Wearable Chemical Ring-Based Sensing Platform for Detecting Chemical Threats

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Supporting Information

ABSTRACT: This work describes a wireless wearable ring-based multiplexed chemical sensor platform for rapid electrochemical monitoring of explosive and nerve-agent threats in vapor and liquid phases. The ring-based sensor system consists of two parts: a set of printed electrochemical sensors and a miniaturized electronic interface, based on a battery-powered stamp-size potentiostat, for signal processing and wireless transmission of data. A wide range of electrochemical capabilities have thus been fully integrated into a 3D printed compact ring structure, toward performing fast square-wave voltammetry and chronoamperometric analyses, along with interchangeable screen-printed sensing electrodes for the rapid detection of different chemical threats. High analytical performance is demonstrated despite the remarkable miniaturization and integration of the ring system. The attractive capabilities of the wearable sensor ring system have been demonstrated for sensitive and rapid voltammetric and amperometric monitoring of nitroaromatic and peroxide explosives, respectively, along with amperometric biosensing of organophosphate (OP) nerve agents. Such ability of the miniaturized wearable sensor ring platform to simultaneously detect multiple chemical threats in both liquid and vapor phases and alert the wearer of such hazards offers considerable promise for meeting the demands of diverse defense and security scenarios.

KEYWORDS: ring, wearable sensor, electronic board, wireless, explosives, organophosphates

Considerable attention has recently been given to the development of wearable sensor technologies.1−4 While initial efforts have been devoted to wearable devices for the monitoring of mobility and vital signs, recent activity has been shifted to the use of wearable chemical sensors for detecting key biomarkers.5−11 Such noninvasive chemical sensing has focused primarily on fitness and healthcare applications in connection to a variety of wearable electrochemical sensors.12−14 With increasing terrorist threats and political instability, there are urgent needs for developing wearable sensing platforms for detecting chemical and biological threats.15,16 New noninvasive chemical sensors are thus critically desired to expand the scope of wearable chemical sensors beyond their current (metabolites/electrolytes) detection capability.

Wearable chemical sensors have relied primarily on the noninvasive monitoring of sweat, saliva, or tears in connection to epidermal (tattoo/textile) devices, mouthguards, and contact lenses, respectively. Particular attention has been given to wearable sensors worn as a patch, wristband, or headband.5,17 Incorporating the electronic interface, energy source, and wireless data transmission capabilities onto these compact and light noninvasive platforms requires a high degree of integration and miniaturization.1,2 Major integration challenges arise due to the different fabrication processes of the different system components. The creation of chemical sensors that can be easily and completely integrated into an individual’s lifestyle, e.g., onto daily fashion accessories, will facilitate a widespread acceptance of wearable sensor technology.18,19

Herein, we demonstrate, for the first time, a fully integrated ring-based analytical platform for real-time field detection of a variety of chemical (explosive, nerve agent) threats toward diverse security applications. While rings represent an extremely attractive wearable platform, they have not been used previously as wearable chemical sensors. To the best of our knowledge, only ring-type pulse oximeters have been reported as wearable sensing devices.20,21 The new wearable chemical detection ring platform relies on complete integration of the wireless stamp-size potentiostatic board and the printed sensing electrodes within the limited constraints of a ring platform. The resulting ring-based device is able to screen the presence of defense and environmental threats in vapor or liquid phases using highly sensitive square wave voltammetry (SWV) and chronoamperometry (CA) techniques. The
amplified requirements. The embedded miniature electronic board thus conditioner, and processing and wireless data transmission within a 3D printed ring case meets the electrochemical, signal conditioning, and processing and wireless data transmission. The embedded miniature electronic board thus entails these electrochemical techniques, along with front-end amplification, microcontroller functions, and wireless radio transmission. To the best of our knowledge, this is the smallest electronic board integrated to a wearable sensor platform with SWV and CA electrochemical capabilities. A semisolid agarose hydrogel was employed to cover the printed sensor surface and promote the analyte diffusion to the electrode. The dual working electrodes were printed using carbon and carbon/prussian-blue inks (Figure 1) to facilitate the surveillance applications aimed at detecting explosives and nerve-agent threats. The high selectivity toward the different targets offers great promise for minimizing various false alarms. Despite the remarkable miniaturization and integration, the wearable ring system offers a highly reliable and robust electroanalytical performance, and hence represents an important step toward decentralized field detection of such chemical threats.

