PDMS thin film (B). QD@PDMS thin films prepared using optimal conditions showing consistent QD distribution as observed under ambient light (C) and UV light (D).

glass slides therefore did not require a PAA layer, as they could be used directly for immersion into water samples and thereafter the fluorescence of the supported thin film could be measured with no pre-treatment needed. This enabled the manufacture of a robust, rugged, and portable fluorescence sensor.

The QD@PDMS films manufactured under optimized conditions were transparent under normal light and had a high fluorescence emission under UV light as seen in Figures 7(c) and 7(d). The optimized films had a homogeneous distribution of QDs, with no bubble formation present which had been encountered with thin films produced using other (non-optimized) parameters (Figures 7(a) and 7(b)). The fluorescence emission measured across the films as shown in Figure 3 had a %RSD of less than 10%.

LQD film replicates were prepared by spin coating 1 mL of the LQD@PDMS solution onto glass slides at a speed of 500 rpm and acceleration of 300 rpm/s for 10 s. Films were cured at a lower temperature of 80 °C for 15 min to prevent bubble formation. The measured thicknesses of the films ranged from 250.44 µm for HQD films to 437.68 µm for a film with no QDs. The differences in thickness between these films can be attributed to differences in viscosities of the spin coating mixture, where films containing QDs had lower viscosities due to QDs being added to the PDMS and curing agent mixture as a dispersion in a solvent (chloroform). The film thicknesses, along with the film masses, were used to calculate the concentration of QDs within the films and were found to be 0.28 and 0.51 mg/mL for LQD and HQD films, respectively. Different excitation wavelengths were tested on the films produced using the optimized parameters as shown in Figure 8a. It was observed that an excitation wavelength of 400 nm led to the highest fluorescence intensity, which was thus used for sensing applications. From Figure 8b it is evident that repeated exposure to this excitation wavelength did not have a major negative impact on the fluorescence emission of the QD@PDMS thin films, as the difference between the maximum and minimum fluorescence emission intensity was 8% over 60 repeated measurements.

Interaction of QD@PDMS with aqueous solutions

Solvents

As the intended application of the QD@PDMS thin films immobilized onto glass slides is in the detection of pollutants in an aqueous matrix, it was important to determine any impact of water itself

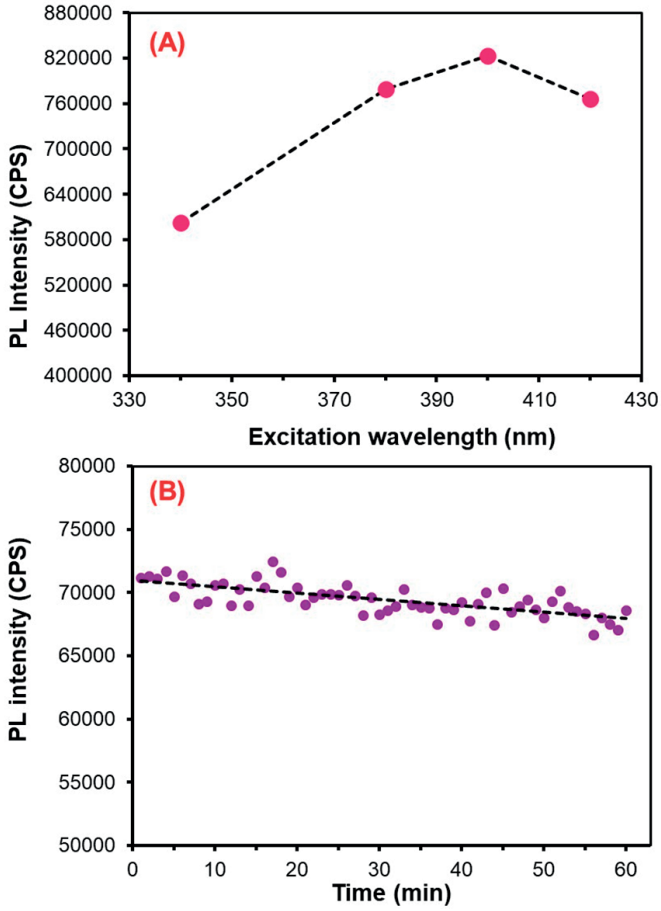

Figure 8: (A) Fluorescence intensity of LQD films obtained for different excitation wavelengths. (B) Repeated measured fluorescence emission of a LQD film every min consecutively for 60 min (400 nm excitation, 610 nm emission and 1.2 nm slit widths).

on the fluorescence of the sensor material. Mixtures of water with ethanol were also tested, as ethanol enhances the solubility of organic pollutants in water. The effect of various solvents on the fluorescence of the films was tested by comparing the fluorescence intensity thereof before and after immersion in various solvents (100% H_2O, 100% ethanol and a mixture of the two, H_2O:ethanol (2:1)) for 24 hours. Although in practice such long exposure times would not be expected for sensing applications, extended tests were performed to ensure that any change in fluorescence during sensing could be ascribed to the presence of pollutants and not the sample matrix.

