Supporting Information

S-1

Quantum Dot and Polymer Composite Cross-Reactive Array for Chemical Vapor Detection

Collin J. Bright[1, 2], Eric C. Nallon[1], Michael P. Polcha[1, 3], Vincent P. Schnee[1*]

1 RDECOM CERDEC Night Vision and Electronic Sensors Directorate, United States Army,
Fort Belvoir, Virginia 22060 United States

2 CACI International Inc.
Arlington, Virginia 22201

3 Fulcrum IT Services,
Centerville, Virginia 20120, United States

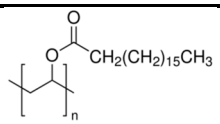
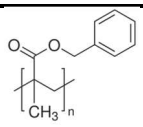
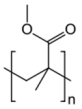
Abstract

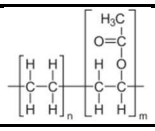
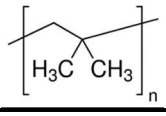
In the full text, a novel study based on a cross-reactive chemical sensing array produced from CdSe Quantum Dots (QD) and multiple organic polymers is presented. In this supporting information, additional details regarding the organic polymers, sensor fabrication, sampling procedures, and data analysis are presented.

Organic Polymers

The structure of each of the five polymers used to modify the QD and their respective abbreviations are shown in Table S-1.

Table S-1: Names, abbreviation and structures of the five polymers used in this work.

Name	Abbreviation	Structure
Poly(vinyl stearate)	OP1	
Poly(benzyl methacrylate)	OP2	
Poly(methyl methacrylate)	OP3	

Poly(ethylene-co-vinyl acetate)	OP4	
Poly isobutylene	OP5	

Sensor Fabrication

The printings solutions were comprised of QDs and a single polymer dissolved in toluene. Typical solutions were 6.5-6.7 mg/mL QD and 2.5-2.75 mg/mL polymer. Solutions were prepared by dissolving 8 mg of polymer in 5 mL of toluene and sonicating at room temperature. The solution was then filtered through a 0.45 µm filter in order to ensure that all particulate matter which might interfere with inkjet printing was removed. This polymer solution (0.25 mL) was then combined with the stock 10 mg/mL QD solution (0.5 mL) to produce the desired concentration of QD and polymer for printing.

Images of the individual drops were captured as they were ejected from the print head by the Jet Lab4's integrated camera. The images were processed using ImageJ, in conjunction with a calibrated microscope slide from Thorlabs which has 25 micron divisions. An image of the drop was captured at multiple points during flight and at various stages in the printing process. The drop diameter was measured at each point. Using a spherical fit, the calculated volume of the drop at each point was used to determine an average drop volume ranging from 40-60 pL. Using this calculated volume, the known number of drops and the known concentration of the print solution, the QD surface concentration was calculated. To confirm the surface concentration of the QDs, absorbance measurements of the residues were made using an Agilent 8453. The measured absorbances were compared to a serial dilution of the QD stock solution. The solid residues and liquid QD solutions were measured on the same instrument using the same custom 4.2 mm diameter aperture. This allowed for comparison of the mass per area to mass per volume to be made.

Quartz Slide Cleaning Procedure

Quartz substrates used for sensor fabrication were cleaned prior to printing by sonication in a (2% wt) sodium dodecyl sulfate solution for 30 minutes, followed by a thorough deionized water rinse and drying in an oven at 100°C. The slides were then sonicated in acetone for 30 minutes and again dried in an oven. Finally, the slides were sonicated for 30 minutes in toluene and dried in an oven before being transferred to a sealed container for storage.

Sampling

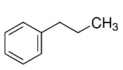
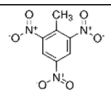
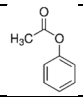
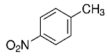
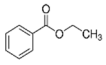
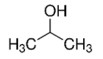
The custom mount which holds the linear fiber array in line with the sample slide and forms a flow channel across the sensing material was attached to an MKS mass flow controller, which precisely regulates rates of laboratory air and analyte vapor to be pulled through the flow channel and across the sensor. The mass flow controller allowed the flow rate to be adjusted up to 100 sccm.

The custom built auto-sampler consisted of two mechanical parts, a linear actuator to provide vertically movement of the sensor assembly and a carousel to select the desired sample vial. Movement of the sensor assembly and sample vials was controlled with two Animatics SmartMotor^{TM} integrated servo

motor systems. A Python script is used to coordinate all aspects of the auto sampler, to include: which vial (of up to 18 possibilities) is to be sampled, the sample name, baseline time, sampling time, recovery time, flow rate, dilution flow rate, input light intensity, integration time, and data logging. Controls are dictated through a user defined CSV file which is read in prior to starting a run.

The analytes used in this study were broken into two groups. The Test Set 1 consisted of substituted benzene compounds, and Test Set 2 included explosives, explosive manufacturing materials, and common interferents. The name abbreviations used in this work and structure for both sets of analytes are listed in Table S-2.

Table S-2: Names, abbreviation and structures of the analytes tested in this work.