Such merging of strengths of the wearable and fashion fields should lead to wearable lifestyle accessories toward a widespread acceptance of wearable sensor technology. The new electrochemical ring platform could thus be readily expanded to field analyses of a variety of other target threat compounds. As will be illustrated in the following sections, the attractive analytical performance of our new “Lab-on-Ring” system paves the way to effective field assays of chemical threats in connection to diverse security and defense applications.

Figure 1. (A) Ring-based sensor platform for detecting explosives and nerve agent threats in both vapor and liquid phases. Images showing (a) ring polymeric case with the integrated electronics and replaceable screen-printed electrodes based on (from left to right) a carbon working electrode (WE 1), an Ag/AgCl reference electrode (RE), a carbon/prussian-blue working electrode (WE 2), and a carbon counter electrode (CE); (b) bottom view of integrated circuit board and coin battery compartment capable of performing SWV and CA; (c) ring sensor worn on wearer’s middle finger. All scales: 15 mm. (B) Schematic representation of the redox detection processes of the different chemical threats on the ring sensor platform, and corresponding vapor-phase detection, showing multiplexed vapor detection of (a) DNT (red) on carbon WE 1 and corresponding background SWV (black) in vapor phase, (b) peroxides detection on the carbon-prussian blue WE 2 (red) along with the background CA (black); (c) MPOx vapor detection on carbon WE 1 (red) along with the background SWV response (black).

EXPERIMENTAL SECTION

Materials and Methods. The Ag/AgCl ink (E2414) and carbon ink (E3449) were purchased from Ercon Inc. (Wareham, MA). The carbon-prussian blue ink (C2070424P2) was obtained from Gwent Inc. (Torfaen, UK). All inks were used as received. Analytical grade salts of potassium phosphate dibasic, potassium phosphate monobasic, and potassium chloride, 30% (w/w) H2O2 standard solution, agarose type I-A (low EEO), 99.9%, Nafion, methyl paraoxon (MPOx), chlorobenzene, and acetone were purchased from Sigma-Aldrich (St. Louis, MO, USA). Polyethylene terephthalate (PET) was used as substrate for the screen-printed electrodes. Glass vials (9.1 cm diameter and 9.6 cm height) were used to generate and confine the explosive vapor. A BlueStik - Reusable Adhesive Putty (DAP Products Inc.) was used to seal the jar cap opening. Organophosphorous hydrolase (OPH) enzyme (10 μg/mL) was isolated from E. coli bacterial strain DH5α (provided by CSIRO, Clayton, Australia).

Screen-Printing Process. The Ag/AgCl, graphite, and carbon-prussian blue inks were stored at 4 °C prior to use. Screen-printing was carried out using a MPM–SVM semiautomatic screen-printer (Speedline Technologies, Franklin, MA). The sensor patterns were designed in AutoCAD (Autodesk, San Rafael, CA) and outsourced for fabrication on three stainless steel through-hole 12″ × 12′′ framed stencils (125 μm thickness) (Metal Etch Services, San Marcos, CA). The inks were applied onto the planar surface of the stencil before printing onto the PET substrate. The printing steps are depicted in Figure 2A. The first step was the printing of the current-collector contact traces and reference electrodes using a Ag/AgCl ink followed by 20 min curing at 85 °C. Subsequently, the carbon ink was used for printing the counter and working electrodes (for the nitroaromatic compounds) through screen-printing and then cured at 85 °C for 10 min. Subsequently, the counter electrode was printed and cured at 85 °C for 10 min. Finally, the working electrode was printed and cured at 85 °C for 10 min.
DNT and H2O2 vapors were generated at room temperature by applying hydrogel displayed a high stability for 2 weeks upon storing the electrodes. Subsequently, the electrodes were allowed to settle for 5 min to solidify and cool.

