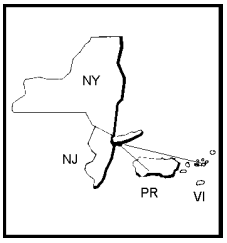

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Development of a Portable Petroleum By-Products Chemical Sensor

Year 1 Report
March 25, 2005

Professor Michael A. Carpenter,
College of NanoScale Science and Engineering

Professor Marina A. Petrukhina,
Department of Chemistry
University at Albany, SUNY
Albany, NY 12203

In cooperation with

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16. Abstract

This study develops nanoparticle based chemical sensors for the sensitive, selective and field portable analyses of soil samples for petroleum spill indicating hydrocarbons (such as benzene, toluene, ethyl-benzenes, xylenes, PCBs, trichloroethylene). The broader impacts of the hydrocarbon sensor research program lies in the future target applications of nanoparticle based chemical sensors. NYS-DOT spends approximately $10-12M/yr on the testing of soil and groundwater samples, which do not include the NYC-DOT.1 By moving the majority of these tests from an off-site analytical lab, to a field portable device the overall cost of construction budgets, will be significantly lower and construction projects will experience fewer delays due to untimely analytical lab reports. Another example leading to a broader impact of the program is for monitoring benzene, toluene, ethyl benzene, and xylenes (BTEX) for applications in groundwater well networks or soil sample analysis. BTEX compounds are indicative of petroleum by-product contamination and currently the US-EPA has regulations for performing a standardized test of groundwater and soil samples using modern analytical laboratory equipment. Off-site analytical lab testing of both groundwater and soil samples are a significant expense of environmental monitoring and cleanup operations throughout the federal and state level Superfund program. Since its inception in 1986, the New York State Superfund program alone has identified, characterized and placed a total of 1,714 sites on the Registry of inactive hazardous waste disposal sites.

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Research Summary

We have proposed to tailor design nanoparticle based chemical sensors for the sensitive, selective and field portable analyses of soil samples for petroleum spill indicating hydrocarbons (such as benzene, toluene, ethyl-benzenes, xylenes, PCBs, trichloroethylene). The broader impacts of the hydrocarbon sensor research program lies in the future target applications of nanoparticle based chemical sensors. NYS-DOT spends approximately $10-12M/yr on the testing of soil and groundwater samples, which does not include the NYC-DOT.[1] By moving the majority of these tests from an off-site analytical lab, to a field portable device the overall cost of construction budgets will be significantly lower and construction projects will experience fewer delays due to untimely analytical lab reports. Another example leading to a broader impact of the program is for monitoring benzene, toluene, ethyl benzene, and xylenes (BTEX) for applications in groundwater well networks or soil sample analysis. BTEX compounds are indicative of petroleum by-product contamination and currently the US-EPA has regulations for performing a standardized test of groundwater and soil samples using modern analytical laboratory equipment. Off-site analytical lab testing of both groundwater and soil samples are a significant expense of environmental monitoring and cleanup operations throughout the federal and state level Superfund program. Since its inception in 1986, the New York State Superfund program alone has identified, characterized and placed a total of 1,714 sites on the Registry of inactive hazardous waste disposal sites. Details of these sites are as follows:[2]

1. A total of 934 sites have been identified that require remediation; growth is approximately 30 sites/yr
2. 215 of these sites require long-term operation, maintenance, and monitoring (OMM) to ensure that remediated sites continue to protect the public health (growth of OMM sites is approximately 30/yr)
3. In the 1999/2000 fiscal year approximately $9 million were spent on site investigation, remediation investigation and OMM, all of which required extensive sampling, monitoring and analysis of soil and groundwater samples
4. To date funds spent or obligated to be spent total approximately $4.61 billion: $3.01 billion by responsible parties, $1.05 billion by New York State and $554 million by the federal government

It is clear that significant cost savings at both the state and federal levels would occur if chemical sensors integrated with pattern recognition techniques were developed for continuous on-site environmental monitoring, specifically for analyzing groundwater well and soil samples. Future advances and phases of the proposed research program would likewise integrate in-situ remediation processes in the event of a detected pollution plume and lead to far less expensive cleanup procedures.

During the first year of the program we have adapted colloidal synthetic chemistry procedures to attach a combination of stabilizing and sensing ligands to the surface of semiconducting quantum dots (QDs). The sensing ligands are designed and utilized to achieve the first level of selective detection of the target hydrocarbons. These tailored QDs have been incorporated into a polymer matrix, which is chosen to achieve a second level of selectivity in the detection the target hydrocarbons. Testing of these tailored QD films has required the development and integration of a reliable sensor testing station so that ppm to % level hydrocarbon concentrations can be delivered and detected using fluorescence spectroscopy techniques. Currently, we have been able to achieve a **15ppm** detection limit for **xylenes** in an ambient air mixture, which is approximately **3 times** the **50ppm** detection limit for **toluene**. This increased sensitivity with the development of selective films for the detection of aromatic hydrocarbons, which only differ by a single methyl group, is justification that our proposed program, which entails the development of tailored QD-polymer films, is a promising technology for the development of a portable petroleum by-products chemical sensor.

During the second year of the program we intend to continue the optimization of the tailored sensing ligands and likewise perform further studies to select an optimal polymer host for the QDs, thereby achieving an increase in sensitivity to ppb levels while enhancing the degree of selectivity we achieved in year 1. These goals will be achieved in part by utilizing parallel analysis techniques which will leverage equipment purchased with the infrastructure funds obtained in year one. Libraries of films will be deposited in a parallel fashion and will be subsequently tested against hydrocarbon exposure events using nearly parallel fluorescence techniques. A design of experiments approach to modifying the film libraries will be utilized for optimizing the sensing ligand, sensing ligand loading, QD density, and polymer host. These parallel techniques will enhance the throughput by at least an order of magnitude thus allowing for the rapid development of hydrocarbon sensing films.

Staffing

Key to the overall success of this program is the research efforts led by two postdoctoral associates. Dr. Oxana Vassiltsova, in Professor Petrukhina's research group has developed and extended QD synthetic procedures to include the use of stabilizing and sensing ligands which are required for the first level of hydrocarbon selectivity. Furthermore, Dr. Vassiltsova has led the efforts in analyzing the tailored QDs using a variety of analytical techniques that include transmission electron microscopy (TEM), NMR, Uv-Vis absorption spectroscopy and fluorescence spectroscopy. Dr. Zhouying Zhao, in Professor Carpenter's research group has developed methods for the incorporation of the tailored QDs into polymer matrices thereby achieving the second

level of selectivity. Likewise Dr. Zhao designed, implemented and optimized the sensor testing station that was used for the detailed exposure tests performed in year 1. Likewise Dr. Zhao has also characterized the QD-polymer films using Uv-Vis absorption spectroscopy and fluorescence spectroscopy. As part of the education program we have also had 2 high school research interns as well as 1 undergraduate research intern and 1 undergraduate student participate in research activities during year one. As part of our growth, during year 2 of the program we intend to hire two Ph.D. graduate students to assist both Dr. Vassiltsova and Dr. Zhao. The internship program for both undergraduates and high school students will continue during year 2.

Funding

During year one we leveraged the investment made by the Department of Transportation by almost an order of magnitude. Specifically, the hydrocarbon sensor program successfully received one year of funding from NYSERDA, $33,000, to develop tailored nanoparticles for the detection of hydrocarbons in aerosol particles. As both the NYS-DOT and NYSERDA programs are related, they will be leveraged to help provide overall support of research staff and supplies for the programs. Furthermore, $1,200,000 in infrastructure funding was raised by Professor Carpenter, through his participation and collaboration in the Syracuse University Environmental Quality Systems New York State STAR Center program. These funds have been used for the purchase of analytical instrumentation and equipment for support of the NYS-DOT program. Proposals are currently pending and will be submitted to both state and federal agencies during year two to promote programmatic growth of the hydrocarbon sensing research initiative, thereby providing continued leverage of the investment made by the Department of Transportation. Hydrocarbon sensors are being sought for use in environmental, indoor air, agricultural, homeland security, the food industry, pharmaceutical and industrial applications. Therefore, through successful fundraising and economic outreach efforts to state and federal agencies along with industrial sponsors, we envision expanding this program into a high technology research center which provides the rapid development of sensors tailored for targeted applications.

Outreach

Presentations on our progress to date have been given at the 2003 National American Chemical Society, 2004 National American Chemical Society, 2003 Northeast regional American Chemical Society, the 2004 regional AMSE meetings, NY Nanotech 2004 and the 2nd Joint Quebec-New York Workshop on Nanotechnology, Albany, NY, 2004. The results have been very well received and both Dr. Oxana Vassiltsova and Dr. Zhouying Zhao were very busy presenting our results at each of these meetings. The results generated during year one are currently under further analysis and we envision that several manuscripts will be drafted and submitted to peer-reviewed scientific journals by July 2005.

Results to Date

QD Synthesis and Characterization

QDs such as CdSe are ideal candidates for sensing applications due to their extremely high surface/volume ratio and sensitivity of their optical properties to the changes in their chemical environment. Surface modification of CdSe nanocrystals by the appropriate anchoring molecules are being explored. This approach will test the ability of donor-substituted aromatic compounds to form π-complexes with electrophilic functionalities of molecules grafted to the surface of QDs by chemisorption or self-assembly. Consequently, any changes in the surface environment of QDs significantly should affect their photophysical and photochemical properties, which will be exploited for the development of sensing technologies.

During the first year of the NYS-DOT program, several methods of QDs synthesis have been tested. The known literature procedures have been adapted to allow both stabilizing and sensing ligands to be attached to the QD surface. Specifically, the known literature procedures have been adapted (1, 2, 3, and 9). Attempts also have been made to adjust the literature methods to our research goals by introducing potential sensor groups on the QDs surfaces (4, 5, 6, 7, and 8). ^{1}H-NMR analysis was used to analyze the degree of ligand attachment.

