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Wireless gas detection with a smartphone via rf communication

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Chemical sensing is of critical importance to human health, safety, and security, yet it is not broadly implemented because existing sensors often require trained personnel, expensive and bulky equipment, and have large power requirements. This study reports the development of a smartphone-based sensing strategy that employs chemiresponsive nanomaterials integrated into the circuitry of commercial near-field communication tags to achieve non-line-of-sight, portable, and inexpensive detection and discrimination of gas-phase chemicals (e.g., ammonia, hydrogen peroxide, cyclohexanone, and water) at part-per-thousand and part-per-million concentrations.

Portable chemical sensors are needed to manage and protect the environment (1), human health (2, 3), and quality of life (4). Examples include sensors for point-of-care diagnosis of disease (5), detection of explosives and chemical warfare agents (6), indication of food ripening and spoilage (7), and monitoring of environmental pollution (1). Connecting sensors with information technology through wireless rf communication is a promising approach to enable cost-effective onsite chemical detection and analysis (8). Although rf technology has been recently applied toward wireless chemical sensing, current approaches have several limitations, including lack of specificity to selected chemical analytes, requirements for expensive, bulky, fragile, and operationally complex impedance and network analyzers, and reliance on extensive data processing and analysis (8–13). We report herein the adaptation of a nascent technology embedded in modern smartphones—near-field communication (NFC)—for wireless electronic, portable, non-line-of-sight selective detection of gas-phase chemicals (Fig. 1 and Movie S1). We demonstrate this concept by (i) incorporating carbon-based chemiresponsive materials into the electronic circuitry of commercial NFC tags by mechanical drawing and (ii) using an NFC-enabled smartphone to relay information regarding the chemical environment (e.g., presence or absence of a chemical) surrounding the NFC tag. This paper illustrates the ability to detect and differentiate part-per-million (ppm) concentrations of ammonia, cyclohexanone, and hydrogen peroxide. We demonstrate the ability to couple wireless acquisition and transduction of chemical information with existing smartphone functions [e.g., Global Positioning System (GPS)] (Movie S1).

Many commercial smartphones and mobile devices are equipped with NFC hardware configured to communicate wirelessly with NFC “tags”—simple electrical resonant circuits comprising inductive (L), capacitive (C), and resistive (R) elements on a plastic substrate (Fig. 1). The smartphone, such as the Samsung Galaxy S4 (SGS4) used in this study, communicates with the battery-free tag by powering its integrated circuit (IC) via inductive coupling at 13.56 MHz (14). Power transferred from the smartphone to the IC is, among other variables, a function of the transmission frequency (f), the resonant frequency (f₀), the quality factor (Q), and the circuit efficiency (η), which in turn are functions of L (H), C (F), and R (Ω) of the smartphone and NFC resonant circuit components (15). Integration of chemiresponsive materials into commercial NFC tags produces stimuli-responsive variable circuit components that affect power transfer between the tag and a smartphone in the presence or absence of chemical stimuli. The resulting programmable chemically actuated resonant devices (CARDs) enable non-line-of-sight smartphone chemical sensing by disrupting or allowing rf communication.

Fabrication and Characterization of CARDs

We render commercial NFC tags chemically sensitive via a simple two-step modification procedure (Fig. 1). First, we disrupt the electronic circuit of the tag, rendering the tag unreadable, by removing a section of the conductive aluminum that connects the IC to the capacitor with a hole puncher. Then, we recomplete the LCR circuit with conductive nanocarbon-based chemiresponsive materials deposited by mechanical abrasion (16) (Fig. 1). We achieve chemical selectivity in sensing by harnessing the established properties of chemiresponsive materials (16–18). This study used two different solid-state chemiresponsive materials—PENCILs (process-enhanced nanocarbon for integrated logic)—that can be conveniently drawn on a variety of surfaces using an established technique (17). For sensing ammonia (NH₃) and hydrogen peroxide (H₂O₂)—common industrial hazards that can be used in improvised explosives—we chose pristine single-walled carbon nanotubes (SWCNTs) compressed in the form of a pencil “lead” (16, 18) (P1); this material exhibits a well-characterized, dose-dependent chemiresistive response toward these analytes. We also chose a solid composite comprising a 4:1 (wt/wt) blend of 2-(2-hydroxy-1,1,1,3,3-hexafluoropropyl)-1-naphthol (HFIPN) with SWCNTs generated via solvent-free mechanical mixing within a ball mill (P2) because this material exhibits high selectivity and sensitivity for