Gel Preparation. A single, conductive semisolid hydrogel was employed for the detection of explosives (DNT, hydrogen peroxide) and organophosphate (OP) vapors. The hydrogel was composed of agarose (0.5% w/v) in (0.1 M) phosphate buffer (PBS, pH 7.4). This mixture was first heated in a small glass vial at 200 °C while stirring to dissolve the agarose, until the solution was clear. Then, 100 μL of the gel was applied to cover the surface of the sensing electrodes. The applied hydrogel was allowed to settle for 5 min to solidify and cool prior to the sensing application. Subsequently, the electrodes were properly attached to the ring sensor, as shown in Figure 2C. The applied hydrogel displayed a high stability for 2 weeks upon storing the electrodes in a sealed container to maintain a constant gel humidity.

Detection of Explosives in Liquid and Vapor Phases. Upon attachment of the sensing electrodes onto the ring platform, a coin battery was inserted along with the connections to the embedded electronic board to initiate the analysis. The vapor detection environment was mimicked using a glass vial with 9.1 cm diameter and 9.6 cm height. The vial had an opening on its lid of the exact size to fit the sensor ring. Sealing of the ring on the lid was accomplished using BlueStik - Reusable Adhesive Putty. The explosives were placed in a secondary open container (35 mm diameter and 10 mm height) inside the vial, and the vial was immediately closed with the lid containing the embedded sensor ring and sealed with paraffin (Figure 4a). DNT and H2O2 vapors were generated at room temperature (within the quiescent sealed container) and used to mimic an explosive vapor environment. SWV detection of DNT was performed at room temperature (22 °C) using the bare carbon electrode as the working electrode. SWV plots were recorded from −0.4 V to −1.2 V with a frequency of 10 Hz, an amplitude of 25 mV and 4 mV steps, using MATLAB through a measuring interface. Chronoamperometry was used for the detection of H2O2. The current was sampled for 100 s at a potential of −0.1 V using the bare carbon-Prussian blue working electrode.

Detection of OP in Liquid and Vapor Phases. The ring-based OPH biosensor was used for the liquid and vapor-phase detection of the methyl paraoxon (MPOx) model OP nerve agent. Prior to the enzyme immobilization and measurement, the working electrode surface was electrochemically cleaned by scanning the potential between 0 and +1.0 V (using 0.01 M acetate buffer; pH 4.5) at a scan rate of 0.1 V/s for 25 cycles. Following this, the surface was modified by casting 3 μL of a Nafion/OPH mixture (1:1 v/v ratio). This was achieved by preparing a 5 μL solution mixture of 1% Nafion in ethanol and a 10 μg/mL OPH in 0.1 M phosphate buffer (pH 7.4 solution). The electrode was allowed to dry at room temperature (22 °C) for 3 h. Subsequently, the surface was coated with a layer of agarose hydrogen (0.5%).

The nerve-agent vapor was generated using a portable Mesh Nebulizer, mini Air 360+A (LFS, Shenzhen, China). The vapor, in the form of small droplets whereas MPOx was a liquid, was directly dispensed onto the ring sensor surface. Liquid and vapor phase OP experiments were carried out inside the fume-hood following strict safety measures. The nitrophenol product of the MPOx−OPH reaction was monitored wirelessly with a smart-device (laptop) via Bluetooth Communication. Experiments were conducted by varying the MPOx concentrations from 0.250 to 1.25 mM in the liquid phase, and from 5 to 15 mM in the vapor phase. Vapor from the nebulizer was applied for 30 s at a 5 cm distance from the vapor source. SWV were recorded at room temperature (22 °C) using the enzyme-modified carbon electrode as the working electrode through the electronic board embedded within the ring. These voltammograms were recorded using MATLAB through a measuring interface between the board and the sensor.
+0.3 V and +1.2 V using a SWV frequency of 10 Hz, amplitude of 25 mV, and a 4 mV step.