Fluorescence enhancement was observed for both LQD and HQD films after interaction with pure H_2O and pure ethanol, whilst slight quenching was found with H_2O:ethanol (2:1) (Table 1). From these experiments, it was determined that the most effective matrix for sensing of organic pollutants was a mixture of water and ethanol in a ratio of 2:1, as this had the smallest effect on the fluorescence of the films as measured before and after the interaction with the different solvents.

Organic water pollutants

Organic chemical contaminants in water include several compound classes including dyes, petroleum, pesticides, pharmaceuticals, PAHs, polychlorinated biphenyls (PCBs) and surfactants.[34,4] Initially a polar organic herbicide, namely atrazine, which is a common contaminant in water, was tested with the optimized LQD and HQD films. Whilst significant quenching was observed for LQD films, there was no statistically significant difference between F_0 and F for the HQD films (Appendices Table A1 and A2). This disparity may be due to the short interaction time of 1 min and also as a result of the hydrophobic nature of PDMS, thus the interaction between the polar analyte and the QD@PDMS films would not be ideal. In addition, the relative quenching of the high concentration of QDs in the HQD films upon interaction with a low concentration of atrazine may be insignificant.

Phenanthrene (Phe) is a non-polar PAH that is formed mainly from the incomplete combustion of organic materials and therefore enters the environment from various sources, which include residential heating, motor vehicle exhaust, coal-tar pitch and asphalt production, coal gasification, liquefying plants, aluminium production, catalytic cracking towers and related activities of petroleum refineries.[35,36,37] The effect on the fluorescence of QD@PDMS thin films when interacted with Phe was thus investigated, as non-polar – non-polar interactions were expected to be more favourable for sensing applications.

The LQD and HQD thin films were interacted with Phe, which is expected to have a strong affinity for non-polar PDMS. Three films each of optimized LQD and HQD respectively were immersed in 4 mL phenanthrene solutions (H_2O:ethanol (2:1)) at varying low concentrations. The fluorescence of the films was measured before and after 24 hours of interaction with the solutions, and again after 25 days of standing on the laboratory bench. Long interaction times were used for these initial performance tests, whilst it is acknowledged that in practice considerably shorter exposure times would be required thus additional optimization is needed to achieve this. Enhancement was observed for LQD and HQD films when interacted with Phe (Table 2), where films tested with solvent blanks showed quenching after these longer interaction intervals, clearly indicating that the solvent did not cause the enhancement which thus resulted from sensing of the target analyte. For LQD films, the F/F_0 value increased as the Phe concentration increased, which correlated to literature where it was previously found that L-cysteine capped CdSeTe/ZnSe/ZnS QDs conjugated to graphene oxide (GO) showed fluorescence enhancement with increasing concentrations of Phe.[24] A similar increase in F/F_0 was not observed for the HQD films, which is likely due to inner filter effects, in that emitted fluorescence was reabsorbed by other QDs in the vicinity of the emitting QD. This was possible due to the higher concentration of QDs in the HQD films.

Table 3 shows the results of LQD and HQD films interacted with filtered, unconcentrated water samples from an inlet to a water treatment plant. The LQD films showed a degree of quenching, whilst the other interactions with this water sample had negligible effects on the fluorescence of the material, but when comparing this to the 100% deionized water (blank) interaction for 24 hours, the fluorescence was quenched significantly. This points to the presence of pollutants in

Table 1: Measured fluorescence (F/F_0) of LQD and HQD QD@PDMS films upon interaction with 100% H_2O, 100% ethanol or H_2O:ethanol (2:1) for 24 hours.

Solvent	100% H_2O	100% Ethanol	H_2O:ethanol (2:1)
F/F_0 for LQD	1.63	1.22	0.93
F/F_0 for HQD	1.78	1.55	0.87

Table 2: Fluorescence (F/F_0) of three LQD and HQD QD@PDMS films after the films upon interaction with Phe solutions of varying concentration in H_2O:ethanol (2:1) for 24 hours.

[Phe]	Solvent blank (0 M)	5.61×10^{-6} M	5.61×10^{-5} M
F/F_0 for LQD	0.93	1.05	1.15
F/F_0 for HQD	0.87	1.09	1.09

Table 3: Measured fluorescence (F/F_0) of LQD and HQD films after being interacted with a filtered, unconcentrated water sample from the inlet of a water treatment plant for 1 min, 1 h and 24 hours.

Sample	Filtered, concentrated (24 h)	Filtered, concentrated (30 min)	H_2O:ethanol (2:1) blank (24 h)
F/F_0 for LQD	$0.75^{\#1}$	$0.87^{\#3}$	$0.93^{\#5}$
F/F_0 for HQD	$0.83^{\#2}$	$1.06^{\#4}$	$0.87^{\#6}$

the water and highlights the potential use of this sensor material for non-targeted screening of pollutants in water. The lower quenching observed for 24 h as compared to 1 min and 1 h interactions may indicate back diffusion of analytes out of the PDMS thin film over longer interaction times.

