



Contact printing of a quantum dot and polymer cross-reactive array sensor



Vincent P. Schnee^{a,*}, Collin J. Bright^b, Eric C. Nallon^a, Michael P. Polcha^c

^a RDECOM CERDEC Night Vision and Electronic Sensors Directorate, United States Army, Fort Belvoir, VA, 22060 United States

^b CACI International Inc., Arlington, VA 22201, United States

^c Fulcrum IT Services, Centerville, VA 20120, United States

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ABSTRACT

Contact printing of Quantum Dot (QD) and organic polymer (OP) composites is explored as an alternate method of fabricating a cross-reactive chemical sensor array. Sensing layers fabricated by inkjet printing and contact printing methods are compared, showing that contact printing methods demonstrate a more uniform distribution of the QDs and higher signal to noise ratios (SNRs) when exposed to chemical vapors. A cross-reactive array was then fabricated with CdSe QDs and five OPs and exposed to the vapor of 15 common laboratory solvents. Principal component analysis (PCA) of the data showed high dimensionality of the sensor array response and linear discriminant analysis (LDA) produced correct classification of the target analytes in 100% of test cases.

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1. Introduction

Quantum Dots (QDs) or semiconducting nanocrystals, with their well known, size dependent properties, offer new avenues to the development of electronic devices. One of the challenges in realizing the potential of QD-based devices is the incompatibility of QDs with traditional microfabrication techniques, such as thermal evaporation, and intolerance of QD layers to solvents limiting the usefulness of photolithography. Some of the device fabrication challenges have been overcome by the development of contact printing using elastomer stamps [1], which allows for the high resolution deposition of QD structures and films [2,3]. Contact printing has been employed to deposit QD films used in light emitting diodes [4,5], full-color displays [6,7], photovoltaics [8], and optical elements [9]. Films of organic polymers have also been demonstrated to make chemical sensors [10,11], electronic features [12], light emitters [13], and solar cells [14,15]. In this work we demonstrate the utility of contact printing for the fabrication of QD/polymer composite chemical sensing layers [16]. We demonstrate that contact printing is a versatile technique that allows chemically diverse QD/polymer composites to be deposited spatially close to one

another to form a cross-reactive array sensor. The first report of a QD cross-reactive array used inkjet printed composites of QD and polymer to distinguish two sets of chemicals, the first, a set of chemically similar substituted benzene compounds and the second, a set of explosives and environment interferents [16]. A subsequent study of a QD based array sensor used varying ligands to create diversity, and accurately identified explosives in solvent to the ppb range [17]. The present work also includes a comparison of contact printed and inkjet printed layers to determine the influence of film morphology on the sensor performance.

2. Materials and methods

2.1. Materials

The CdSe quantum dots (QDs) used in this study were Lumidot CdSe 480 core-type QD, purchased from Sigma-Aldrich (St. Louis, MO). All QDs were received in toluene (5 mg/mL) and stabilized with hexadecylamine. Other than solution concentration, no modifications were made to the QD. The Lumidot 480 QDs have a diameter of 2.1–2.3 nm and a maximum emission wavelength of 475–485 nm.

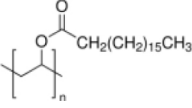
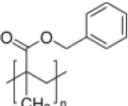
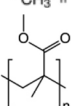
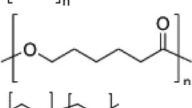
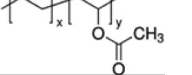
Five organic polymers were used to produce QD composites: poly(vinyl stearate), poly(benzyl methacrylate), poly(methyl methacrylate), poly(caprolactone) and poly(ethylene-co-vinyl

* Corresponding author.

E-mail address: vincent.p.schnee.civ@mail.mil (V.P. Schnee).