Safety Note. Due to the toxicity of OP compounds, a double-layered glovebox, placed inside the fume hood with continuous air flow, was used for all the experiments. An airtight polymer box was placed inside the glovebox with a circular hole to insert the Nebulizer inlet. A mannequin arm with the ring sensor on its finger was placed inside the box. Experiments were conducted by following strict safety measures, wearing safety goggles and a respiratory mask.

Electronics. A miniaturized potentiostat performing the SWV and CA operations was developed by the stacking of two electronic printed circuit boards (PCBs). Figure 2B,a and b, shows the top and bottom PCBs of the wearable ring system and the electronic circuitry, respectively. The PCB contained a controller CC2640 from Texas Instruments (TI, Dallas, TX), which had an integrated Bluetooth Low Energy (BLE) function to enable wireless communication between the sensor and a host device, such as a smartphone or laptop. For SWV, the potential between working and reference electrodes was swept linearly in time, with superposition of a square wave on to a staircase waveform. A reference waveform was generated by a digital-to-analog converter (DAC) DAC8563 from TI. A feedback loop compares the output of the DAC with the buffered potential of the reference electrode and controls the potential with a driver circuit. The DAC had 16-bits resolution to enable precise voltage sweep, and was controlled by the controller via serial peripheral interface (SPI). A trans-impedance amplifier (TIA) was used to convert the forward and reverse currents at the working electrode into voltages. The output of the trans-impedance amplifier was sampled and digitized by an analog-to-digital converter (ADC) integrated in the controller. The final current was calculated as a difference between the forward and reverse currents. The sampling timing of the ADC, as well as the trigger for changing the output of the DAC, was controlled by a timer function in the controller. For CA measurements, the output of the DAC was set to a constant value to apply a fixed potential (~0.1 V) between working and reference electrodes. The current at working electrode was measured by the trans-impedance amplifier and digitized by the ADC. For both SWV and CA, the sensor current signals were first stored in the controller, and then transmitted to the host device as BLE packets. The data was displayed using a custom-made graphic interface in the host laptop. A three-electrode system was employed by manually switching the working electrode connector to the desired electrode. The PCB electronic board was powered by a rechargeable Li-ion 3.6 V coin battery, with a battery lifetime of 7.5 h considering continuous operation.

RESULTS AND DISCUSSION

Sensor Ring Concept. The ring-based sensor system overcomes the limited constraints of a ring platform and consists of two parts: a set of printed sensors and a circuit board for signal processing and wireless transmission of data. The board contains a battery-powered stamp size potentiostat that is suitable for performing mobile and wearable electrochemical analyses. The new wearable ring platform (Figure 1A, a) relies on the full integration of the wireless electronic backbone with microfabricated screen-printed sensing electrodes for carrying out amperometric and voltammetric measurements of explosive and OP chemical threats in liquid and vapor phases. The sensor was mounted on the cap of the ring, facing the external environment. The electrochemical sensor strips were screen-printed on PET substrate to allow an exchangeable and low-cost electrode surface for detecting the different target threats. The presented electrode design had dual working electrodes (each with an area of 9.55 mm²). One of the working electrodes was fabricated using carbon ink (WE 1) and the other one using carbon/Prussian-blue ink (WE 2). The counter electrode (CE) and reference electrode (RE) were screen-printed using carbon ink and Ag/AgCl ink, respectively. As illustrated in Figure 1A, the compact dimensions of the polymeric ring case (28 × 27 × 12 mm³) contains all the electronic circuitry required to generate and process the electrochemical signal and wirelessly transmit the data to a smart device (phone or laptop). This sensor-ring wearable platform (Figure 1A) is light and easy to wear, containing a metallic hoop to fit a human finger (Figure 1A, c). On top of the hoop, a 3D printed case incorporated the potentiostat PCB and the battery. Figure 1A, b shows the back view of the electronic board capable of performing the SWV and CA electrochemical techniques. A 3.6 V rechargeable coin battery is used to power the electronic board. Thus, all the electronics and related power supply and sensing electrode transducers are fully integrated in the wearable ring device.

