U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND
CHEMICAL BIOLOGICAL CENTER

ABERDEEN PROVING GROUND, MD 21010-5424

CCDC CBC-TR-1684

# Inkjet-Printed Light-Emitting Diode Circuits for Self-Detoxifying Textiles

**Hui Wang**
**Wesley O. Gordon**
**Gregory W. Peterson**
**Christopher J. Karwacki**

**RESEARCH AND TECHNOLOGY DIRECTORATE**

**John Landers**

**LEIDOS, INC.**
**Abingdon, MD 21009-1261**

**Anne Walker**

**OAK RIDGE INSTITUTE FOR SCIENCE & EDUCATION**
**Belcamp, MD 21017-1543**

**August 2021**

| REPORT DOCUMENTATION PAGE | | *Form Approved*<br>*OMB No. 0704-0188* |
|---|---|---|

| | | |
|---|---|---|
| **1. REPORT DATE** *(DD-MM-YYYY)*<br>XX-08-2021 | **2. REPORT TYPE**<br>Final | **3. DATES COVERED** *(From - To)*<br>Mar 2019–Nov 2019 |

| | |
|---|---|
| **4. TITLE AND SUBTITLE**<br>Inkjet-Printed Light-Emitting Diode Circuits for Self-Detoxifying Textiles | **5a. CONTRACT NUMBER** |
| | **5b. GRANT NUMBER** |
| | **5c. PROGRAM ELEMENT NUMBER** |
| **6. AUTHOR(S)**<br>Wang, Hui; Gordon, Wesley O.; Peterson, Gregory W.; Karwacki, Christopher J. (DEVCOM CBC); Landers, John (Leidos); and Walker, Anne (ORISE) | **5d. PROJECT NUMBER**<br>2019 IDEAS Program |
| | **5e. TASK NUMBER** |
| | **5f. WORK UNIT NUMBER** |
| **7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**<br>DEVCOM CBC, ATTN: FCDD-CBR-PF, APG, MD 21010-5424<br>Leidos, Inc.; 3465 Box Hill Corporate Center Dr., Abingdon, MD 21009-1261<br>Oak Ridge Institute for Science & Education; 4692 Millennium Dr., Suite 101, Belcamp, MD 21017-1543 | **8. PERFORMING ORGANIZATION REPORT NUMBER**<br>CCDC CBC-TR-1684 |
| **9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)**<br>DEVCOM CBC, ATTN: FCDD-CBR-PF, APG, MD 21010-5424 | **10. SPONSOR/MONITOR'S ACRONYM(S)** |
| | **11. SPONSOR/MONITOR'S REPORT NUMBER(S)** |

**12. DISTRIBUTION / AVAILABILITY STATEMENT**
Approved for public release: distribution unlimited.

**13. SUPPLEMENTARY NOTES**

**14. ABSTRACT: (Limit 200 words)**

A current science and technology thrust is the minimization of physiological and logistical burdens by the modernization of our protective capabilities. We present a strategy to reduce this burden by incorporating low-power circuitry into swatches capable of powering an array of light-emitting diodes (LEDs) for the photo-decontamination of sulfur mustard (HD). LEDs were incorporated into photosensitizer-containing fabrics and connected by inkjet-printed circuits on the fabrics. Several different types of fabrics were tested for compatibility with inkjet printing. We found that the fiber size of the fabrics affected the success of inkjet printing the circuits. Circuits on fabrics with smaller fiber sizes often had better conductivity. The most effective material we designed was boron–dipyrromethene–polyvinylidene fluoride (BODIPY–PVDF) electrospun nanofibers with inkjet-printed circuits. When the LEDs were powered on, the BODIPY–PVDF nanofibers were capable of decontaminating 96% of 2-chloroethyl ethyl sulfide, an HD simulant, in 1 h.

**15. SUBJECT TERMS**

| | | |
|---|---|---|
| Chemical warfare agent (CWA) | Light-emitting diode (LED) | Detoxification |
| Sulfur mustard (HD) | Smart textile | Photo-decontamination |
| Boron–dipyrromethene (BODIPY) | Inkjet-printed circuit | |

| | | | | | |
|---|---|---|---|---|---|
| **16. SECURITY CLASSIFICATION OF:** | | | **17. LIMITATION OF ABSTRACT** | **18. NUMBER OF PAGES** | **19a. NAME OF RESPONSIBLE PERSON**<br>Renu B. Rastogi |
| **a. REPORT**<br>U | **b. ABSTRACT**<br>U | **c. THIS PAGE**<br>U | UU | 22 | **19b. TELEPHONE NUMBER** *(include area code)*<br>(410) 436-7545 |

Blank

# PREFACE

The work described in this report was authorized under the 2019 Innovative Development of Employee Advanced Solutions (IDEAS) Program at the U.S. Army Combat Capabilities Development Command Chemical Biological Center (Aberdeen Proving Ground, MD). The work was started in March 2019 and completed in November 2019.