Test Set 1					
Toluene (Tol)		Chlorobenzene (ClB)		Nitrobenzene (NitroB)	
Ethylbenzene (EtylB)		Bromobenzene (BrB)		1,2-Dinitrobenzene (12DNB)	
Propylbenzene (PropylB)		Iodobenzene (IB)		1,3-Dinitrobenzene (13DNB)	
O-Xylene (OX)		Phenol (Phenol)		1,4-Dinitrobenzene (14DNB)	
Benzonitrile (BZN)		3-Nitrotoluene (3NT)			
Test Set 2					
2,4,6-Trinitrotoluene (TNT)		Phenyl Acetate (PhAc)		4-Nitrotoluene (4NT)	
Ethyl Benzoate (EthyBZ)		Cyclohexanone (CXN)		Benzyl Alcohol (BZOH)	
Chloroform (CHCl3)	$CHCl_3$	Acetone (Acetone)		Isopropanol (IPA)	
Ammonium Nitrate (AN)	NH_4NO_3	Methanol (MeOH)	CH_3OH	Gasoline* (Gas)	
Kerosene* (Kene)					

Data Analysis

During each trial, the start and stop times of each baseline measurement and the time of each movement of the sensor assembly or sample vial were recorded, enabling each trial to be divided into three periods: baseline, sampling and recovery. A notional representation of the three sampling periods can be seen in Figure S-1. The time and intensity information for each of the three periods were captured for each sample during each sampling event and used as the basis for much of the post processing.

The baseline period begins with the sensor is being exposed to laboratory air, typically for 60 seconds. During this time, the sensor is allowed to collect a 'baseline' sensor response. In order to calculate the baseline reading, average response for each ROI is calculated from initiation of the sample, until the vial is moved into place and the sensor head is lowered into the vial. It should be noted that in order to eliminate any variation in the calculated baseline value, the first and last 50 data points (3.33 seconds at 15 Hz) are not included in the calculation.

The sampling period begins when the sensor assembly is lowered into the vial, allowing the vacuum to draw the analyte vapor across the sensor. During sampling, there is a rapid response of the sensing material's emission intensity to the analyte vapor. The response is seen as an increase or decrease in fluorescence, and depends on the analyte sampled as well as the QD/polymer composite present.

When the sensor assembly is removed from the vial, the sampling period is complete and the recovery period begins. During the recovery period, the sensor is once again exposed to laboratory air and allowed sufficient time to return to a 'baseline' state. During the recovery period, the signal intensity is monitored as the sensor returns to a 'baseline' state.

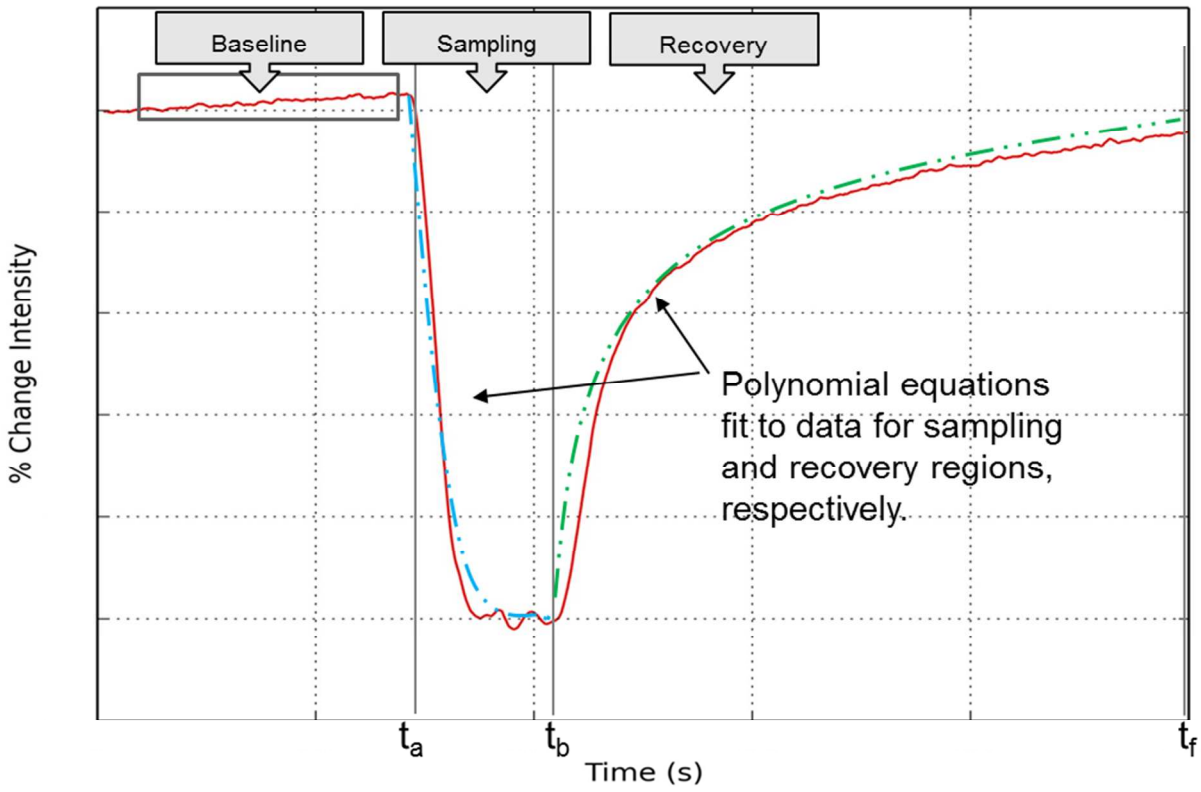


Figure S-1. Notional representation of sensor response, showing I) Baseline region, II) Sampling region and III) Recovery region. Polynomial equations are fit to the data for the sampling and recovery regions of the data. The coefficients of the equations are used to distinguish between analytes.