The new fully integrated ring sensor system offers rapid parallel on-site detection of explosive and OP nerve agent vapors as well as in the liquid phase. Figure 1B illustrates the detection of dinitrotoluene (DNT) (a) and of the MPOx model nerve agent (c) at WE1 using square-wave voltammetry and of hydrogen peroxide (H₂O₂) at WE2 using chronopotammetry (b). A conductive semisolid agarose gel, covering the four-electrode area, facilitates the vapor diffusion to the sensing area as well as the conductive electrolyte matrix essential for completing the electrochemical cell. As illustrated in Figure 1Ba, vapor of the nitroaromatic explosive analogue DNT yields a well-defined cathodic response with two characteristic peaks corresponding to the reduction of the nitro groups to amino groups (red); in contrast, no peaks are observed in the absence of explosive analogue (in black). Similarly, the presence of the H₂O₂ and MPOx vapors resulted in well-defined amperometric and SWV response, respectively (Figure 1B, b and c; red). The latter displays a well-defined anodic voltammetric peak, corresponding the oxidation of the p-nitrophenol product of MPOx enzymatic reaction. No response is observed in the absence of the peroxide or MPOx vapors (black).

Electronic Integration on the Ring Platform. The wearable ring platform combines both electrochemical sensors on the upper cap that seals the ring, and a miniaturized potentiostat (performing SWV and CA) within its case (Figure 1A). As illustrated in Figure 2A, different printing steps were used to fabricate the electrochemical sensor strip, which included the sequential printing of Ag/AgCl layer, the carbon and carbon-Prussian blue layers, followed by printing an insulating layer to confine the sensor area and protect the current collector traces. Two electronic printed circuit boards (PCBs) were developed and stacked to fit into the compact ring. Figure 2B, a shows the top and bottom PCB of the ring-system electronic circuitry. This remarkably small potentiostat (15 × 15 mm² in size, including battery) is capable of performing both SWV and CA measurements independently. The PCB contained a potentiostat circuit (Figure 2B, iii) designed for three-electrode system: working (WE), counter (CE), and reference (RE) electrodes (Figure 1A,a). A microcontroller unit (MCU) controlled the SWV potential scanning between the WE and the RE (Figure 2B,b, ii). The applied potential could also be fixed to a specific value for the chronoamperometric (CA) operation. The MCU integrates an analog-to-digital converter (ADC) for measuring the current at the WE, and a Bluetooth Low Energy (BLE) host device, connected to a small chip antenna Figure 2B,b, i, for wireless communication to a mobile device. A custom-made graphical-interface software in the laptop controls the potentiostat wirelessly, and displays the resulting electroanalytical data.
Despite the remarkable miniaturization of the board and its different micro components, the developed PCB provides a robust, reproducible, and reliable electrochemical performance.

The sensor assembly, detailed in the Experimental section, is shown in Videos S1 and S2. Following the final integration of electronic components (Figure 2C, iv), the agarose gel (containing the 0.1 M PBS electrolyte) is deposited on top of the sensor surface and the ring sensor system is ready for its analytical mission (see Experimental section).