Blank

# CONTENTS

PREFACE ..... iii

1. INTRODUCTION ..... 1

2. EXPERIMENTAL METHODS ..... 3

2.1 Decontamination Efficiency Evaluation ..... 3
2.2 BODIPY–Polyvinylidene Fluoride (PVDF) Fibers ..... 3
2.3 BODIPY-Coated ACUs ..... 3
2.4 Inkjet Printing ..... 3
2.5 Lamination ..... 3
2.6 Screen Printing ..... 3
2.7 Circuit Design and Attachment of Micro-LEDs ..... 4

3. RESULTS ..... 4

4. CONCLUSIONS ..... 7

LITERATURE CITED ..... 9

ACRONYMS AND ABBREVIATIONS ..... 11

# FIGURES

1. Reactive fabrics ....................................................................................................2
2. Design of self-decontamination textile fabrics incorporated with inkjet-printed circuits and LEDs ....................................................................................2
3. Evaluation of different substrates for inkjet printing with silver ink..................................4
4. Left: inkjet-printed circuit on an electrospun PVDF–MOF composite ..............................5
5. Printed surfaces as a function of number of passes of the same design .............................6
6. Measured light properties of a surface-mount technology (SMT) micro-LED (left inset) using an integrated sphere (right inset) .............................................................6
7. Left: SMT micro-LED used for this study...........................................................................7
8. Reactivity studies with 2-CEES comparing BODIPY-impregnated fabrics containing inkjet-printed circuits that were exposed to a blue LED light source ..........................................................................................7

# INKJET-PRINTED LIGHT-EMITTING DIODE CIRCUITS FOR SELF-DETOXIFYING TEXTILES

## 1. INTRODUCTION

Protection of Soldiers against chemical warfare agents (CWAs) is crucial in a battlefield environment. Current protective clothing relies on the use of high-surface-area, carbon-based technology that is capable of adsorbing agents.[1] The mechanism of protection relies on the ability of activated carbon that has been impregnated with metals to absorb the chemicals; however, this material lacks the ability to sufficiently decontaminate chemical threats. Although carbon-based protective clothing technology provides the advantage of acting as an impermeable barrier for the permeation of chemicals, it also has the disadvantage of acting as a barrier to water transport arising from the wearer's perspiration. It thereby negates the natural evaporative cooling mechanism of the human body. This leads to raised body temperatures, which make this protective clothing uncomfortable for the wearer. Furthermore, when the carbon itself becomes contaminated, care must be taken to remove the protective garment or to wash it with decontamination solution before removing it. This is because the carbon can become saturated with agent, which then poses the risk of the agent leaching from the carbon.

Textiles capable of self-decontamination are therefore advantageous over textiles that can only capture and adsorb chemical threats. Efforts have been made to develop semipermeable garments or membranes that are self-decontaminating but have nonzero moisture vapor transport rates.[2,3] Methods to produce self-decontaminating fabrics have included incorporating reactive sorbents such as metal oxides[4–6] or metal–organic frameworks (MOFs) for the decontamination of CWAs[7–10] into fabrics.[11,12] For example, photocatalytic materials such as $TiO_2$ were incorporated into cotton to create antibacterial and self-cleaning fabrics.[13,14] In other work, semiconducting inorganic nanoparticles were incorporated into fibers for purposes of decontaminating CWAs. In a demonstration for decontamination of CWAs, $TiO_2$ was also incorporated into a nonwoven nanofibrous mat produced using an electrospinning method.[15] Additionally, membranes were prepared that exhibited self-sealing properties upon contact with CWAs.[16]

We recently demonstrated the self-decontamination of textile fabrics and polymer films with the incorporation of a fluorescent dye. Upon irradiation of an external light-emitting diode (LED), the dye generated reactive oxygen species and effectively decontaminated sulfur mustard (HD) (Figure 1).[17] The photo-decontamination rates were extremely fast: the half-life was less than 1 min, which is much faster than has been observed for non-photo-catalyzed decontaminations. However, the LED was a separate entity and was not incorporated into the fabric. Here, we propose to incorporate low-power circuitry into fabrics capable of powering an LED array for the photocatalysis of HD (Figure 2).