1) CdSe QDs with tetradecylphosphonic acid (TDPA)[3]

This method of synthesis was tested to produce QDs ranging in size from 1.8 to 3nm, since TDPA and HDA are known as strong ligands, thus limiting the particle growth. CdO (64.2 mg, 0.5 mmol) was placed into a three-neck flask containing 4 ml of TOPO and 3 ml of HDA. The mixture is heated to ca. 270˚ C under a nitrogen flow. Upon addition of 0.227 g (2.1 mmol) of TDPA a colorless solution was formed. At 250˚ C, 7.5 ml of a 0.3 M solution (2.25 mmol) of Se powder in TOP was swiftly injected. At the desired nanocrystal size, the reaction was stopped by removal of the heating bath. Purification was carried out by two cycles of precipitation with methanol and redispersion of the nanocrystals in toluene.

This synthetic method with TDPA and HDA was successful and afforded very small QDs ranging in size from 1.8 to 3 nm (Figure 1). The size of CdSe particle synthesized was determined based on analysis of the Uv-Vis absorption properties according to Yu et al..[4]

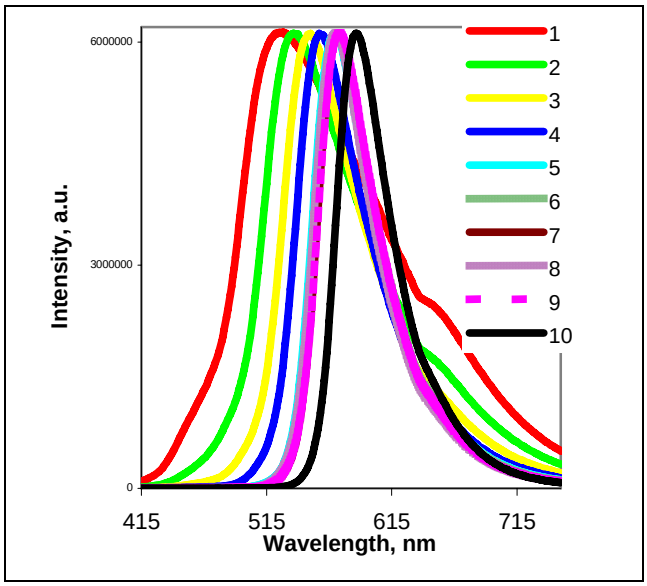


Figure 1: Photoluminescence (PL) spectra of set of CdSe QDs. Sizes ranges from 1.8 nm up to 3 nm

2) Set of CdSe QDs from 2.3 up to ~ 10.4 nm in diameter

To produce a wider size range of QDs we performed the synthesis of CdSe QDs as described above, but only with TOPO and HDA as the protecting ligands. We produced the smaller sized particles, however the luminescence of larger particles was less efficient and the absorption maxima for these large particles were also not very pronounced. Luminescence maxima for those QDs were in a range from 517 nm up to 667 nm (Figure 2&3).

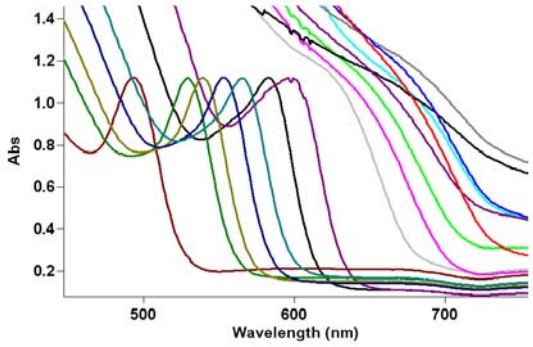


Figure 2: Absorption spectra of CdSe QDs

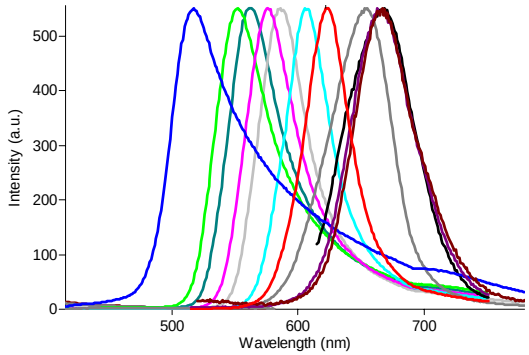


Figure 3: Luminescence spectra of CdSe QDs, λ_{ex}=400 nm

3) CdSe QDs with TOP/TOPO

This method was tested to get CdSe QDs containing only TOP/TOPO surface-bound ligands and were used both as our reference QDs (to compare it with CdSe QDs with grafted sensing ligands) and for ligand exchange reactions (to attach sensing ligands).

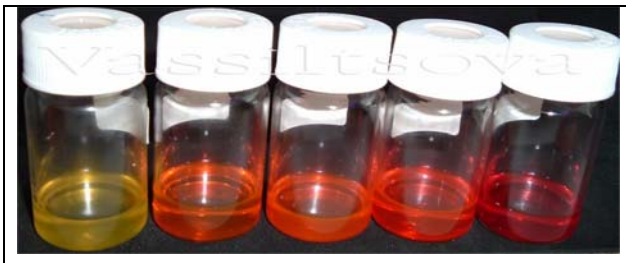


Figure 4: Photo of different sized synthesized CdSe QDs

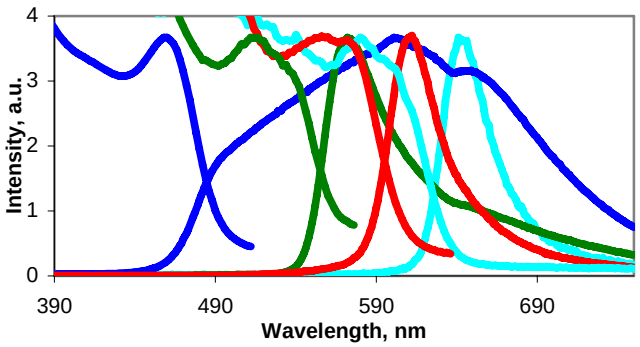


Figure 5: Absorption and luminescence spectra of set of CdSe QDs with only TOP/TOPO on the surface. Particle diameter ranges from 1.8 nm up to 4 nm.

A selenium stock solution was prepared by mixing 0.178 g of Se in 7.5 ml of TOP. 10 g of TOPO and 0.064 g of CdO were placed under nitrogen flow and heated to 350˚ C. At this temperature the Se stock solution was swiftly injected into the reaction vessel in a single step. The reaction temperature was adjusted to 250˚ C immediately after the injection. The reaction was stopped 5 min after the injection, and heat was immediately removed. The reaction mixture was allowed to cool to ~30-50˚ C, and methanol was added to precipitate the nanocrystals. As a result of the above synthetic procedure, a set of QDs ranging in size from 1.8 to 4nm was produced with the optical properties displayed in Figures 4 and 5.

4) CdSe with stearic acid[5] or perfluorostearic acid (PFSA)

As our goal was to modify the surface of CdSe QDs by perfluorinated and nonfluorinated carboxo-bound ligands, we chose this synthetic method which used stearic acid as a surface bound ligand, and later substituted it with PFSA. With this procedure we were able to synthesize both small and large QDs with high PL yield and good stability. QDs emitting well separated wavelengths were chosen for incorporation into polymer films as described later.

The synthesis of CdSe was performed in the mixture of TOPO, HDA and stearic acid (or PFSA). In a typical reaction procedure CdO (0.0127 g, 0.1 mmol) and stearic acid (0.1140 g, 0.4 mmol) were loaded into a 25 mL three-neck flask and heated to 150˚ C under a nitrogen flow. After CdO was completely dissolved, the mixture was allowed to cool to room temperature. TOPO and hexadecylamine (HDA), 3.44 g for each, were added to the flask, and the mixture was heated to 280˚ C to form an optically clear solution. At this temperature, the Se solution containing 0.079 g (1 mmol) of Se dissolved in 2.920 g of TOP was swiftly injected into the reaction flask. After the injection, the temperature was set at 250˚ C. For all reactions, the total mass of the reaction mixture was fixed as 10 g, and 10 times the amount of the selenium precursor was used in comparison to the cadmium precursor.

This procedure resulted in stable QDs ranging in size from 3.2 up to ~ 9.2 nm in diameter with emission maxima from 569 nm up to 681 nm (Figures 6&7). We have chosen 3 different types of QDs and incorporated them in polymer films.

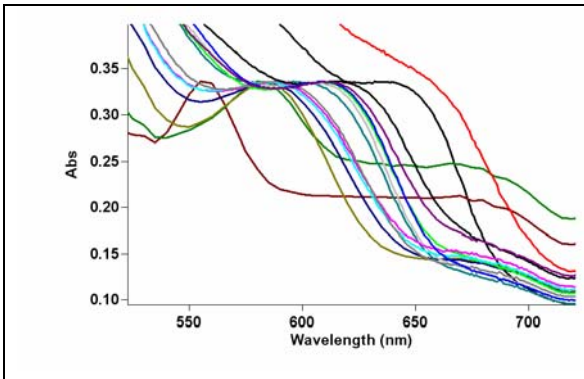


Figure 6: Absorption spectra of CdSe QDs

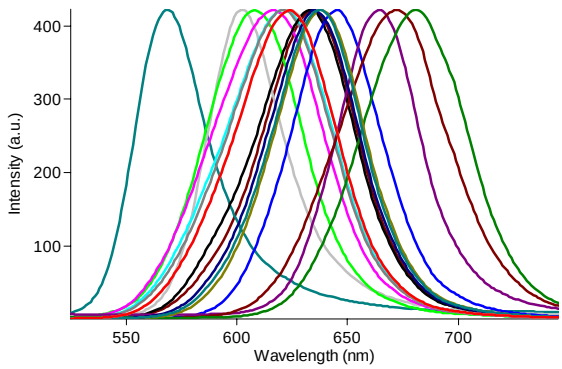


Figure 7: Luminescence spectra of CdSe QDs , λ_{ex}=400 nm

The low sublimation temperature of a new potential surface-bound molecule, PFSA (135˚ C), its limited thermal stability and low solubility in organic solvents all have affected the reaction pathway to achieve PFSA substituted QDs and did not result in the preparation of stable QDs. We therefore concluded that PFSA should be added to the pre-formed QD system through ligand exchange procedures and not during the direct high temperature CdSe synthesis.