Table 1

Names, abbreviations and structures of the five organic polymers used to produce QD composites in this work.

| Name | Abbreviation | Structure |
|---------------------------------|--------------|--|
| Poly(vinyl stearate) | OP1 |  |
| Poly(benzyl methacrylate) | OP2 |  |
| Poly(methyl methacrylate) | OP3 |  |
| Poly(caprolactone) | OP4 |  |
| Poly(ethylene-co-vinyl acetate) | OP5 |  |

acetate); named OP1-5 respectively in the text and were all used as received from Sigma-Aldrich (St. Louis, MO). Table 1 shows the structure of each of these polymers and their respective abbreviations. The organic analytes tested against the array (acetone, acetonitrile, chloroform, methylene chloride, cyclohexanone, dimethyl sulfoxide, diethyl ether, 2-propanol, methanol, mesitylene, o-xylene, pyridine, tetrahydrofuran, and toluene) were purchased from Sigma-Aldrich at the highest purity. The water sample was collected from the in-house deionization system with a resistance of 18 M Ω at generation.

2.2. Inkjet printed sensor fabrication

Quartz substrates, 25 × 75 × 1 mm, with the short edges having an optical polish, were obtained from Pyromatics (Mentor, OH) and used to fabricate the sensor. The substrates were cleaned prior to printing, dried in an oven and transferred to a sealed container for storage. Inkjet print solutions were comprised of QDs and a single polymer dissolved in toluene. For the sensitivity study, OP2 was selected as the polymer matrix. The print solution was 5 mg/mL QD and 3.3 mg/mL polymer. The QD/polymer solutions were printed onto the cleaned substrates using a MicroFab Jet Lab4 (Plano, TX) print station. The print head used is equipped with a 40 μ m orifice and the print substrate was heated to 60–65 °C. Each QD/polymer composite was printed in an array of 10 × 20 ‘pixels’ that were centered 0.5 mm apart. Each pixel was formed from 40 to 120 individual drops of the print solution to reach the desired surface concentration. There were five printed areas on the substrate with a 5 mm space between adjacent areas and each area contained only one QD/polymer composite and covered an area of roughly 5 × 10 mm. In order to produce the defocused drops, the print settings were altered to produce a non-uniform drop and the substrate was left at room temperature during the printing process.

2.3. Contact-Printed sensor fabrication

To produce the contact printed films a 3 step process was used: first, solutions of QD and polymer were made in a range of concentrations (2.5–20 mg/mL QD in toluene), being careful to ensure that the ratio of QD to polymer in these solutions was the same as the ratio of QD to polymer used for inkjet printing solutions. Second, the solutions were spun coated onto polydimethylsilox-

ane (PDMS) stamps which were made from Sylgard 184 Silicone Elastomer Kit (Dow Corning) with a 10–1 ratio of elastomer to curing agent. Finally, the stamps were cut into ~5 mm wide strips and transferred to quartz substrates using contact transfer methods [13]. In order to aid in the transfer process, a thin layer of a non-fluorescing polymer (poly isobutylene [PIB]) was applied to the cleaned quartz slides prior to contact printing. The absorbance of each contact printed region was measured to ensure that the variation in concentration of solutions coupled with the selected spin speed produced films with QD concentrations similar to the surface concentrations of the inkjet printed solutions.

2.4. Sampling

After fabrication, the sample was placed into the sensor assembly previously described [16]. The sample set used for analysis included 15 common laboratory solvents. To create the test sample for the array testing, a small amount (ca. 0.5 g) of each chemical was placed into a 40 mL scintillation vial and placed into the carousel of the auto-sampler. Each vial is fitted with a tight fitting Teflon plug with a magnetic cap that is removed by the auto-sampler during the sampling process introducing the headspace vapor of the solvent with a background of laboratory air to the sensor. The vapor concentration of each sample was close to the saturation point but not determined analytically. For tests that focused on the sensitivity of films, a bubbler containing the analyte of interest, nitrobenzene, was used to generate repeatable fully saturated vapor in the headspace of the vial. A mass flow controller was used to deliver a calibrated amount of laboratory air into the bubbler through a ceramic diffuser. Vapor that evolved was contained in the vial which the sensor assembly was allowed to sample. This system was found to deliver the analyte vapor to the sensor in a variable, yet reproducible manner.

Data collection was performed using a custom built automatic sampling system (auto-sampler) which relied on a Python script to control two mechanical parts based on user inputs. The first part is a linear actuator that vertically moves the sensor assembly to and from the analytes, and the second, a carousel with 18 compartments for sample vials. Using the auto-sampler, many repetitions can be performed in a standardized and consistent manner, generating large volumes of highly reproducible data. Post processing,

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