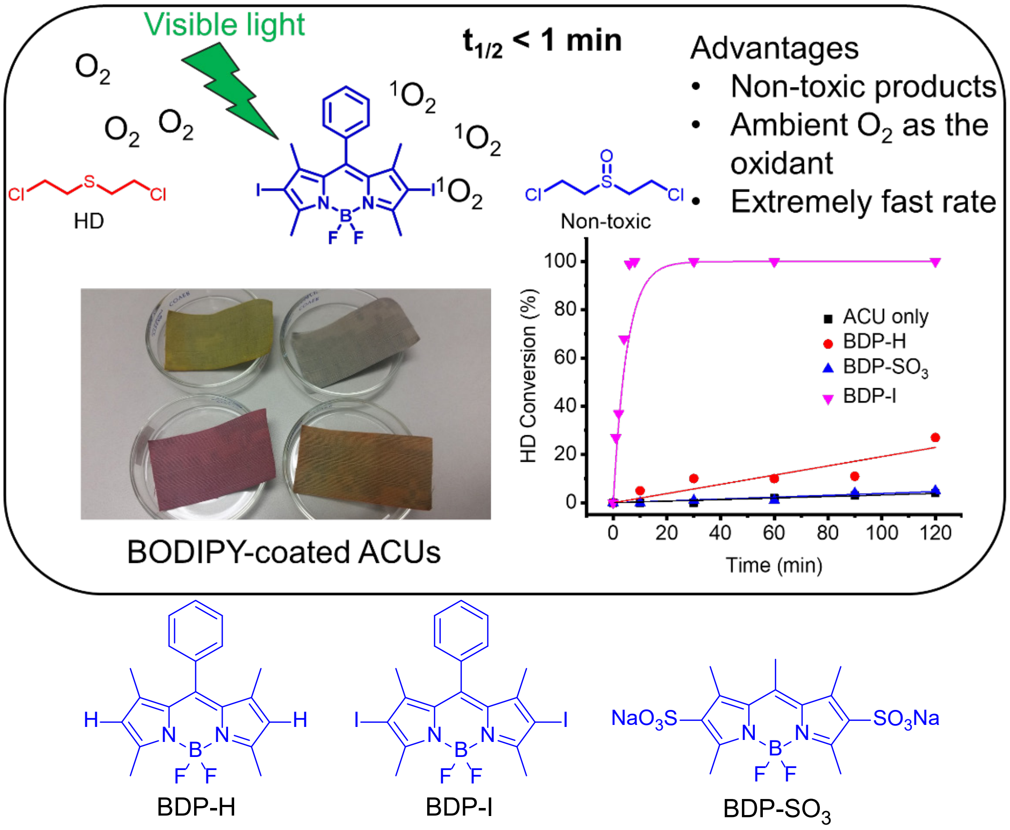

Figure 1. Reactive fabrics. Top: reaction mechanism for conversion of HD to sulfoxide with boron–dipyrromethene (BODIPY) dye. Bottom, left: Army combat uniform (ACU) fabrics impregnated with different BODIPY dyes. Bottom, right: HD conversion with different ACU-impregnated BODIPY dyes. $t_{1/2}$, half-life.

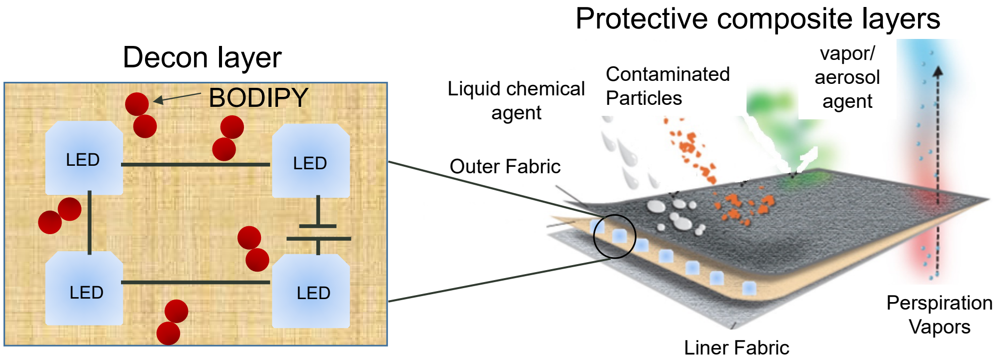

Figure 2. Design of self-decontamination textile fabrics incorporated with inkjet-printed circuits and LEDs.