The filtered water sample after concentration by SPE was small in volume thus necessitating the consecutive testing thereof, as indicated in Table 4 by superscripts. Filtration and SPE would have removed potential interferences in the measurements as well as pre-concentrated the analytes. LQD films had a greater quenching of fluorescence when compared to the fluorescence measured using HQD films, which may have been due to the inner filter effect. For LQD films this was again a significant reduction in fluorescence intensity (determined by the t-test at a 95% confidence level) compared to the change in fluorescence of the blank when the film was interacted with H_2O:ethanol (2:1) for 24 h. This therefore also suggests the presence of organic pollutants in the water sample, again indicating the potential use of the material for non-target screening of water samples.

The fluorescence mechanism of the QD@PDMS requires further elucidation to better understand and predict changes in fluorescence when this material is brought into contact with various solvents and analytes. Photoinduced fluorescence enhancement (PFE) of CdSe and CdSeTe/ZnS QDs, for example, has been observed in a wide range of environments, including aggregated QD monolayers[38], aqueous and organic solutions[37] thin polymer films[39], or when these QDs are exposed to ambient light (unintentional illumination by room light).[40] Surface-environmental effects including photoinduced surface passivation by water molecules[38] and photoinduced oxidation[40] should be further investigated.

It is important to note that other organic pollutants, particularly non-polar compounds, present in water samples may potentially interact with the QD@PDMS thin films and impact on their fluorescence as a result. The compounds of relevance would vary depending on the source water, for example wastewater may have a high loading of organic contaminants of anthropogenic origin, whilst natural organic matter derived from plant and animal matter[41] may be more prevalent in river water samples. Relative uptake and/or interaction of organic compounds by the thin films would thus need to be determined and their selectivity towards target analytes investigated for a particular application, in order to assess the viability of use of the QD@PDMS thin films to screen for the presence of the analytes and to semi-quantify them using fluorescence. The later would require the generation of calibration curves using matrix-matched standard solutions at application-relevant concentrations.

CONCLUSION

Hydrophobic CdSeTe/ZnS QDs were successfully synthesized by the organometallic hot-injection method as confirmed by fluorescence and UV-Vis spectroscopy, and HRTEM. The presence of hydrophobic surface moieties enabled the incorporation of the QDs into PDMS thin films. A robust spin coating method for preparing thin films comprised of CdSeTe/ZnS core/shell QDs immobilized into PDMS was developed. The thin films of 250 and 438 μm thickness were prepared for two different QD concentrations, respectively, as the presence of the QDs changed the viscosity of the spin coating mixture. The excellent homogeneity of the fluorescence of these thin films opens the door to their use for pollutant sensing applications. Moreover, the approach is rugged and practical, as it allows for direct immersion of the thin films supported on glass slides into water samples, followed by placement thereof into a fluorescence spectrophotometer for analysis. The QD@PDMS thin films were found to be photostable over 60 repeated fluorescence excitation cycles, with only an 8% decrease in fluorescence emission intensity. The findings of this study reveal the potential of QD@PDMS thin films in detecting organic pollutants present in water although this application is constrained due to the sensitivity of fluorescence intensity to the measurement microenvironment and conditions. These challenges may be addressed in part by storing the films in the dark after synthesis and prior to use, whilst future work into the possible use of various capping agents to passify the surface of the C/S QDs and enhance their stability prior to their incorporation into the thin films should be investigated.

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Table 4: Measured fluorescence (F/F_0) of LQD and HQD films after being interacted consecutively (from 1 to 6 as shown by superscripts) with a filtered, concentrated (SPE) water sample taken from the inlet of a water treatment plant for 24 h, and then for 30 min.

Sample	Filtered, unconcentrated (1 min)	Filtered, unconcentrated (1 h)	Filtered, unconcentrated (24 h)	100% H_2O blank (24 h)
F/F_0 for LQD	1.07	0.86	1.00	1.63
F/F_0 for HQD	1.03	1.03	1.06	1.78

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APPENDICES

Table A1: Three LQD films tested per atrazine concentration with F/F_0 values obtained from the spot in the middle of the film (N = 1), (λex= 400 nm, λem= 610 nm, 2 nm slit widths).

[**Atrazine**]	**2×10^{-7} M**	**8×10^{-7} M**	**12×10^{-7} M**
Film 1	0.96	0.74	0.68
Film 2	1.01	0.61	0.74
Film 3	0.84	0.76	1.10
Average	0.94	0.70	0.84

Table A2: Three HQD films tested per atrazine concentration with F/F_0 values obtained from the spot in the middle of the film (N = 1), (λex= 400 nm, λem= 610 nm, 2 nm slit widths).

[**Atrazine**]	**2×10^{-7} M**	**8×10^{-7} M**	**12×10^{-7} M**
Film 1	1.08	1.76	1.08
Film 2	1.17	1.33	1.00
Film 3	0.81	0.91	1.09
Average	1.02	1.33	1.06