**Liquid Phase Screening of Explosives and Nerve Agent.** The ring-sensor device holds great promise for on-site detection of explosives (DNT and peroxide) and nerve agents. The sensing ability of the ring-based device was first evaluated toward screening these threats in the liquid phase. Figure 3A displays the disposable screen-printed sensor, integrated with ring platform, along with the wireless data transmission to a mobile device. Figure 3B, a illustrates square-wave voltammograms obtained for different concentrations of the nitroaromatic DNT compound over the 10−100 ppm range. These voltammograms reveal two well-defined redox (reduction) processes, at −0.7 and −0.9 V (vs the printed Ag/AgCl reference), characteristic of stepwise reduction of DNT. The corresponding DNT calibration plots for both peaks are also shown in Figure 3B, a (right). The first signal (at −0.7 V), displaying the most favorable characteristics, was selected for subsequent analytical work. As indicated from these calibration plots, the peak currents are directly proportional to the DNT concentrations over the entire 0−100 ppm range (Figure 3B, a). The ring sensor offers good linearity ($r^2 = 0.99$), high sensitivity of 4.55 μA·ppm$^{-1}$, and a limit of detection (LOD) of 4 ppm, indicating its suitability for rapid on-site screening of nitroaromatic compounds. Note the favorable signals for the first 10 ppm DNT addition. Similarly, the new platform was tested for liquid-phase measurements of the peroxy explosive precursor H$_2$O$_2$. Figure 3B, b illustrates the chronoamperograms for H$_2$O$_2$ detection along with the corresponding calibration plot. The current increases linearly upon increasing the hydrogen peroxide concentration in 2 mM steps, leading to a highly linear calibration plot ($r^2 = 0.98$) over the 2−10 mM range with a slope of $−1.8$ μA·mM$^{-1}$ and LOD of 1 mM. To further extend the applicability of this new ring device, we also evaluated the liquid-phase detection of the neurotoxin OP compound and pesticide MPOxi in connection to the OPHi-printed electrode ring biosensor. Figure 3B, c shows voltammograms obtained for five 0.25 mM concentration MPOxi increments in PBS from 0.25 to 1.25 mM. A well-defined anodic peak, corresponding to the oxidation of the nitro-phenol product of the MPOxi−OPHi enzymatic reaction, is observed. The resulting peak current increases linearly ($r^2 = 0.98$) with the corresponding MPOxi concentration (Figure 3B) with LOD of 200 μM. Overall, Figure 3 illustrates that the ring platform displays an attractive performance toward detecting explosives and nerve agents in the liquid phase. Simple modifications of the working electrodes and electrochemical conditions would allow the detection of additional threats.