# 2. EXPERIMENTAL METHODS

## 2.1 Decontamination Efficiency Evaluation

2-Chloroethyl ethyl sulfide (2-CEES; 2 µL) was evenly applied onto an ~2 × 2 cm piece of boron–dipyrromethene (BODIPY)-containing fabric, which was placed in a glass jar containing inkjet-printed circuits and LEDs. The jar was sealed completely, and the LEDs were powered on for 60 min. After irradiation, 1.5 mL of acetonitrile-$d_3$ was added to the jar, and the mixture was vortexed for 2 min to ensure efficient extraction of the products and unreacted 2-CEES from the materials. The extracted solution was then analyzed by $^1$H nuclear magnetic resonance (NMR) to determine the percentage of 2-CEES that was decontaminated.

## 2.2 BODIPY–Polyvinylidene Fluoride (PVDF) Fibers

PVDF fibers containing BODIPY were prepared by electrospinning. Briefly, 1.0 g of PVDF (mol wt, 534,000 g/mol) and 10 mg of BODIPY were dissolved in 4 g of dimethylformamide/acetone (4:1 w/w). The solution was added to a syringe with a 22 gauge needle and dispensed from the syringe at a rate of 1 mL/h at a voltage of 12.5 kV. A rotating drum collector covered with aluminum foil was set at a rate of 300 rpm at a distance of 10 cm from the tip of the needle. Electrospinning was performed at 35 °C.

## 2.3 BODIPY-Coated ACUs

BODIPY-coated ACUs were prepared using a dip-coating method. Specifically, a 3 mM solution of BODIPY photosensitizer methanol was prepared in a 100 mL glass jar. ACUs were cut into small pieces and immersed in the solution for 24 h. BODIPY-coated ACUs were taken out of solution to dry at ambient temperature. This immersion-and-drying process was repeated twice. Finally, the BODIPY-coated ACUs were dried in an oven (50 °C) overnight.

## 2.4 Inkjet Printing

Inkjet printing was performed using a Squink printer and silver ink (BotFactory; Long Island City, NY). Circuit designs were printed on a variety of substrates including Kapton polyimide film (DuPont de Nemours; Wilmington, DE), cellulose, Ecoflex biopolymer (Ludwigshafen, Germany), ACU, cotton, electrospun PVDF fibers, and electrospun PVDF composite fibers.

## 2.5 Lamination

Lamination of the Intexar decals (DuPont) was achieved by pressing with a clothing iron set at a temperature of ~180 °C.

## 2.6 Screen Printing

Screen designs were achieved by placing an ultraviolet (UV)-curable emulsion film over a 250 mesh screen. The desired design was printed on regular printer paper, laid over the emulsion screen, and exposed to UV light for some duration. The light that penetrated (i.e., the unprinted portion of the paper) hardened the underlying emulsion film. Afterward, the emulsion film was washed with water to remove the uncured polymer and leave behind the desired design. The ready-to-use screen print was laid over cloth, and Vortex conductive ink (GSG; Dallas, TX) was squeegeed back and forth several times.

## 2.7 Circuit Design and Attachment of Micro-LEDs

A simple circuit design was made using Inkscape software (open source) and sent to DuPont's Intexar division. Using a proprietary method, the company provided iron-on decals that could be directly laminated to fabrics. Micro-LEDs were attached with a conductive glue.

## 3. RESULTS

Throughout the course of this work, several factors emerged that were critical to obtaining highly conductive and continuous circuit designs on fabrics. They include (1) the compatibility of the ink with the printed substrate; (2) the number of times the design was printed (passes); and (3) in the case of fabrics, the fiber diameter. The feasibility of placing conductive circuits onto fabrics was first demonstrated using the Botfactory Squink conductive inkjet printer. Various substrates were tested (Figure 3) on different geometrical surfaces such as films and woven and nonwoven textiles. A primary consideration was the compatibility of the silver ink with the substrate. For example, if the ink had good wetting properties with the substrate, then a continuous design could be printed. However, if there was poor compatibility (i.e., poor wetting) with the substrate, then the ink tended to bead, and a continuous pattern could not be achieved (Figure 3c, inset).