5) CdSe QDs with pyrenebutyric acid (PBA)

The method of synthesis of QDs was developed in order to place sensing ligand PBA on the surface of CdSe QDs. CdO (51.4 mg, 0.4 mmol), 227.6 mg (0.8 mmol) of stearic acid and 230.7 mg of PBA were placed into a three-neck flask and heated to 150ºC under nitrogen flow. After CdO was completely dissolved, the mixture was allowed to cool to room temperature. 3 g of TOPO and 1.5 g of HDA were added to the flask and the mixture was heated to ca. 300˚ C under nitrogen flow. At this temperature Se solution containing 316 mg of Se powder in 2.1 mL of TOP was swiftly injected. At the desired nanocrystal size, the reaction is stopped by removal of the heating bath. Aliquots were mixed with methanol and the precipitated QDs were separated by centrifugation. The process of dispersion in methanol and centrifugation was repeated several times. This method of synthesis was also used for the subsequent acids described later.

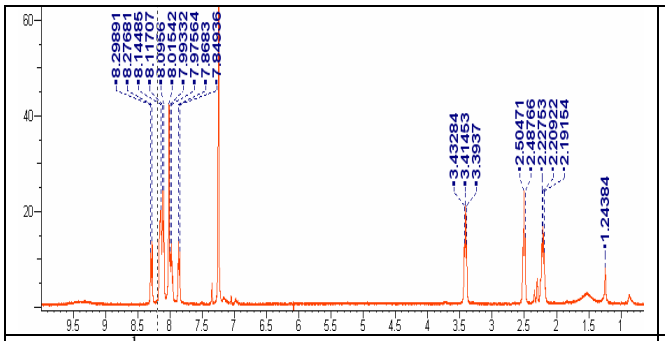


Figure 8: ^{1}H NMR of PBA in $CDCl_3$

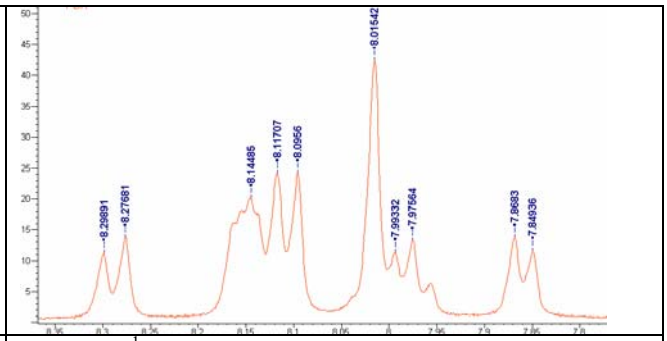


Figure 9: ^{1}H NMR of PBA in $CDCl_3$

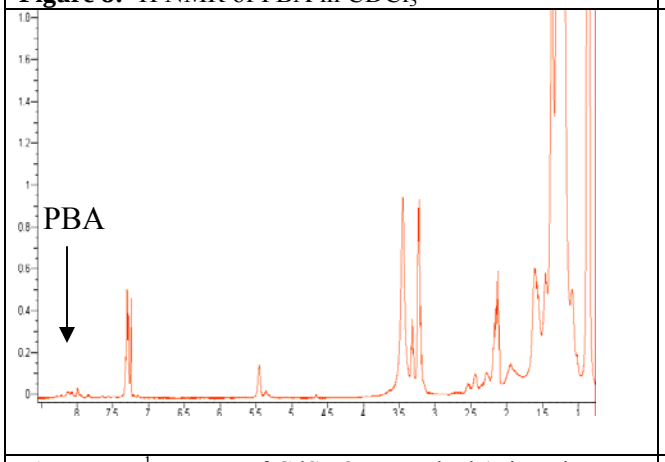


Figure 10: ^{1}H NMR of CdSe QDs washed 1 time, in $CDCl_3$

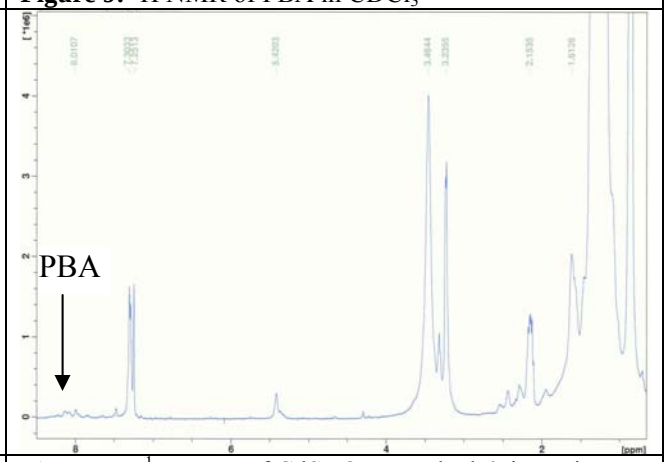


Figure 11: ^{1}H NMR of CdSe QDs washed 6 times, in $CDCl_3$

Comparison of ^{1}H-NMR spectra of PBA and CdSe QDs allowed us to conclude that PBA was present in CdSe QDs solution even after washing excess of ligands by methanol 6 times (Figure 8-11). With each of these subsequent washings the QDs luminescence became less intense, see figure 12, due to a reduction in the QD concentration within the remaining solution. In Figure 12 the peak at 475nm is due to PBA excimer formation, and as can be seen the excimers are not washed away. We have synthesized QDs of sizes from 2.5 nm up to 10 nm. But for large particles (bigger than 4 nm) luminescence from QDs disappears, and only luminescence from PBA excimer remains. By modifying the synthetic procedure we were able to produce QDs with concentrations of bound PBA, see NMR spectra in Figure 16, that did not form excimers, as indicated in the lack of a peak at 475nm in the luminescence spectra shown in Figure 17. We have also been able to correlated high concentrations of PBA with a reduction in the QD luminescence.

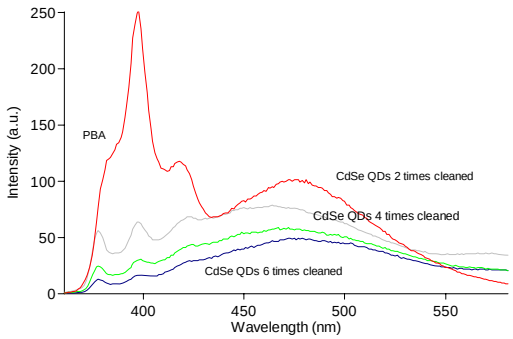


Figure 12: Luminescence spectra of several times washed CdSe QDs and PBA, λ_{ex}=300 nm

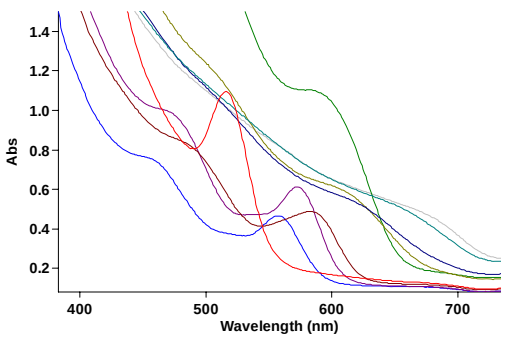


Figure 13: Absorption spectra of CdSe QDs (with PBA) of different sizes: from 2.5 nm up to 10 nm

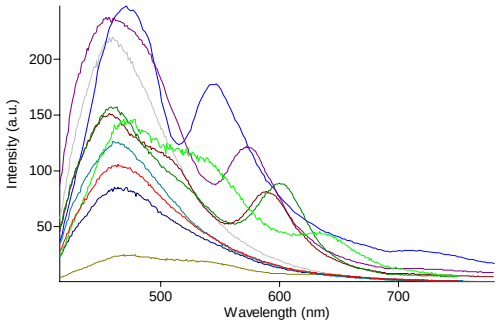


Figure 14: Luminescence spectra of CdSe QDs (with PBA) of different sizes: from 2.5 nm up to 10 nm, λ_{ex}=400 nm.

