

Self-Organized Frameworks on Textiles (SOFT): Conductive Fabrics for Simultaneous Sensing, Capture, and Filtration of Gases

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S Supporting Information

ABSTRACT: Wearable electronics have the potential to advance personalized health care, alleviate disability, enhance communication, and improve homeland security. Development of multifunctional electronic textiles (e-textiles) with the capacity to interact with the local environment is a promising strategy for achieving electronic transduction of physical and chemical information. This paper describes a simple and rapid approach for fabricating multifunctional e-textiles by integrating conductive two-dimensional (2D) metal-organic frameworks (MOFs) into fabrics through direct solution-phase self-assembly from simple molecular building blocks. These e-textiles display reliable conductivity, enhanced porosity, flexibility, and stability to washing.



The functional utility of these integrated systems is demonstrated in the context of chemiresistive gas sensing, uptake, and filtration. The self-organized frameworks on textiles (SOFT)-devices detect and differentiate important gaseous analytes (NO, H_2S , and H_2O) at ppm levels and maintain their chemiresistive function in the presence of humidity (5000 ppm, 18% RH). With sub-ppm theoretical limits of detection (LOD for NO = 0.16 ppm and for $H_2S = 0.23$ ppm), these constitute the best textilesupported H₂S and NO detectors reported and the best MOF-based chemiresistive sensors for these analytes. In addition to sensing, these devices are capable of capturing and filtering analytes.

INTRODUCTION

Wearable electronics¹⁻³ hold promise in enhancing health monitoring,^{4,5} alleviating disability,⁶ and tracking of environmental pollution.⁷ Electronic textiles (e-textiles) have the potential to advance the impact of wearable electronics through breathable devices and garments capable of electronically transduced interactions with the local environment.⁸⁻¹⁰ This electronic signal transduction can be harnessed to create Smart Fabric Sensors (SFSs)¹¹ that report applied pressure,¹² strain,¹³ heart rate,¹⁴ or presence of a chemical.^{15,16} While physical SFSs typically rely on the flexibility and tunability of the fabric platform to enhance device performance,¹¹⁻¹⁷ chemical SFSs often employ fiber-integrated stimuli-responsive materials (e.g., conductive polymers, carbon nanotubes, graphene),^{15,16,1} that either do not affect or diminish the sensing response compared to other substrates.^{17,18} A movement toward developing SFS technology based on synergy rather than compromise - wherein the sensor performance is enhanced by the textile platform — is an essential step in expanding the scope and practical viability of wearable chemical sensors.¹

An emerging class of conductive multifunctional nanomaterials based on metal-organic frameworks (MOFs) holds remarkable potential in electronic applications $^{22-25}$ as chemir-esistors, $^{26-30}$ supercapacitors, 31,32 and electrocatalysts. $^{33-35}$ These porous, $d-\pi$ conjugated, crystalline frameworks can be prepared through modular bottom-up self-assembly of organic ligands with metallic nodes to generate extended conductive solid-state materials.²³ The structural and functional tunability

afforded by the diversity of available ligands and nodes can impart rationally designed functionality into the assembled framework at the monomer stage.³⁶⁻³⁸ Integration of conductive MOFs into textiles to create SFSs that synergistically integrate the desirable features of conductive MOFs (electronic response to stimuli and high surface area) with the porosity and flexibility of the textile substrate can greatly enhance the functional utility of e-textiles.