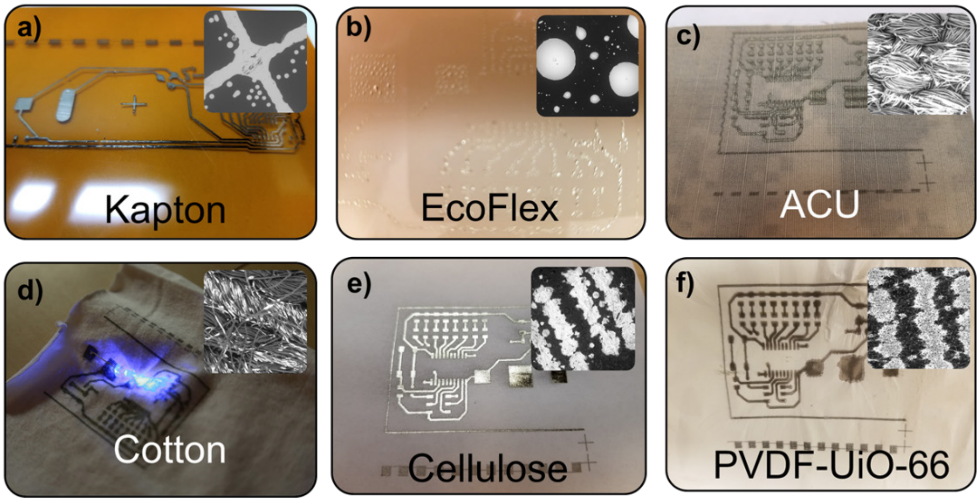

Figure 3. Evaluation of different substrates for inkjet printing with silver ink. (a) Kapton polyimide substrate; (b) Ecoflex silicon elastomer, commonly used in flexible electronics; (c) army combat uniform; (d) cotton fabric; (e) cellulose; and (f) electrospun PVDF. Insets show the scanning electron micrographs (SEMs) of printed substrates. SEM for cotton was for five passes. Optical image for cotton was for >10 passes. SEM scale bar: (a) 200 µm; (b–f) 300 µm. Source for cotton optical image: Gay Pinder (DEVCOM C5ISR).

By far the easiest substrate to inkjet print on was the Kapton polyimide substrate, which demonstrated resistance on the scale of 1–100 Ω. This was expected, given it is the substrate that BotFactory recommends for printing. Turning our attention to woven textiles such as ACU and cotton fabric, we found it was difficult to print continuous patterns, and it was more difficult on woven fabrics with larger-diameter yarns (ACU being more difficult than cotton). One exception to this was when we printed more than 10 passes onto the cotton fabric. However, we deemed this approach wasteful, and we experienced limited success (Figure 3f). Nevertheless, we were able to connect and power an LED onto the printed cotton fabric.

To further demonstrate that fiber size is critical in obtaining a printed circuit, we compared two types of cellulose substrates: cotton fabric and paper. The latter consisted of a nonwoven fabric (Figure 3b) with fiber diameters several magnitudes smaller than those found in cotton fabric. The realization that smaller fiber sizes result in better deposition led us to test the ability to inkjet print onto electrospun fibers, which have fiber diameters on the scale of 10–100 nm. Electrospun fibers were produced by incorporating PVDF with two separate entities to yield composite fibers (Figure 4). The first was PVDF with the MOF UiO-66, a commonly studied additive for Warfighter protection. The second additive was the BODIPY dye. Both composites demonstrated the ability to inkjet print continuous and conductive circuits.

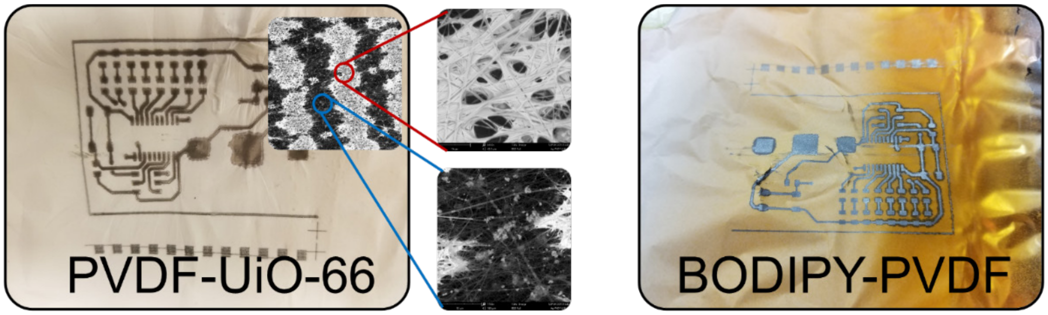

Figure 4. Left: inkjet-printed circuit on an electrospun PVDF–MOF composite. Inset shows SEMs of the deposited circuit. Areas in white represent the ink, and areas in black represent the unprinted cellulose. Right: printed circuit on electrospun BODIPY–PVDF fibers.