Significance

This paper describes the first example of an adaption of near-field communication (NFC) technology—in 0.5 billion modern smartphones and mobile devices installed in 2014—toward portable, wireless, non-line-of-sight gas phase chemical sensing. We demonstrate the ability to convert inexpensive commercial NFC tags into chemical sensors that detect and discriminate analytes at part-per-thousand and part-per-million concentrations. This effort merges rational design of conductive nanostructured materials for selective chemical sensing with portable and widely distributed NFC technology to deliver a new method of acquiring chemical information about an NFC tag’s local environment. This paper introduces a concept for distributed chemical sensing by the growing number of people that carry NFC-enabled smartphones, tablets, and other smart devices.
cyclohexanone (C₆H₁₀O) vapors (a common constituent of plastic explosives) (17, 19, 20). HB pencil lead (P3) was chosen as a negative control because it shows a negligible response toward the concentrations of analytes used in this study. These materials exhibit predictable drift and consistent stability in their electrical resistance (Rₛ) when deposited on the surface of the NFC tags (Figs. S2 and S3).

We used a network analyzer to determine f₀ and Q of the NFC tags at various stages of modification by measuring the rf reflection coefficient, S₁₁ (Fig. 2 and Fig. S4) (21). In tandem, we also used SGS4 to test the readability of the tags (“on”/“readable” and “off”/“unreadable”) and a multimeter to estimate the electrical resistance (Rₛ) of the connection between the capacitor and the integrated circuit within the NFC tag (Fig. S5). Fig. 2A shows a plot that exhibits six notable features. First, in the absence of any device, the S₁₁ spectrum displays a flat baseline (Fig. 2A, 1). Second, unmodified NFC tags (Rₛ = 0.3 Ω ± 0.0 Ω) are SGS4-readable (on) and display a resonant frequency of 13.67 ± 0.01 MHz and Q = 35 ± 1 (Fig. 2A, 2). Third, tags where the electrical connection between the integrated circuit and the capacitor has been disrupted by hole punching (Rₛ = 23.3 ± 0.8 MΩ) are SGS4-unreadable (off) and display f₀ = 14.29 ± 0.01 MHz and Q = 85 ± 2 (Fig. 2A, 3). Fourth, when the electrical circuit is recompleted using P2, the resulting CARD-2 (Rₛ = 16.5 ± 1.0 kΩ) becomes SGS4-readable (on) and has f₀ = 14.26 ± 0.02 MHz and Q = 21 ± 1 (Fig. 2A, 4). Fifth, when this CARD-2 is exposed to vapors of cyclohexanone (~5,000 ppm), a significant change in both f₀ and Q is observed. After 5 s of exposure, f₀ shifts to 14.30 ± 0.01 MHz and Q increases to 32 ± 1 (Fig. 2A, 5), and the tag becomes SGS4-unreadable (off). After 1 min, f₀ remains at 14.30 ± 0.00 MHz; Q increases to 51 ± 2 (Fig. 2A, 6), and the tag remains SGS4-unreadable (off).

Readability of CARDS by the smartphone can be rationalized by estimating the percent of incident power transferred (Pᵣ) from the smartphone to the tag or CARD (Fig. 2B and Fig. S6). For the purposes of this study, the distance of the smartphone to the CARD and the orientation of the smartphone with respect to the CARD were kept constant (Methods); however, in a non-laboratory setting distance and orientation would have to be taken into consideration. The commercial NFC tag (Fig. 2B, 2) absorbs nearly 77% of the rf signal delivered from the smartphone. The disrupted circuit, however, absorbs only 14% of the rf signal from the phone; this amount is insufficient for effective smartphone–tag communication and the tag is unreadable by the SGS4 (Fig. 2B, 3). Incorporation of a chemiresponsive material from P2 into this tag creates CARD-2, resulting in the amount of absorbed rf signal increasing to 23%—a sufficient amount of power transfer to enable rf communication (on) (Fig. 2B, 4). Subsequent exposure of CARD-2 to C₆H₁₀O decreases the absorbed rf signal to 19% and results in CARD-2 becoming unreadable by SGS4 (Fig. 2B, 5). Prolonged exposure of CARD-2 to the...
analyte for 1 min leads to a further decrease in absorbed rf signal from the phone (16%) (Fig. 2B, 6). Thus, $P_t$ between smartphone and CARDS decreases with increasing $R_s$.