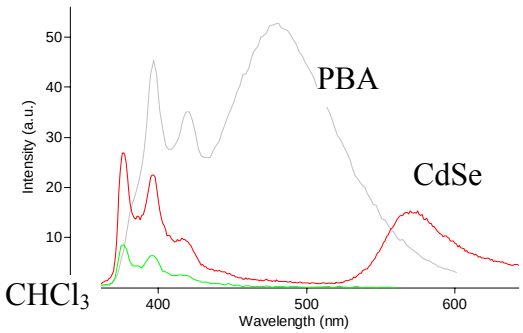


Figure 15: Luminescence spectra of $CHCl_3$, CdSe, PBA, λ_{ex}= 330 nm

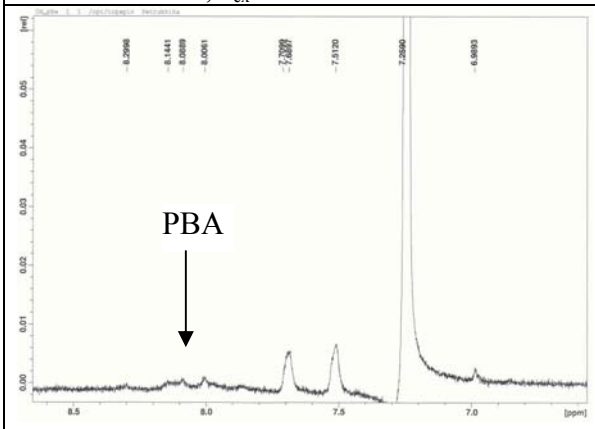


Figure 16: ^{1}H NMR spectra of CdSe QDs with PBA on the surface

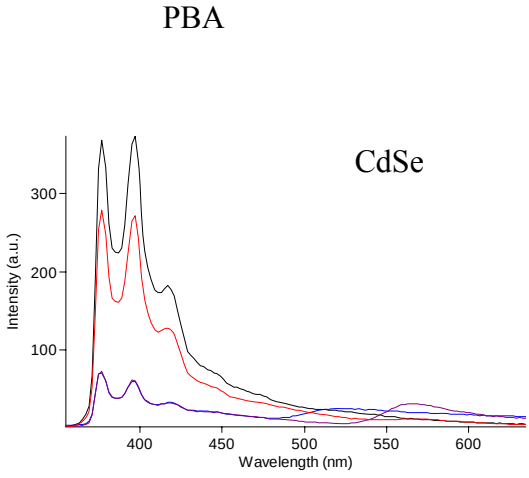


Figure 17: Luminescence spectra of CdSe QDs λ_{ex}= 340 nm

6) CdSe QDs with Benzylbutyric acid (BBA)

As our goal was to modify the surface of CdSe QDs by perfluorinated and nonfluorinated arene carboxo-bound ligands, we chose this method using benzylbutyric, benzoic,

pentafluorobenzoic acids as surface bound ligands. It is necessary to mention in the synthesis of CdSe with BBA even during the heating of CdO with BBA it is possible to observe fast dissolution of CdO even at 150ºC that means that BBA interacts with CdO. BBA is adsorbed on the surface of CdSe QDs, since it is possible to observe it in ^{1}H NMR spectra of CdSe QDs solutions (Figure 18-20). In luminescence spectra of BBA it is possible to observe 2 maxima (Figure 21) at 280 and 560 nm. The peak at 280nm corresponds to known peaks observed for BBA. The maximum at 560 nm was not observed in the literature for BBA and cannot be attributed to excimer formation, since excimer emission is usually in the range 430-480 nm. In luminescence spectra of CdSe QDs of different sizes it is possible to observe emission maximum in the case of small particles at 460 nm, which could be attributed to BBA excimer (Figure 23). In other cases no excimer maxima was observed.

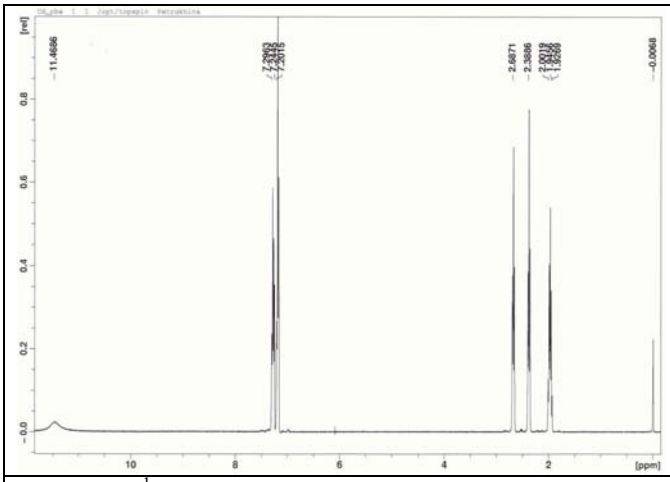


Figure 18: ^{1}H NMR spectra of BBA in $CDCl_3$

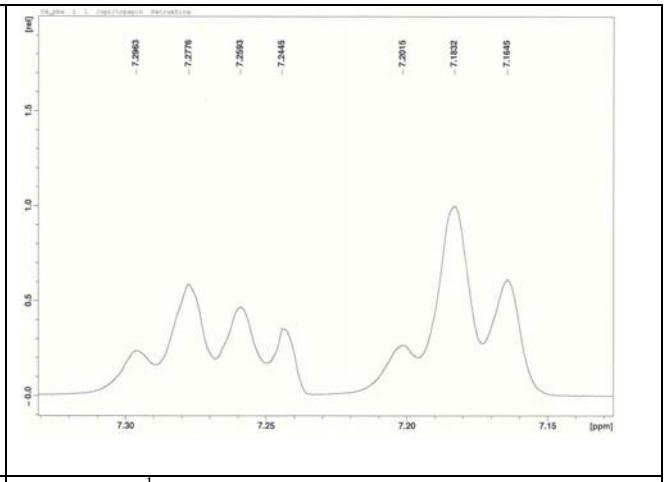


Figure 19: ^{1}H NMR spectra of BBA in $CDCl_3$

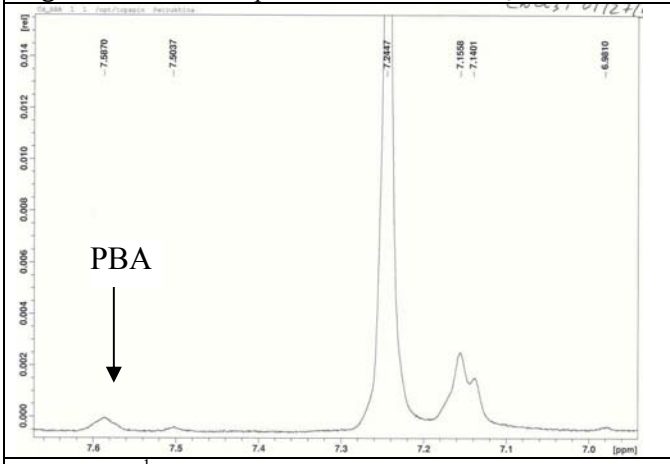


Figure 20: ^{1}H NMR spectra of CdSe QDs with BBA in $CDCl_3$

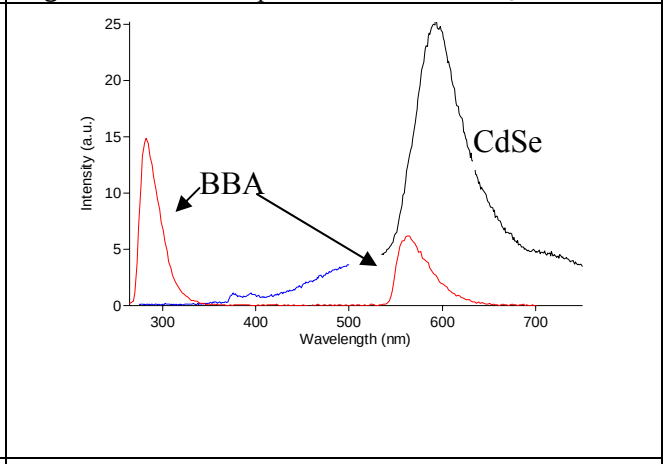


Figure 21: Luminescence spectra, λ_{ex}= 260 nm of CdSe QDs and BBA

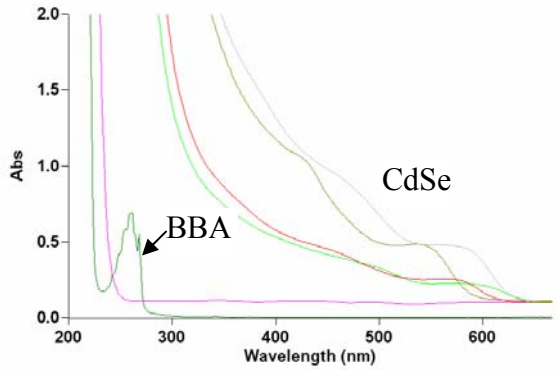


Figure 22: Absorption spectra of CdSe QDs, BBA in acetonitrile, $CHCl_3$

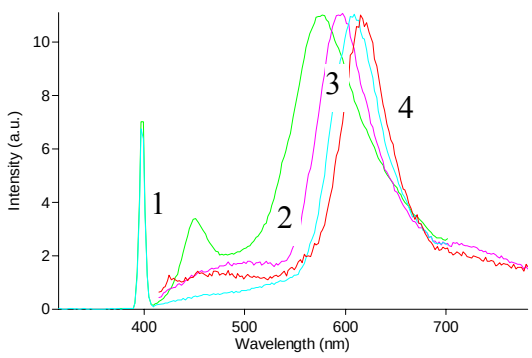


Figure: 23 Luminescence spectra, λ_{ex}= 400 nm of different size CdSe QDs with BBA on the surface

7) CdSe QDs with Benzoic acid (BA)

Another sensing ligand we used was BA. As with BBA, BA easily react with CdO during synthesis. In luminescence spectra we did not detect formation of BA excimer (Figure 25). In ^{1}H NMR spectra of BA and CdSe in $CDCl_3$ (Figure 26) it is possible to observe chemical shift of BA signals, indicative of BA attachment to CdSe QDs. Also one can conclude that there is equilibrium between BA on the surface and in solution (Figure 26). Addition of known amount of CH_2Cl_2 to CdSe QDs sample allows the determination of the bound BA with respect to bound TOPO. (Figure 27) Integration of CH_2Cl_2 let roughly estimate amount of BA and TOPO on the surface. According to this estimation there are about 1 molecule of BA and 122 molecules of TOPO.