To decrease the electrical resistance, we attempted to study the number of passes on cellulose paper. We compared three substrates using one, two, and seven passes of the same circuit design (Figure 5). With each pass, the circuit demonstrated lower electrical resistance, owing to better adhesion to the prior pass and printing on areas where the ink did not previously adhere. However, a trade-off began to develop with a higher number of passes: the circuit tended to smear, which caused short circuits between electrical components that should otherwise have been isolated from each other. Thus, a balance should be considered when choosing a substrate and the number of passes to be performed, in order to achieve low electrical resistance and thereby prevent shorts in the circuit.

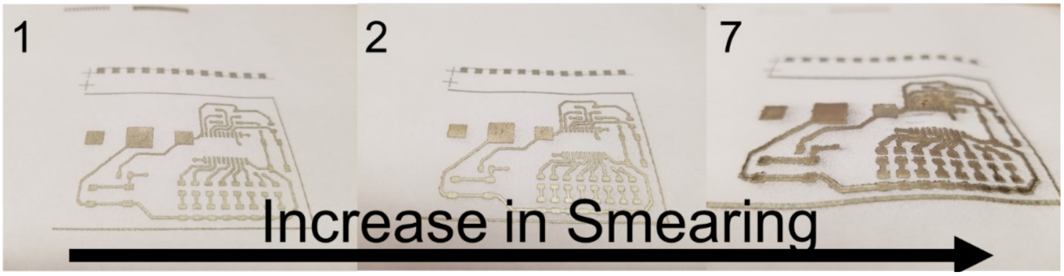

Figure 5. Printed surfaces as a function of number of passes of the same design. Substrate was cellulose for each. Number on each image indicates the number of passes.

We tried two alternative approaches for generating electrical circuits on textiles. The first approach involved screen printing a conductive carbon paste onto fabric. Although this approach (not presented here) allowed for versatility in design, the resultant electrical resistance was too high to allow for the powering of an LED (~10 MΩ). The second alternative was the use of stretchable and flexible decals that could be ironed directly onto fabric. As a proof of concept, a simple circuit was designed and sent to DuPont's Intexar division. Decals were fabricated and sent back. Figure 7 shows the power and light properties of a micro-LED (light properties of which are shown in Figure 6) as well as the incorporation of the micro-LED onto the flexible decal. This provided a simple approach for incorporating flexible circuits onto fabrics. However, the polymer backing of the decal is water impermeable, which is an impediment to the development of breathable protective garments. In future work, we will consider removing the polymer section of the decal that does not contain the flexible circuit, to maintain breathability.

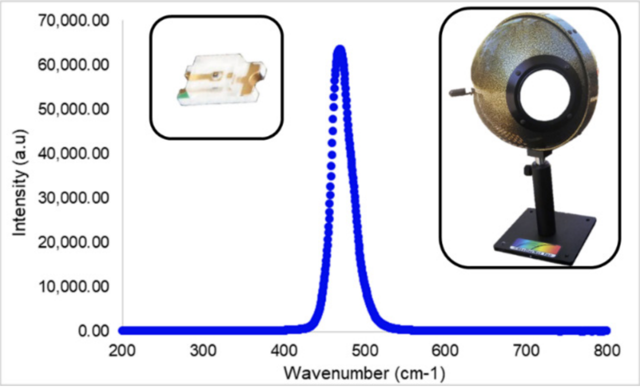

Figure 6. Measured light properties of a surface-mount technology (SMT) micro-LED (left inset) using an integrated sphere (right inset). Wavelength peak position was measured to be ~480 $\mathrm{cm}^{-1}$.