**Vapor Phase Screening of Explosives and Nerve Agent.** Following the successful demonstration of liquid phase screening of explosives and nerve agents, the sensor ring was evaluated for its ability to detect vapor-phase explosives and OP nerve agent agents. All experiments were performed using strict safety protocols described in the Experimental section. Vapor phase explosives detection experiments were carried out by employing the setup shown in Figure 4A, a and b, using of DNT and H$_2$O$_2$. The chemical agent (MPOxi) vapor detection was performed using the setup shown in Figure 4A, c. Such vapor phase measurements were facilitated by coating the sensor surface with a conductive layer of solid-state electrolyte agarose hydrogel (0.5% agarose gel in 0.1 M PBS pH 7.4), which allowed the vapors to diffuse onto the sensor surface. A sealed glass container (volume: 480 mL) was used to enclose the explosive samples and avoiding any vapor leakage. As shown in the Figure 4A, b, the container was sealed with a lid on which the sensor-ring platform was embedded and tightly sealed. The DNT vapor was generated from DNT powder, while the peroxy vapor was generated from H$_2$O$_2$ solution. Both vapors were generated at room temperature. Figure 4A, c illustrates the setup for the nerve agent vapor detection. In this case, the vapor was generated by using a hand-held nebulizer. All data were wirelessly transmitted to a laptop via Bluetooth. Figure 4B, a−iv illustrates the vapor-phase detection of DNT using the ring sensor system. SWVs were first recorded in the absence of DNT followed by the presence of different amounts of DNT. The SWV shown in Figure 4B, a, i corresponds an absence of DNT powder. In this case, no signal was observed after the incubation time (60 min). However, there was a slight increase in the background current over the time, which was most likely
The hydrogel stability test is shown in Figure S1. The sensor showed a slight current decrease over the first few hours, followed by stable performance over 5 h period. The agarose gel displays good stability when the sensor and analyte are confined within a sealed container, with the sensor displaying well-defined stable peaks over the 24 h experimental period. Figure S1A, a and B, illustrates that both SWV and CA signals remained stable when the sensor is in a sealed container, even after 48 h. On the other hand, as illustrated in Figure S1A, b and B, b, some increase of the SWV and CA signals is observed after 3 h in open air, reflecting that the agarose gel is dried under open air after this period. It is important to note that most of the experiments carried out over less than 2 h during which excellent stability is observed. Figure 4B, a, ii–iv displays voltammetric DNT detection through vapor generation after 1 h incubation by different amounts of DNT; 5, 50, and 100 mg, respectively. The resulting current signals (of the two SWV increments), were thus employed to generate vapors, and their corresponding electrochemical response was recorded. In all measurements, the MPOx vapor was sprayed constantly for 15 s at a distance of 5 cm from the sensor surface.

Figure 4B, c, i–iv illustrates the vapor-phase voltammetric response obtained upon spraying the ring sensor system with MPOx. A well-defined peak response, representative of p-nitrophenol oxidation, is observed at ~ +0.90 V (vs Ag/AgCl), indicating the positive detection of the MPOx vapor. The MPOx peak currents are proportional to the concentrations used for generating the vapor (5 to 15 mM, ii–iv). In contrast, no peaks are observed in the absence of MPOx (black curve of Figure 4B, c, i). The OPH sensor electrode was applied for single use to minimize potential cross-reactivity and false alarm.

Figure 4C, a shows the temporal dependence of the SWV signal generated by 100 mg DNT after 0, 30, and 60 min incubation times. The voltammograms were recorded every 30 min for the same sample in the sealed container. After each incubation period, the DNT vapor accumulated on the hydrogel, resulting in a relative increase of the peak current. A similar protocol was employed for the time dependence of the H$_2$O$_2$ and MPOx vapor detection (Figure 4C, b–c). For the OP time-dependence experiment, the nebulizer was sprayed for 15, 30, and 45 s to generate the MPOx vapors. For all samples, the current value increased with time, confirming the accumulation behavior. The computationally estimated current–time dependence can be seen in Figure S2, along with...
description of mathematical approaches adopted. The wearable ring sensor was also used to examine reproducibility of explosives and nerve agent analyses. Satisfactory performance and reproducibility (Figure S3) were found, considering the fabrication steps and the manually controlled gel thickness. Precision tests for vapor phase studies indicated good intersensor reproducibility values, with RSD < 8.4%, < 5.3%, and < 5.1% \((n = 3)\) for DNT, \(\text{H}_2\text{O}_2\), and MPOx, respectively. The presence of a diamond-like stone crystal on the sensor strip has no effect on the electrochemical response (Figure S4). While DNT measurements were carried out at the bare carbon WE1 electrode, MPOx was monitored at the OPH/Nafion-modified WE1 electrode. It should be pointed out that due to the largely different peak potentials of DNT and MPOx, such modified electrode can discriminate between DNT and MPOx, leading to well-defined MPOx anodic peak and characteristic DNT reduction peaks that could allow a simultaneous monitoring on the same surface (not shown). Nevertheless, it is desired to perform these measurements separately (with DNT detection at the bare electrode) as the nitrophenol OPH product can lead also to a small reduction peak. We also evaluated the cross reactivity between WE1 and WE2. These experiments showed that the analytes (MPOx and DNT) of WE1 do not affect the peroxide detection at the WE2, and that the MPOx detection at WE1 is not affected by hydrogen peroxide (not shown).