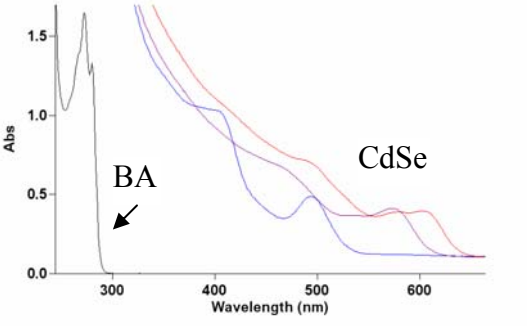


Figure 24: Absorption spectra of CdSe QDs with BA

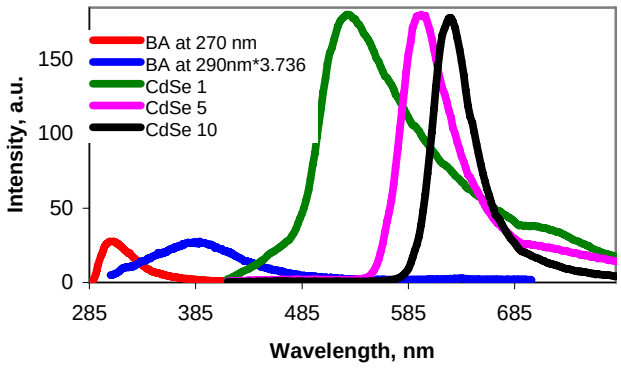


Figure 25: Luminescence spectra of CdSe QDs with BA, λ_{ex}=400 nm; and BA λ_{ex}=270 and 290 nm

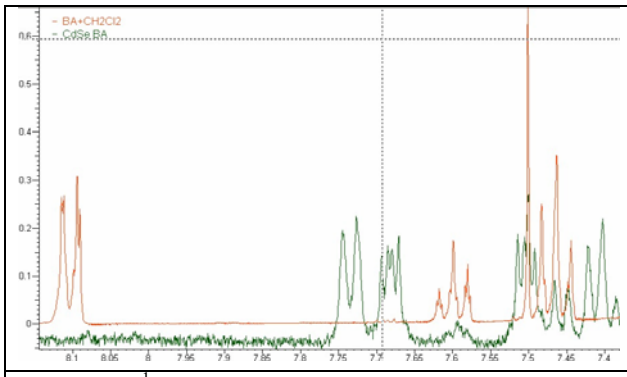


Figure 26: ^{1}H NMR spectra of BA and CdSe in $CDCl_3$

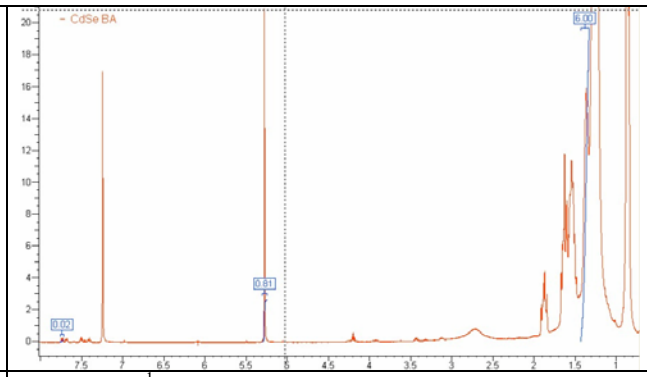


Figure 27: ^{1}H NMR spectra of CdSe + CH_2Cl_2, in $CDCl_3$

8) CdSe QDs with Perfluorobenzoic acid (FBA)

Using FBA instead of BA should provide better sensing properties of CdSe QDs. Intensity of luminescence excitation spectrum of CdSe QDs with FBA is very high and covers emission spectrum of FBA. In luminescence emission spectra of CdSe QDs with FBA on the surface one can observe high intensity of FBA excimer. It is necessary to note, that while increasing the QD size, the excimer emission (at 470 nm) decreases (Figure 29). Depending on the excitation wavelength intensity ratio of FBA excimer and CdSe QDs luminescence can vary.

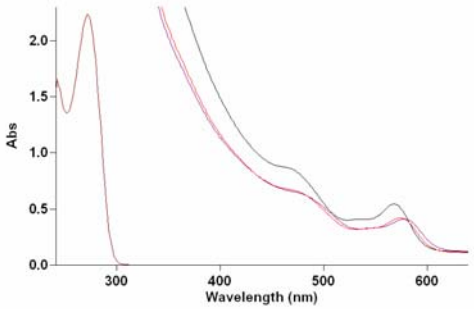


Figure 28: Absorption spectra of CdSe QDs with FBA

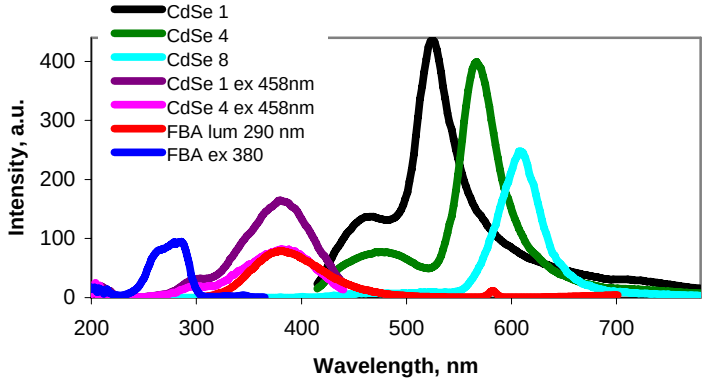


Figure 29: Luminescence excitation (λ_{em}= 380 nm, blue) and emission (λ_{ex}=290 nm, red) spectra of FBA. Luminescence excitation (λ_{em}= 458nm) and emission (λ_{ex}=400 nm) spectra CdSe QDs with FBA on the surface

9) CdSe QDs synthesized from preorganized clusters $Li_4[Cd_{10}Se_4(SPh)_{16}]$

Thiophenol (PhSH) was chosen as another type of sensing ligand, which has strong binding to CdSe surface. Synthesis of CdSe QDs from preorganized complex $Li_4[Cd_{10}Se_4(SPh)_{16}]$ was used to bind PhSH on the QDs surface.

Approximately 55 g of HDA (hexadecylamine) was degassed under vacuum at 120ºC. To the stirred solution of HDA under N_2 was added 1.0 g (0.28 mmol) of previously synthesized $(Li)_4[Cd_{10}Se_4(SPh)_{16}]$[6] using standard airless techniques, and the solution temperature was raised to 220-240ºC (1ºC/min). Growth rates depend on the initial reactant concentration and can be followed by absorption spectroscopy. At the desired

crystal size, the reaction mixture was cooled by 20ºC and left overnight to narrow the size distribution by annealing the nanocrystals. The CdSe was isolated by selective precipitation by addition of 100 mL of anhydrous MeOH and centrifugation. Excess HDA was removed by subsequent resuspension in MeOH and isolation by centrifugation.

This method of QDs synthesis also allows narrowing CdSe QDs size distribution (Figure 30). NMR spectroscopy proves presence of thiophenol and hexadecylamine on the surface of CdSe QDs (Figure 31).

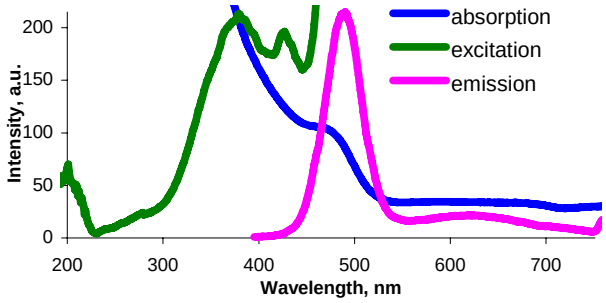


Figure 30: Absorption, excitation (λ_{em}=380 nm) and emission spectra of CdSe QDs with thiophenol, λ_{ex}=490 nm

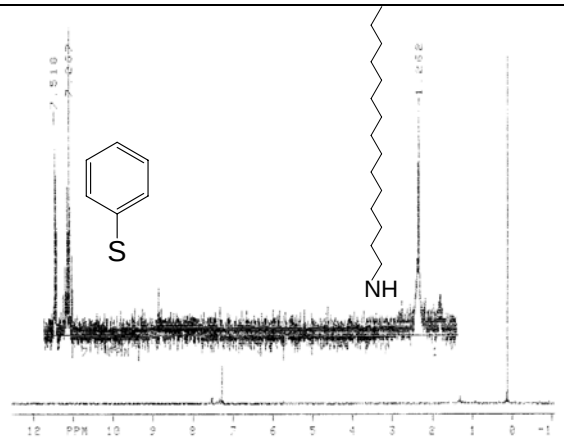


Figure 31: ^{1}H NMR spectra of PhSH-modified CdSe nanoparticles in $CDCl_3$

10) CdSe/ZnS[7] QDs

In order to improve stability and PL properties of CdSe QDs, a shell protected QDs were synthesized. A mixture of CdO 0.05 g (0.39 mmol), HDA 7.09 g (30 mmol) and TOPO 7.09 g (18 mmol) was heated up to ~340º C under N_2 flow on a Schlenk line. After the formation of a CdO–HDA complex, the system was allowed to cool to 260º C. As the temperature stabilized at 260º C for around 3–5 h, Se/TOP Se 0.0375 g (0.475 mmol) in 13.43 ml (50 mmol) TOP was quickly injected (<2 s) into the hot CdO/HDA/TOPO solution to proceed with the nucleation and the growth of CdSe nanocrystals. Subsequently, the Zn/S/TOP shell stock solution was injected to the core solution via the syringe, while the temperature remained at 230º C for the growth of CdSe/ZnS quantum dots. The injection of shell stock solution was divided into five portions at ~20 s intervals to minimize the nucleation of shell particles[8]. Upon injecting all the Zn/S/TOP shell stock solution, the reaction mixture was allowed to cool and stir at 110º C for a period of 1–2 h. The final molar ratio between Cd/Se (core) and Zn/S (shell) was kept constant, typically ~1:4.