**Semi-quantitative Detection of Ammonia with a Smartphone and CARDS**

After establishing the correlation between $R_s$, $P_t$, and the readability by the smartphone, we tested the ability of CARDS to detect and wirelessly communicate repeated chemical exposure to 35 ppm NH$_3$ gas. To program CARDS ($n = 3$) for NH$_3$, we integrated P1 with initial $R_s = 16.1 \pm 0.6$ kΩ into the LCR circuit using the modification method described in Fig. 1, resulting in CARD-1A. We measure $R_s$ and test the SGS4 readability of CARD-1A in response to four consecutive exposures to 35 ppm NH$_3$ gas (Fig. S7). For clarity, Fig. 3A summarizes the effect of NH$_3$ (35 ppm) on the resistance and phone readability of a single CARD-1A. Within 1 min of exposure to 35 ppm NH$_3$, CARD-1A experienced $\Delta R_s = 5.3 \pm 0.7$ kΩ and became unreadable (turned off) when probed by the phone. Removal of NH$_3$ and recovery under ambient air led to a rapid recovery of $R_s$ and retrieval of phone readability of CARD-1A. After a 20-min recovery under ambient atmosphere, the $R_s$ of CARD-1A recovered to 17.4 $\pm$ 0.6 kΩ ($\Delta R_s = +1.2 \pm 0.3$ kΩ from the value of $R_s$ before exposure).

Correlating the readability of CARD-1A by SGS4 with $R_s$ enabled us to estimate that the on/off threshold ($R_s$) for P1 when exposed to NH$_3$ was 20.8 $\pm$ 1.0 kΩ (Supporting Information and Table S1). Below this critical value of $R_s$, CARD-1A was readable by the SGS4, and we have established that it is unreadable when $R_s > R_s$. The well-defined value of $R_s$ in the wireless communication between the smartphone and CARDS fabricated with P1, coupled with the established concentration-dependent response of SWCNTs to NH$_3$, enables semiquantitation. To demonstrate this concept, we fabricated, in triplicate, two types of CARDS designed to turn off in response to crossing different threshold concentrations of NH$_3$: 4 ppm (just below the threshold of human detection of NH$_3$ based on smell) (CARD-1B; initial $R_s = 19.2 \pm 0.2$ kΩ) and 35 ppm (National Institute of Occupational Safety and Health (NIOSH) short-term exposure limit (STEL)) (CARD-1A; initial $R_s = 16.3 \pm 0.5$ kΩ) (Fig. 3B and Fig. S8).

Before exposure to NH$_3$, both CARDS were readable by the phone. Exposure to 4 ppm NH$_3$ only turns CARD-1B off, whereas exposure to 35 ppm NH$_3$ turns both CARDS off. This concept is general: With sufficient information about the concentration-dependent response of the chemiresponsive sensing elements in the presence of the analytes of interest, CARDS can be programmed to turn on or off at the designated thresholds of various analytes.

**Discrimination of Analytes with an Array of CARDS**

The fabrication of arrays of CARDS containing different chemiresponsive materials can also enable the detection and discrimination of multiple analytes using NFC communication (Fig. 4). We used three different sensing materials (P1–P3) to produce distinct $\Delta R_s$ upon interaction with NH$_3$ gas (35 ppm), cyclohexanone vapor (335 ppm), H$_2$O$_2$ vapor (~225 ppm), and H$_2$O vapor (~30,000 ppm). We produced an array of four types of CARDS (each type in triplicate) and used these devices to detect single exposures of the analytes. To detect NH$_3$, we used CARD-1A (initial $R_s = 16.3 \pm 0.6$ kΩ) designed to turn off upon exposure to 35 ppm NH$_3$ and turn back on upon recovery under ambient conditions (Fig. 4A, 1). Importantly, CARD-1A does not turn off in the presence of the other analytes at the concentrations tested (Fig. 4A, 2–4).