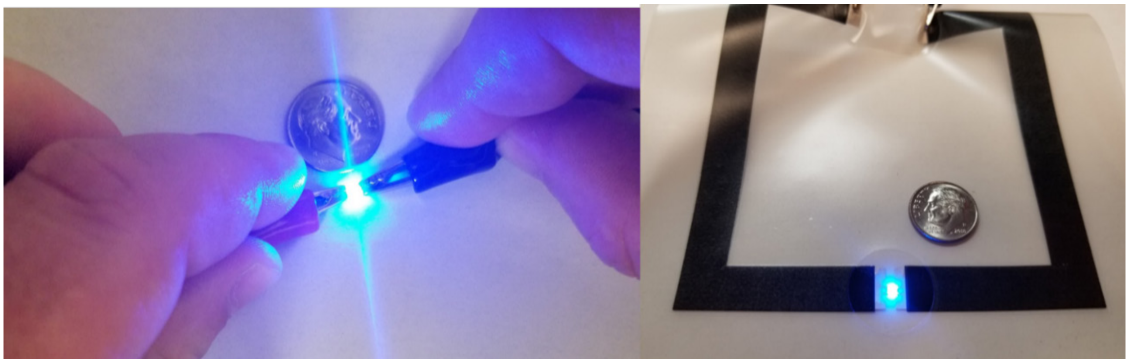

Figure 7. Left: SMT micro-LED used for this study. Right: SMT LED integrated into a simple flexible circuit.

Finally, we compared the ability to degrade the HD simulant 2-CEES with two fabrics that contained inkjet-printed circuits: ACU and PVDF. Both fabrics were impregnated with BODIPY dye, and a dose-extraction procedure was performed for an incubation time of 1 h. The results are displayed in Figure 8. The results revealed that upon exposure to blue LED irradiation, only the printed circuit on the PVDF showed any significant degradation, and nearly 96% of the HD simulant was removed after just 1 h.

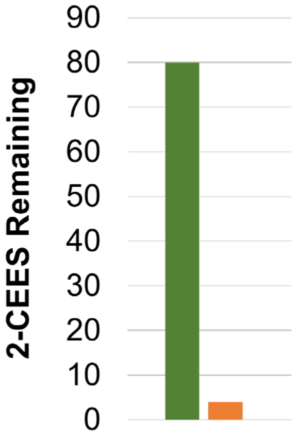

Figure 8. Reactivity studies with 2-CEES comparing BODIPY-impregnated fabrics containing inkjet-printed circuits that were exposed to a blue LED light source.
Green is ACU, orange is PVDF. Dose times were 1 h.

## 4. CONCLUSIONS

Overall, we demonstrated that inkjet-printing circuits onto fabrics is a viable technique for designing self-decontaminating fabrics. Many factors affected the success of inkjet printing on fabrics, including the fabric type, the fiber size, and the number of passes that were printed. In addition to inkjet printing, we tried other methods for designing self-decontaminating fabrics, such as lamination and screen printing. These methods provide alternative options to inkjet printing and have their own advantages and disadvantages as compared with inkjet printing. Future research should be focused on developing better circuit designs as well as further reducing the logistical burden of the fabrics, by lowering the weight of the LEDs and the power source. This would yield a truly functional self-decontaminating garment that not only protects the Warfighter against CWAs, but also does not add a logistical burden.

# LITERATURE CITED

1. Lodewyckx, P. Adsorption of Chemical Warfare Agents. In *Activated Carbon Surfaces in Environmental Remediation*; Bandosz, T.J., Ed.; Elsevier: Amsterdam, 2006; Vol. 7, Chapter 10, pp 475–528.

2. Bui, N.; Meshot, E.R.; Kim, S.; Peña, J.; Gibson, P.W.; Wu, K.J.; Fornasiero, F. Ultrabreathable and Protective Membranes with Sub-5 nm Carbon Nanotube Pores. *Adv. Mater.* **2016,** *28* (28), 5871–5877.

3. Benaddi, H. Polymeric Composition Acting as Barrier to Noxious Agents. U.S. Patent US7736664B2; 15 June 2010.

4. Wagner, G.W.; Koper, O.B.; Lucas, E.; Decker, S.; Klabunde, K.J. Reactions of VX, GD, and HD with Nanosize CaO: Autocatalytic Dehydrohalogenation of HD. *J. Phys. Chem. B* **2000,** *104,* 5118–5123.

5. Wagner, G.W.; Chen, Q.; Wu, Y. Reactions of VX, GD, and HD with Nanotubular Titania. *J. Phys. Chem. C* **2008,** *112,* 11901–11906.

6. Panayotov, D.A.; Paul, D.K.; Yates, J.T. Photocatalytic Oxidation of 2-Chloroethyl Ethyl Sulfide on $TiO_2$–$SiO_2$ Powders. *J. Phys. Chem. B* **2003**, *107,* 10571–10575.

7. DeCoste, J.B.; Peterson, G.W. Metal–Organic Frameworks for Air Purification of Toxic Chemicals. *Chem. Rev.* **2014**, *114*, 5695−5727.