Zn/S/TOP shell stock solution was prepared by dissolving $Zn(CH_3)_2$ ~156 µl (0.312 mmol) and hexamethylsilathiane $(TMS)_2S$ ~162 µl (0.137 mmol) in TOP 12 ml (48 mmol) at room temperature. The use of very volatile and reactive $(TMS)_2S$ as a sulfur

precursor requires a separated glove box that is currently unavailable. Other sulfur-containing sources should be considered and tested.

For the above-described core/shell formation, the precursor concentrations were largely diluted by TOP and HDA, resulting in a significant reduction of the particle growth rate. The resulting nanocrystals with selected diameters and shell thickness could thus be extracted at different aging times. Isolation and purification of crystallites was made in $CHCl_3/CH_3OH$ system. For characterization purposes, several aliquots of 100 µl of reaction mixture were taken by syringe and diluted by 2 ml of $CHCl_3$. First few of them are of the CdSe particle solution, next – right after the injection of ZnS precursors, last – 5 minutes after injection.

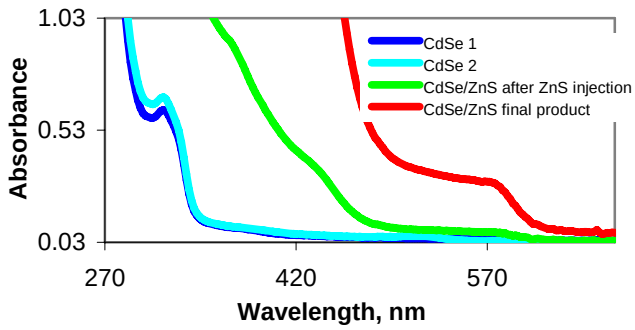


Figure 32: Absorption spectra of CdSe and CdSe/ZnS QDs in the process of their growth

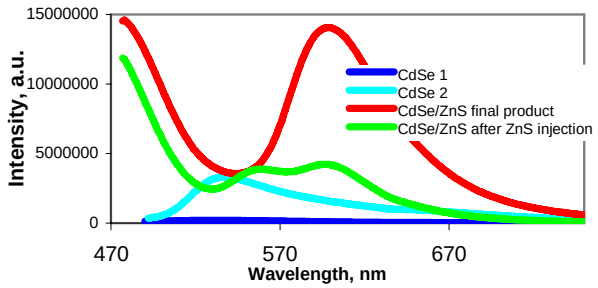


Figure 33: Photoluminescence spectra of CdSe and CdSe/ZnS QDs λ_{ex}=377 nm

Based on the data obtained we can conclude that initially formed CdSe nanoparticles are about of 1 nm in diameter (absorption band at 316 nm, Figure 32). Importantly, photoluminescence emission of QDs covered by ZnS is increased compared to the unprotected CdSe particles as shown in Figure 33.

11. TEM Analysis

The QDs have been analyzed using transmission electron microscopy, for investigation of the size distribution and corresponding crystallinity. As is shown in Figure 34 the QD are nominally 2 nm in diameter and as detailed in the HRTEM shown in the inset the QDs have a high degree of crystallinity. Dr. Oxana Vassiltsova received training on TEM instrumentation during the 2nd stage of the program and will be performing these measurements to confirm the size distribution calculated from the optical analysis.

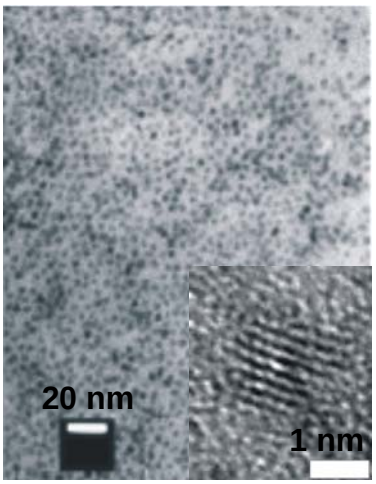


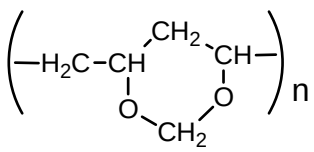
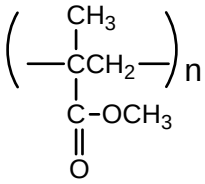
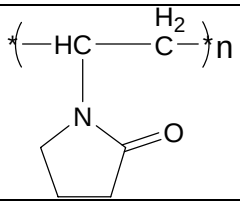
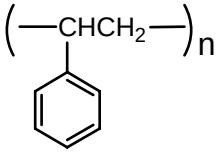
Figure 34: TEM micrograph of CdSe QDs, HRTEM of single QD shown in inset

Incorporation of QDs into Composite films

Incorporation of the tailored QDs into a polymer matrix is a key step towards developing a quantum dot based chemical sensor. The polymer matrix will not only

serve as protection against oxidation of the semiconductor quantum dot but will also be used for a level of selectivity in the sensing process. Specifically the polymer hosts, as detailed in Table 1, have been chosen to preferentially adsorb the chemical class of interest (hydrophobic or hydrophilic hydrocarbons). We will be investigating methods of depositing libraries of QD-polymer material formulations to be printed. This library of films will then be tested in a parallel fashion using the sensing system described in the next section.

Table 1

Formvar	Poly(methyl methacrylate)	Polyvinyl pyrrolidone	Polystyrene
			

Several samples of CdSe QDs prepared as above have been used for the polymer encapsulation experiments. We have prepared composite films by incorporating the QDs into two types of polymers, Formvar and PMMA as depicted in Table 1.

Deposition of Nanocomposite Sensing Films

Semiconductor quantum dots/ polymer sensing films of micron-range thickness were prepared by drop coating of CdSe/PMMA solutions (in chloroform) on Si substrates. The QD concentration in the polymer matrix was designed to achieve a strong fluorescence output and an enhanced surface passivation for the dots at the same time. The detailed dot size and mole concentration in the polymer matrix are listed in Table 2, where the dots were covered with three respective surfaces groups in additional to TOPO ligand.

	CdSe-SA/PMMA	CdSe-FBA/PMMA	CdSe-BA/PMMA
Size (nm)	2.8	3.6	3.6
Concen. (mol/g)	6.7×10^{-7}	4.4×10^{-7}	2×10^{-7}

Sensor Testing Station Results

A micro-testing chamber has been installed and is shown in Figure 35. The test chamber is designed using 2.75" conflat vacuum components and has an internal volume of 20ml. The nanocomposite films are mounted in the chamber and gases of various compositions can be passed over the samples. A Varian Eclipse spectrofluorometer with a fiber coupling attachment is used for the fluorescence

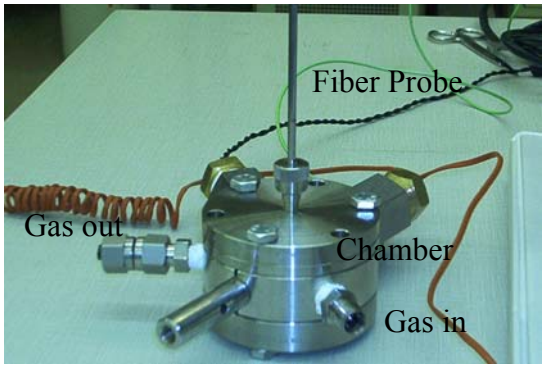


Figure 35: Test chamber used for QD exposure experiments

analysis of single nanocomposite films. In order to perform hydrocarbon (HC) exposure tests, a reliable HC vapor source is required. In this test, a vapor producing system via a Kontes bubbler and Environics gas mixing system was designed and integrated to deliver HC vapor to a 20cc stainless test cell with the vapor concentration adjustable from several ppm to several percent by changing of the gas flow rate. Both pressure and temperature of the bubbler is monitored to ensure a reliable vapor concentration delivered.

The HC response properties of the films were characterized by monitoring peak fluorescence intensity change of the QDs while the gas environment of the test cell was varied from pure N_2 to a HC vapor in N_2 through the computer controlled vapor producing system and the Environics gas mixing system. The total test gas flow, pressure and temperature were maintained at 1200sccm, 760 Torr and ~ 25 ºC, respectively. A Varian Eclipse Spectrofluorometer, Figure 36, was employed to record the fluorescence intensity via an optical fiber assembled accessory, which utilizes a bifurcated optical fiber bundle to direct a single (choosing 350nm in this test) excitation wavelength from a Xenon light source to the sample and collect emitted fluorescence light from the QDs for detection by a monochromator and a photomultiplier tube detector housed within the Eclipse spectrofluorometer.