While integration of conductive MOFs into textiles for the purposes of developing functional electronic sensors has not been previously established, interfacing nonconductive MOFs with fibers and fabrics,^{39–44} polymers,^{45,46} nanoparticles,⁴⁷ biomaterials,^{48,49} and chemically modified supports,^{41,45} is well documented.^{50–52} Methods of solvothermal growth,^{50–52} liquid-phase epitaxy,^{50–52} spray-coating,⁴² film casting,⁵¹ postsynthetic attachment,^{40,51} electrochemical deposition,^{51,53} atomic layer deposition,⁴⁶ and direct precipitation^{43,51} can produce hybrid systems with enhanced function in selective chemical separation, sequestration, and filtration,^{50–52,54–56} resistance to biofouling,⁵⁷ stabilization of biomolecules,^{48,49} and controlled release of catalysts.⁴¹ Moreover, introduction of lithographic⁵⁸⁻⁶² and inkjet printing techniques⁶³ can create patterns of surface-attached MOFs with controlled lateral resolution with potential utility in solid-state devices. Many of these systems, however, are not conductive and consequently

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are incapable of direct electronic transduction of their function. Inspired by these performance metrics with nonconductive MOFs in other areas, we reasoned that developing effective methods for integrating conductive MOFs with textiles can lead to SFSs with enhanced performance in gas sensing and filtration.

This paper describes a one-step fabrication of flexible, textilesupported devices based on conductive MOFs (Figure 1A,B).^{64,65} The direct self-assembly of 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) or 2,3,6,7,10,11-hexaaminotriphenylene (HATP) organic ligands with metallic nickel(II) nodes from solution onto natural (cotton) and synthetic (polyester) fabrics produces textiles that are conformally coated with conductive MOF crystallites at the fiber-level: Ni₃(2,3,6,7,10,-



Figure 1. Fabrication of MOF devices and sheet resistance of SOFTsensor devices. (A) Starting materials for SOFT-sensors from organic triphenylene-based ligand (HHTP or HATP), metallic node (Ni-(OAc)₂ or NiCl₂), and fabric swatch (cotton shows no conductivity). Photograph of cotton swatch is shown. (B) Solvothermal condensation of these reagents in water produces conductive SOFTdevices: textiles coated with nanoporous MOF. Macroscopic through molecular level detail is shown, from a photograph of cotton SOFTsensor postreaction (top left), to scanning electron micrographs detailing MOF coating on fibers (bottom left), and characteristic MOF nanorod texture (bottom right), to space-filling model of MOF (top right). (C) Sheet resistance measurements for SOFT-swatches. 11-hexahydroxytriphenylene)₂ or Ni₃(2,3,6,7,10,11-hexaiminotriphenylene)₂ (Ni₃HHTP₂ or Ni₃HITP₂), respectively (Figure 1C).^{64,65} To the best of our knowledge, this work constitutes the first use of direct self-assembly to deposit conductive MOFs on textiles.

The MOF-based e-textiles reported herein display at least seven unique characteristics for functional materials design: (i) They are the first example of using conductive MOFs as functional components in e-textiles. (ii) They exhibit enhanced porosity by combining mesoporosity of the textile and microporosity of the conductive MOF. (iii) They represent the first demonstration of simultaneous detection, capture, preconcentration, and filtration of gases in MOF-based chemiresistive device architectures. (iv) They are flexible, washable (in water and acetone), and stable to heat. (v) They retain their functional integrity, conductivity, and gas sensing capability in the presence of humidity (at least 5000 ppm of H_2O). (vi) These systems show that ligand specific differences (HITP vs HHTP) in MOF design can be useful attributes for controlling the unique chemiresistive response of these materials toward analytes. (vii) In terms of magnitude of chemiresistive response, self-organized frameworks on textiles (SOFT)-devices constitute the best SFS NO and H₂S detectors reported and the best MOF-based chemiresistive NO and H₂S sensors with theoretical limits of detection (LOD) of 0.16 ppm for NO and 0.23 ppm for H_2S .

This technology fundamentally advances functional materials design, MOF-based electronics, and methods for integrating electrically conductive stimuli-responsive materials into solidstate devices. We believe that these characteristics are of value for the researchers interested in bottom-up design and synthesis of stimuli-responsive materials, the design of wearable electronics with enhanced capabilities in chemical detection, personal protection, and gas sequestration.