To detect H$_2$O$_2$, we fabricated a “turn-on” sensor having an initial condition of being off by mechanically abrading P1 to obtain initial $R_s = 23.4 \pm 0.9$ kΩ (CARD-1C). CARD-1C turned on and became readable by the SGS4 when it was exposed to the equilibrium vapor of H$_2$O$_2$ (35 wt% in water) and turned back off as it recovered under ambient atmosphere (Fig. 4B, 2). Although the exposures of CARD-1C to water, cyclohexanone, and NH$_3$ led to small to moderate $\Delta R_s$ ($\Delta R_s = +1.5 \pm 0.6$ kΩ for water), these exposures did not invoke a change in its readability by SGS4 (Fig. 4B, 1, 3, and 4).

To detect cyclohexanone, we fabricated a “turn-off” sensor CARD-2 with an initial condition of being on by mechanical abrasion of P2 at initial $R_s = 18.9 \pm 0.6$ kΩ on the surface of the tag. CARD-2 turned off within 1 min of exposure to 335 ppm cyclohexanone (Fig. 4C, 3). The readability of CARD-2 by SGS4 was reversible as it turned back on within 1 min of recovery under ambient air. The value of $R_s$ for CARD-2, however, did not recover to its initial value of $R_s$; rather, it settled at $R_s = 15.3 \pm 0.9$ kΩ after equilibrating for 10 min. We hypothesize that this mismatch of $R_s$ may be due to solvent-assisted rearrangement of the sensing material. Importantly, although exposure of CARD-2 to H$_2$O, H$_2$O$_2$, and NH$_3$ produced small $\Delta R_s$ (Fig. 4C, 1, 2, and 4), they did not alter the readability of this sensor by the smartphone.
As a negative control, we fabricated CARD-3 by mechanical abrasion of P3 to obtain $R_s = 18.0 \pm 0.6 \, \text{k}\Omega$; this tag remained readable and did not change its readability in response to analytes used in this study (Fig. 4 D, 1–4). This tag was an important component of an array-based sensing scheme because it validated the integrity of the reader-tag communication protocol and provided a static handle in a codification scheme.

The binary on/off readability of CARDs by the smartphone can be a powerful approach for converting analog physical inputs (presence or absence of a chemical vapor within a defined threshold) into a digitized output (1 and 0, respectively) that conveys meaningful information about the local chemical environment of the sensor tag and is capable of differentiating concentration thresholds, (e.g., NIOSH STEL) within the local environment of the sensor tag and is capable of differentiating multiple concentrations of one analyte or multiple analytes using multi-CARD logic. The general sensing strategy involving wireless communication between NFC tags and smartphones is modular and can be generalized to incorporate many types of chemiresponsive materials to enable selective detection of diverse chemical changes. Nevertheless, addressing the significant challenges that remain to realize the full potential of this wireless sensing approach will require a cross-disciplinary effort of (i) chemical and materials science innovations to improve the sensitivity and selectivity of chemiresponsive materials to chemical analytes, (ii) improving device-to-device performance reproducibility by advancing the state-of-the-art of nanostructured carbon deposition techniques, and (iii) enabling continuum measurement CARD readout capabilities. The combination of chemical sensing with other capabilities within the smartphone (e.g., GPS) may enable additional utility in applications involving tracking and tracing. As a result of the portability and increasingly ubiquitous use of smartphones and mobile devices, we envision that this platform will enable applications in personalized and widely distributed chemical sensing where the acquisition of chemical or physical information was previously unavailable.