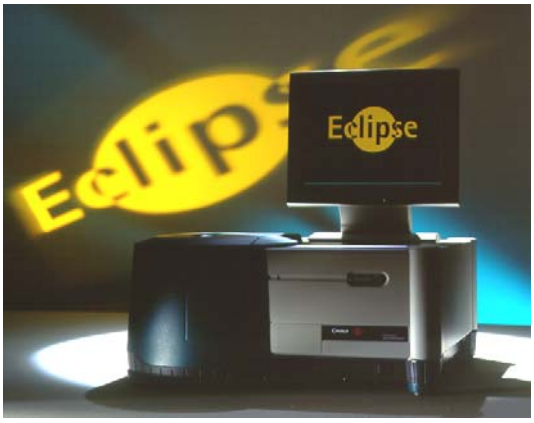


Figure 36: Varian spectrofluorometer to be used for parallel testing of QD film libraries

The current testing chamber, Figure 35, only allows for one sample at a time to be investigated. **During year 2** of the program we intend to increase our efficiency by depositing an array of films with QDs of varied composition and mass loading, different polymer hosts and polymer viscosities. This **library** of films, deposited in a **parallel** fashion could

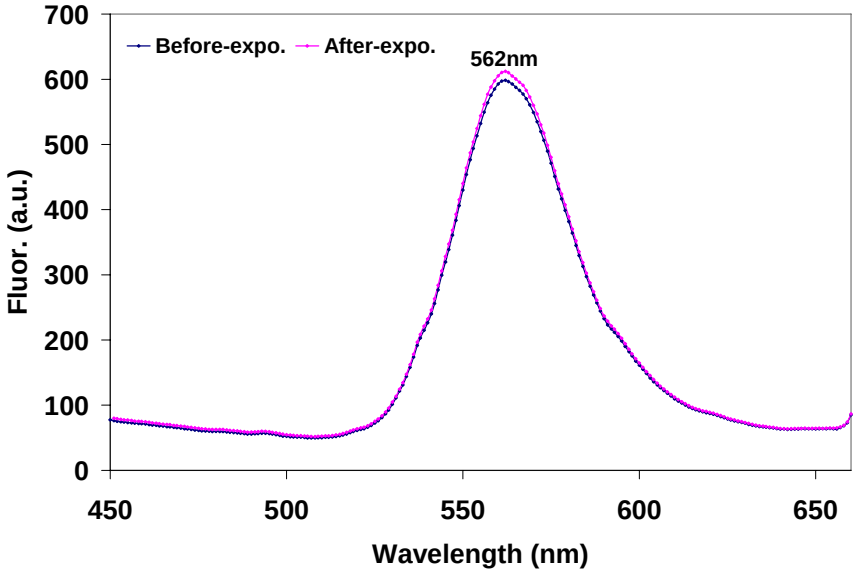


Figure 37: A comparison of fluorescence of a CdSe-SA/PMMA film before and after hydrocarbon exposure

then be tested in a **parallel fashion** and **speed** the testing and analysis by **orders of magnitude**, as only films that tested with positive sensing attributes for the chemicals of interest would be processed for a detailed materials analysis. The Varian Eclipse system will allow for the optical fluorescence testing of a library of films, up to 12 elements in the deposited array, as a function of a change in the gaseous hydrocarbon environment. A miniature testing chamber has been designed, that will be placed in a standard micro-well plate holder accessory for analysis with the Varian Eclipse system.

Figure 37 displays the fluorescence spectrum of a CdSe-SA/PMMA film before and after HC exposure, where SA serves as a surface-stabilizing group. The spectra show good repeatability, indicating the efficient reversibility from the HC exposure.

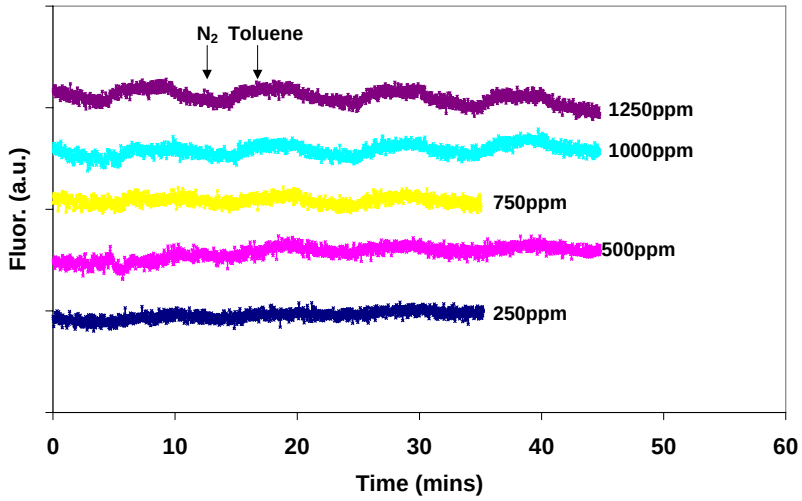


Figure 38: Toluene response of a CdSe-SA/PMMA film as a function of time

The peak (562nm) fluorescence intensity resulting from excitation at 350nm, was monitored in the exposure test with toluene and xylenes. Figure 38 shows that the fluorescence intensity reversibly increases upon exposure to toluene at concentration levels from ~ a thousand down to hundreds of ppm. The sensitivity to toluene is approximately 250 ppm. When exposed to xylenes, the fluorescence reversibly increases over a similar ppm concentration range (Figure 39), while the sensitivity of the film for xylenes is increased to approximately 100ppm, a factor of 2.5 higher than that for toluene.

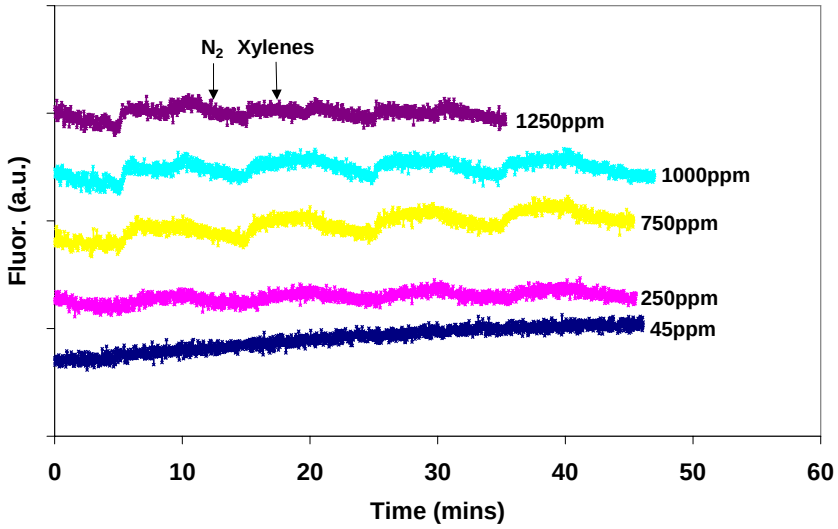


Figure 39 Xylenes response of a CdSe-SA/PMMA film as a function of time

In contrast to the above response, when exposed to high concentrations, i.e. percent level

concentrations of HCs, the fluorescence intensity displays a significant decrease rather than an increase in fluorescence intensity for both toluene and xylenes vapors, as shown in Figure 40. The decrease in fluorescence results from an interaction of the PMMA matrix with the hydrocarbon chemicals, which results in a swelling of the polymer film, and likewise induced a drop in the fluorescence intensity. The matrix swelling effect became noticeable at levels as low as ~1250ppm for xylenes, as indicated in Figure 39 by the decrease in signal change at the higher xylene concentrations.

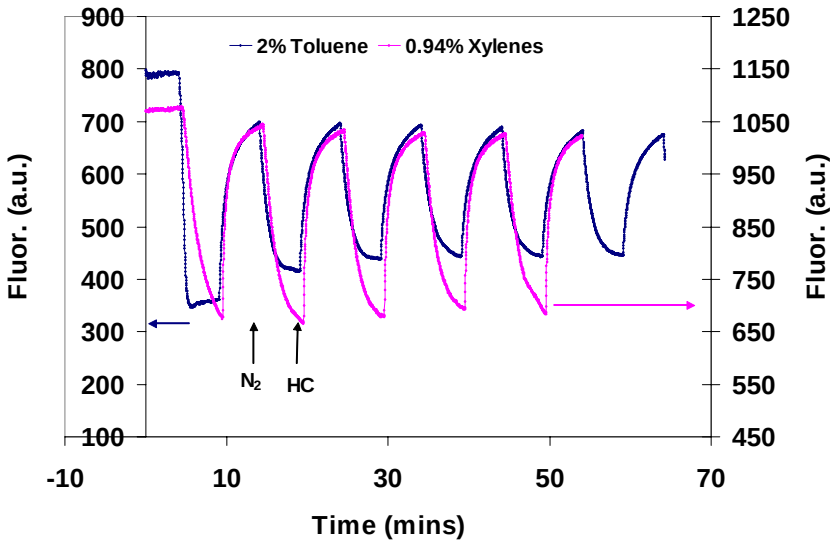


Figure 40: Responses of a CdSe-SA/PMMA film toward exposure to high concentrations of toluene and xylenes

In order to improve the sensitivity of the QDs towards the targeted HCs, aromatic sensing groups of fluorobenzoic acid (FBA) and benzoic acid (BA) were grafted to the QD surface, with an expectation of an increase in the sensitivity towards the detection of the HCs. Figure 41 displays the fluorescence spectrum of a CdSe-FBA/PMMA film before and after a HC exposure, which again indicates the stability of the films. The QD fluorescence peak at 587 nm was monitored under the excitation of the same 350nm light for the exposure experiments. The broad peak at 458nm arises from FBA group.

What is particularly promising is that these tailored QD-polymer films demonstrate an increased sensitivity to less than 15ppm for xylenes (Figure 42) and less than 50ppm for toluene (Figure 43), a factor of more than five enhancement in the sensitivity compared to the above SA-grafted QDs. This film also presents an improved selectivity for xylenes over toluene, as shown in Figure 44, for 50ppm concentrations.