8. Liu, Y.; Howarth, A.J.; Vermeulen, N.A.; Moon, S.-Y.; Hupp, J.T.; Farha, O.K. Catalytic Degradation of Chemical Warfare Agents and Their Simulants by Metal–Organic Frameworks. *Coord. Chem. Rev.* **2017,** *346,* 101–111.

9. Liu, Y.; Howarth, A.J.; Hupp, J.T.; Farha, O.K. Selective Photooxidation of a Mustard-Gas Simulant Catalyzed by a Porphyrinic Metal–Organic Framework. *Angew. Chem. Int. Ed.* **2015,** *54,* 9001–9005.

10. Atilgan, A.; Islamoglu, T.; Howarth, A.J.; Hupp, J.T.; Farha, O.K. Detoxification of a Sulfur Mustard Simulant Using a BODIPY-Functionalized Zirconium-Based Metal–Organic Framework. *ACS Appl. Mater. Interfaces* **2017,** *9,* 24555–24560.

11. Smith, M.K.; Mirica, K.A. Self-Organized Frameworks on Textiles (SOFT): Conductive Fabrics for Simultaneous Sensing, Capture, and Filtration of Gases. *J. Am. Chem. Soc.* **2017,** *139,* 16759–16767.

12. Chen, Z.; Ma, K.; Mahle, J.J.; Wang, H.; Syed, Z.H.; Atilgan, A.; Chen, Y.; Xin, J.H.; Islamoglu, T.; Peterson, G.W.; Farha O.K. Integration of Metal–Organic Frameworks on Protective Layers for Destruction of Nerve Agents under Relevant Conditions. *J. Am. Chem. Soc.* **2019,** *141,* 20016–20021.

13. Xu, B.; Ding, J.; Feng, L.; Ding, Y.; Ge, F.; Cai, Z. Self-Cleaning Cotton Fabrics via Combination of Photocatalytic $TiO_2$ and Superhydrophobic $SiO_2$. *Surf. Coat. Technol.* **2015,** *262,* 70–76.

14. Wu, D.; Long, M.; Zhou, J.; Cai, W.; Zhu, X.; Chen, C.; Wu, Y. Synthesis and Characterization of Self-Cleaning Cotton Fabrics Modified by $TiO_2$ through a Facile Approach. *Surf. Coat. Technol.* **2009,** *203* (24), 3728–3733.

15. Jones, W.E.; Liu, J.; Bernier, W.E.; Tollin, J.B.; McCarthy, D.; Obuya, E.; DeCoste, J. Metal Oxide Nanofibrous Materials for Photodegradation of Environmental Toxins. U.S. Patent US20170056873 A1; 2 March 2017.

16. Rykaczewski, K.; Burgin, T. Self-Sealing and Self-Decontaminating Materials, Methods of Making, and Methods of Use. U.S. Patent US 20170321373 A1; 9 November 2017.

17. Wang, H.; Wagner, G.W.; Lu, A.X.; Nguyen, D.L.; Buchanan, J.H.; McNutt, P.M.; Karwacki, C.J. Photocatalytic Oxidation of Sulfur Mustard and Its Simulant on BODIPY-Incorporated Polymer Coatings and Fabrics. *ACS Appl. Mater. Interfaces* **2018,** *10*, 18771–18777.

# ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| 2-CEES | 2-chloroethyl ethyl sulfide |
| ACU | army combat uniform |
| BODIPY | boron–dipyrromethene |
| CWA | chemical warfare agent |
| HD | sulfur mustard |
| LED | light-emitting diode |
| MOF | metal–organic framework |
| NMR | nuclear magnetic resonance |
| PVDF | polyvinylidene fluoride |
| SEM | scanning electron micrograph |
| SMT | surface-mount technology |
| UV | ultraviolet |

# DISTRIBUTION LIST

The following individuals and organizations were provided with one electronic version of this report:

U.S. Army Combat Capabilities Development
Command Chemical Biological Center
(DEVCOM CBC)
FCDD-CBR-PF
ATTN: Wang, H.
Maxwell, A.

DEVCOM CBC 2019 IDEAS Program
ATTN: Burkhalter, K.

DEVCOM CBC Technical Library
FCDD-CBR-L
ATTN: Foppiano, S.
Stein, J.

Defense Technical Information Center
ATTN: DTIC OA

U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND
CHEMICAL BIOLOGICAL CENTER