**Selectivity of the Ring Sensor System.** Specific detection of the target nitroaromatic explosives compound (DNT), peroxide, and OP nerve agents is needed for the development of a ring-based sensor with no false alarms. The sensor must display selectivity toward the target analytes even in the presence of a large excess of coexisting interfering vapors. Such selectivity was evaluated by performing blind tests in the presence of a wide variety of common vapors. Figure 5 illustrates the electrochemical response of the sensor ring system toward potential interfering compounds along with the target DNT, \(\text{H}_2\text{O}_2\), and OP vapors (A, B, C, respectively). For example, SWV analysis of DNT vapor (generated using 1 h incubation with 100 mg DNT powder), exhibits two character-

![Image](https://via.placeholder.com/150)

**Figure 5.** (A, B) Specificity of the sensor ring toward the detection of explosive vapors after 60 min vapor generation in a sealed container. (A) SWV response of (i) toluene, (ii) aniline, (iii) 100 mg DNT, (iv) phenol, and (v) chlorobenzene on the carbon electrode. (B) CA for 2 mL of (i) methanol, (ii) isopropanol, (iii) 5% \(\text{H}_2\text{O}_2\) (iv) water, and (v) ethanol. (C) Specificity toward nerve-agent vapor: SWV response of (i) 70% ethanol (ii) 90% methanol on PE electrode. (iii) 5 mM MPOx, (iv) 70% IPA, and (v) acetone after spraying the OPH-carbon electrode surface for 15 s using a nebulizer. See experimental conditions for details.

**CONCLUSIONS**

We have demonstrated for the first time a fully integrated wireless ring-based multiplexed chemical sensor platform for simultaneous monitoring of several (explosive and nerve-agent) security threats. The present work addressed also the growing needs for merging the strengths of fashion and wearable fields to create wearable lifestyle accessories toward a widespread acceptance of wearable sensor technology. To realize these goals, we have introduced the sensor ring concept based on embedding powerful wireless electrochemical sensing capabilities on a ring platform. Such integration of the ring-based sensor system with a remarkably miniaturized wireless electronic interface facilitates real-time selective threat detection in both liquid and vapor phases with minimal false alarms. The attractive performance of the ring-based electrochemical platform can rapidly alert the wearers about possible security threats in their surrounding environment. This platform could be readily reconfigured and expanded for decentralized analyses of other hazardous environmental or security agents in connection to different printable transducer inks and bioreceptors.

Although the new wearable ring platform represents a major advance in decentralized electrochemical detection of hazardous agents, several challenges remain to overcome for widespread field applications. For example, the duration of the sensing operation is currently limited by the stability of the agarose layer and hence alternative sensing electrolyte layers should be investigated toward higher stability and extended operations. Note that the low-cost screen-printing electrodes can be replaced rapidly. Second, while only one of the WE was connected to the sensing circuitry at any given time, the use of dual potentiostat would allow the simultaneous detection of multiple threats. The concept could be further expanded to a multielectrode array printed on a single ring cap, along with embedded multipotentiosiastic circuitry, for expanding the scope of such threat detection. All potential interferences should be screened for understanding and eliminating their effect and to ensure negligible false alarms. Further improvements in the detection limits and speed would provide.
improved alert regarding potential exposure to the various threats. Overall, such a fully integrated ring-based wearable platform holds considerable promise for meeting rapidly growing defense and security sensing needs.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssens.7b00603.

Sensor stability analysis; detailed calculation and simulation of DNT vapor concentration over time; DNT sensing reproducibility; impact of ring decoration and modification on the sensing capability (PDF)

Inserting the electronic board inside the ring (AVI)

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Notes
The authors declare no competing financial interest.

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