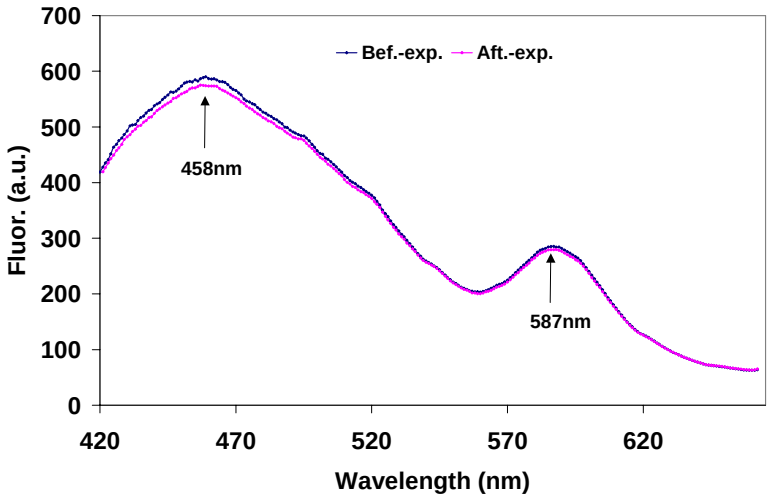


Figure 41: A comparison of fluorescence of a CdSe-FBA/PMMA film before and after hydrocarbon exposure

Figure 45 compares the sensing capability of the different

sensing groups attached to the QD surface towards 50ppm of xylenes. It is clear that the aromatic group modified QDs have a higher sensitivity to xylenes compared to that of the stearic acid sensing ligands. Furthermore, there is a slight increase in sensitivity for the fluorinated benzoic acid sensing ligand over the non-fluorinated benzoic acid sensing group.

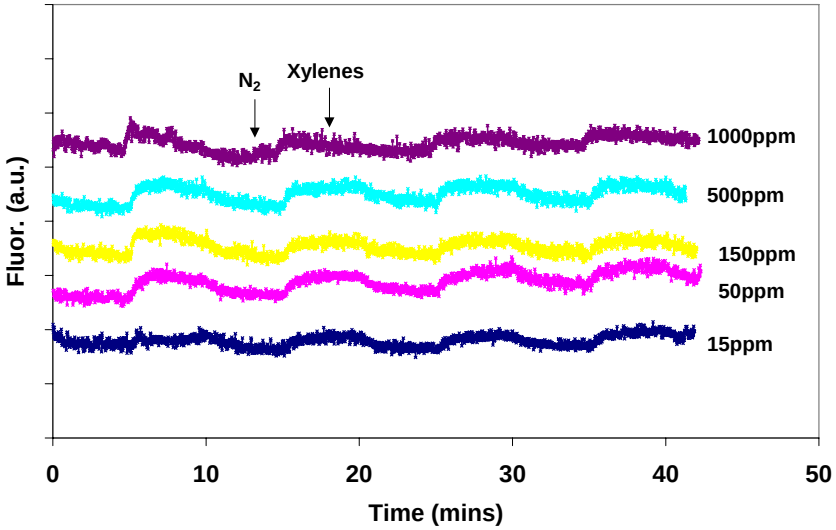


Figure 42: Xylenes response of a CdSe-FBA/PMMA film as a function of time

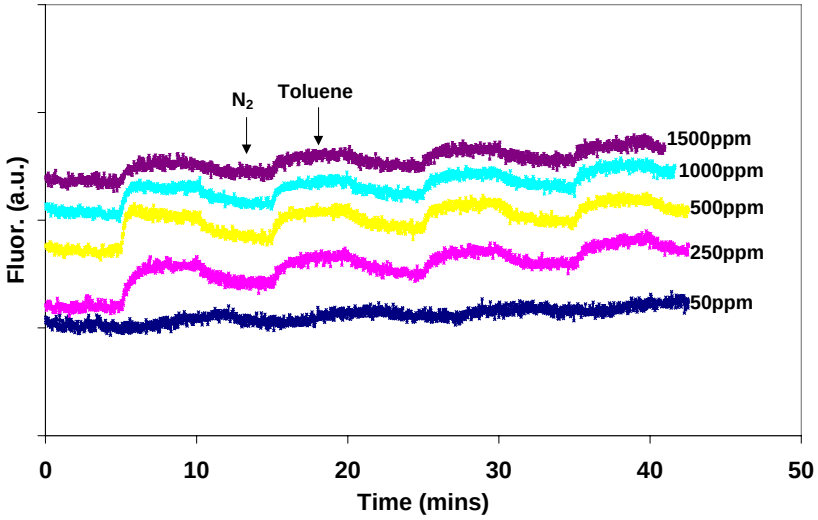


Figure 43: Toluene response of a CdSe-FBA/PMMA film as a function of time

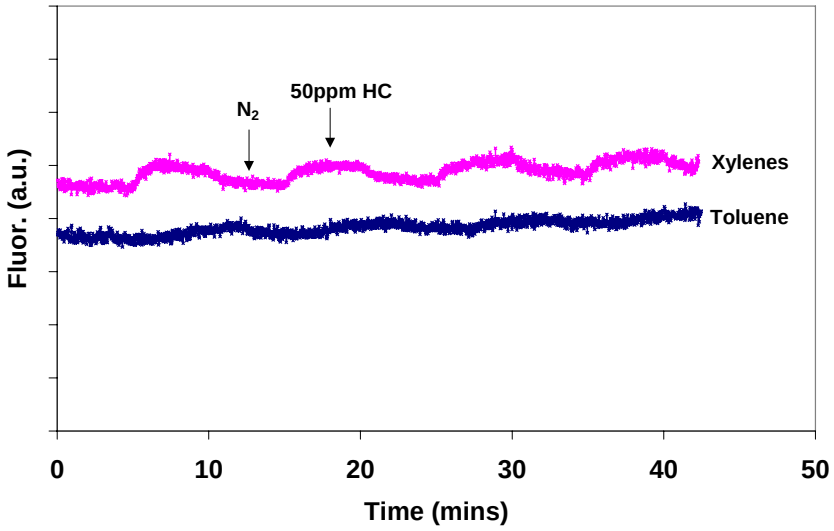


Figure 44: A comparison of sensitivities of a CdSe-FBA/PMMA film toward 50ppm xylenes and toluene

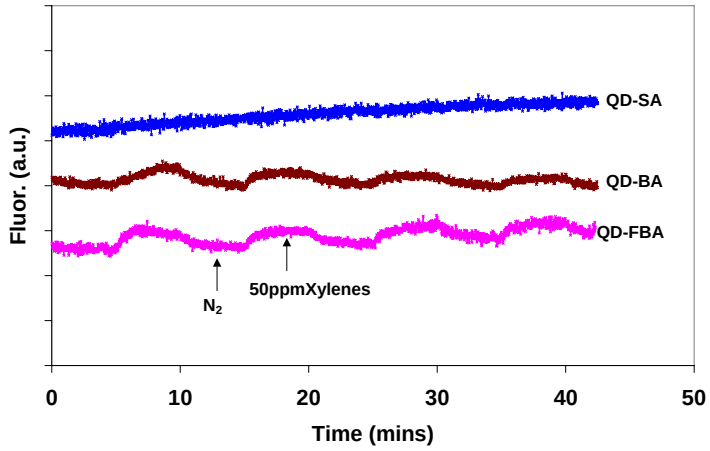


Figure 45: A comparison of sensing capabilities of aromatic group tailored and non-tailored QDs films toward exposure to 50ppm xylenes

Sensor Testing and Polymer Film Formation: Future Work

- Further tailor CdSe QDs with different surface functional groups that allow for higher sensitivity and selectivity toward targeted chemicals
- Stabilize existing CdSe-FBA (BA) systems with enhanced quantum efficiency and stability for following tests in a real carrier gas, air
- Perform extensive research on the QD/polymer system to optimize the nano-composite films by determining a most appropriate polymer matrix that will permit a high solubility of QD, a good passivation for the QD, a high chemical resistance and enhanced mechanical stability

- Investigate dependences of the sensing capability on film thickness, QD concentrations and film microstructures
- Characterize the sensing properties as a function of temperature, relative humidity and background gases
- Enhance sensitivity, selectivity reliability, lifetime and durability of the sensing films by smart sensor array designs
- Develop parallel deposition and testing techniques to increase throughput by an order of magnitude, thus enhancing the rate at which the selective and sensitive films are developed

Conclusions

In summary, we have completed the first year of the research program for the development of a portable petroleum by-products chemical sensor. While the contract start date is listed as Aug. 2003, we did not receive a signed and activated contract to begin these studies until Aug. 2004, and were operating on partial funding since March 2004. Even with these delays the progress described in this report is very promising, as we have demonstrated the ability to synthesize and characterize QDs of sizes ranging from 1.8 nm up to 10.4 nm in diameter. Emission wavelengths are in the range from 517 to 681 nm. CdSe QDs covered by ZnS surface were synthesized as well. Synthesized nanoparticles are stable, uniform and have good crystallinity (as proven by TEM) and have bright emission. We adapted several techniques of QDs synthesis with grafting of several new sensing ligands on the QDs surface. Attachment of these ligands to the surface of QDs was confirmed using ^{1}H-NMR analysis. QDs with grafted sensing ligands on the surface were incorporated into various polymer matrices to form QDs-based composite films. We have begun exposure tests of these films that have shown a high degree of selectivity and sensitivity to xylenes and toluene at ppm concentrations. What is particularly promising is that by tailoring the sensing ligands attached to the QD surface, we are able to achieve a factor of 5 enhancement in the sensitivity of the QD-polymer film. For example, for the perfluorinated benzoic acid ligand, fluorescence intensity changes are more pronounced than for nonfluorinated benzoic acid, which has different electrophilic properties. Selected systems have been tested in high hydrocarbon concentration range (up to 1%) and low concentration range (up to 15 ppm). At high hydrocarbon concentrations, polymer matrix swelling effects are attributed to the observed fluorescence intensity changes. At low hydrocarbon concentrations the main contribution in fluorescence intensity changes is due to formation of π-complexes of aromatic hydrocarbons with the sensing ligand on the QDs surface, which result in the luminescence changes of the QDs. The results obtained at this stage strongly support the proposed concept and show the potential of surface modified QDs for sensing applications.

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