### Methods

**Conversion of a Commercial NFC Tag into a Programmable CARD.** The circuit of an NFC tag was disrupted at the location indicated in Fig. 1 using a circular hole puncher (hole diameter 2 mm; Bead Landing). A hole was punched through the tag, effectively removing a portion of the conducting aluminum film (along with the underlying polymeric substrate) connecting the integrated circuit to the capacitor. The circuit was recompleted via mechanical abrasion by drawing a line with an appropriate PENCIL to bridge the two disconnected ends of aluminum (17). An iterative process of mechanical abrasion of the PENCIL followed by measuring $R_s$ (Fig. 5S) with a multimeter (Fluke 114 TRMS multimeter) was repeated until the desired initial $R_s$ value was achieved. When P1–P3 are deposited on the surface of the NFC tag by mechanical abrasion they exhibit predictable drift characteristics, which allowed for the drawing of tags to predetermined specifications (Figs. S2 and S3). To prevent potential inhalation of particulates generated by the abrasion of PENCIL on NFC tags, this process was carried out in a fume hood. The resulting device was allowed to equilibrate until a stable reading ($\Delta R_s < 0.2 \, \text{k}\Omega/10 \, \text{min}$) was achieved (~30 min). All experiments were conducted within 5 h of making a CARD.

**Programming a CARD-Induced Smartphone Response.** As indicated in Movie S1, a response that is unique to a specific tag can be invoked upon successfully establishing communication between the tag and the phone (on/readable) by...
preprogramming a tag-phone relationship before fabrication of a CARD. This study used the freely available application Trigger (Egomotion Corp.) to establish the phone-tag relationship. First, the unique identification number (UID) of a tag is registered with the smartphone by scanning it via NFC. Second, a task (or tasks) is assigned to that specific UID. For example, a task that can be achieved with the use of Trigger is to open another application, such as a note-taking application, that has a predefined message written on it. Other possible tasks that can be invoked include opening the email application with a prewritten message, opening a maps application that displays the current location of the smartphone, and so forth. By programming Trigger to invoke a unique task for each unique tag UID, once the tag has been converted to a CARD meaningful information about the CARD’s chemical environment can be conveyed to the user. Although outside of the scope of this study, this strategy could be improved by creating a customized application that allows more sophisticated smartphone actions in a less cumbersome user-interface architecture.

Method for Determining Reflection Coefficient and Readability of CARDS with a Smartphone. The reflection coefficient spectra (S11) were collected with a network analyzer (Agilent E5061B). A loop probe was affixed to the outside of a jar cap (250 mL; VWR) using electrical tape and a tag or CARD was placed on the inside of the same jar cap using double-sided tape (Fig. S4). Two jars were used for the experiment; one that was empty (i.e., filled with ambient air) and one that contained cyclohexanone (10 mL) and filter paper. The reflection coefficient spectra were measured and recorded once when the cap was on the empty jar, once after the cap was on the jar containing cyclohexanone for 5 s, and once after the cap was on the jar containing cyclohexanone for 1 min (Fig. 2A).

The readability of the tag or CARD was determined by removing the tag from the jar cap, placing it on a piece of open-cell foam (thickness 4.5 cm), and approaching the sensor tag with a Samsung Galaxy S4 running Android version 4.3 with the NFC Reader application (Adam Nybäck) open, held with its back parallel to the sensor tag. A sensor tag was considered on/readable if the UID could be retrieved within 5 s or less of holding the smartphone at a ~2.5-cm distance above the tag. Conversely, the tag was considered off/unreadable if the UID could not be retrieved under the same conditions. All measurements were performed with the phone oriented such that the parallel plate capacitor of the CARD was perpendicular to the long edge of the phone. The phone was held parallel to the surface on which the tag rested.

Correlating Effects of Chemical Exposure on R, and Smartphone Readability of the CARD. A CARD was attached to one side of a plastic Petri dish using 8768,-1C, -2, and 3, and three types of vapors (NH3, H2O2, and cyclohexanone), SG54 can correctly identify the presence of 35 ppm NH3 as 1000, the presence of vapor of 35% H2O2 dissolved in water as 0100, and the presence of 335 ppm cyclohexanone as 0010. As one of the most commonly encountered interferents, we emphasize that the presence of H2O2 vapor would not invoke a response from the sensor tags used in this study (0000). To enable a four-bit depth measurement, four individual CARDS need to be placed on a surface. The CARDS used in this study cover an area of 20.3 cm2 each. Thus, four CARDS, which cannot be stacked on top of each other, would cover an area of 81.2 cm2.

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