RESULTS AND DISCUSSION

Introducing continuous conductivity while maintaining the functional integrity of the textile platform requires integration of conductive materials at the fiber level.⁹ Multifunctional conductive nanomaterials have served as productive targets for developing SFSs,^{8–18} but their deposition strategies are often limited in continuous fiber-scale integration or require specialized instrumentation. A strategy that maintains the simplicity of bottom-up deposition while achieving conformal fiber-scale integration of conductive sensor materials, such as direct self-assembly from molecular components, is highly desirable.

We chose two MOFs with high bulk electrical conductivities (0.01-2.0 S/cm):^{64,65} metal catecholate and imino cross-linked frameworks, Ni₃HHTP₂ and Ni₃HITP₂, respectively. The reactive starting materials readily assemble into conductive d- π conjugated scaffolds in solvothermal reaction conditions (Figure 1B). We adapted procedures from our earlier report detailing the direct assembly of conductive MOFs onto chemiresistive devices on the surface of polymeric films equipped with carbon-based electrodes.²⁹ This paper demonstrates that the method of direct assembly can be generalized to achieve the integration of conductive MOFs into textiles with unique SOFT-device architecture.

Fabrication of Devices. We chose textiles for the immobilization of functional MOF-based materials because fabrics are chemically modifiable (as shown by dyeing processes),⁶⁶ physically tunable (roughness and thickness),⁶⁷

chemically diverse (natural and synthetic),⁶⁷ often low-cost and renewable, and compatible with straightforward integration directly into the existing infrastructure of cloth garments, coverings, and commercial goods.^{8–10,67,68} To prepare SOFTdevices, commercial textiles were cut into swatches (1 cm \times 2 cm). We focused our efforts on natural woven cotton fabric (0.243 mm thick), due to the precedent for cotton serving as an effective platform for e-textiles.^{8–11} To display the generality of the method, we also tested synthetic nonwoven polyester batting (0.643 mm thick, compressed) and found these devices to perform indistinguishably from the cotton-based SOFTdevices (see sections SVIII and SXIII).

To achieve the assembly of MOFs on fabrics, we added solid molecular precursors (organic ligand and metallic node) directly to a vial containing the fabric swatch (one swatch per vial), and added water such that all reagents and textiles were fully dampened (0.033 M with respect to triphenylene ligand). For Ni₃HITP₂, ammonium hydroxide (6 equiv with respect to HITP) was also added to the reaction vessel.⁶⁵ The mixtures were subjected to sonication (5 min) and stirred overnight at 80 °C. We allowed the resulting SOFT swatches to cool in the reaction mixture, then isolated, washed thoroughly with water (1 × 2 mL) and acetone (1 × 2 mL), and drip dried the devices in air (18 h).

SOFT-devices comprised an average of 7–8% MOF (by weight), corresponding to 4–6 mg of MOF per cm³ of textile (see Supporting Information section SII for full experimental details). Textile-supported MOF constituted 16–30% of the total mass of MOF prepared (section SX), taking into account both the SOFT-device and the precipitated MOF powder isolated from the reaction solution. The characterization of bulk MOF powder samples matched reported analysis (See sections SII–SVI in the Supporting Information).^{64,65}

Characterization of Devices. To characterize the successful integration of MOFs into textiles, bulk MOF (isolated from the SOFT-device reaction solution) was compared to MOF incorporated into devices using powder X-ray diffraction (PXRD: section SIV), scanning electron microscopy (SEM: section SV), and energy-dispersive X-ray spectroscopy (EDS: section SVI). Key PXRD peaks corresponding to Bravais planes oriented perpendicular to the 2D plane of the nanomaterial were present for both bulk and SOFT-samples, suggesting long-range "honeycombed" order in a slipped parallel packing motif, as expected.^{64,65} The PXRD traces for the MOF-coated fabrics, however, were convoluted by the fabric substrate, which presents a series of sharp peaks and broad amorphous regions, and while suggestive of MOF presence, were not conclusive. Identity and morphology of the MOFs was confirmed by EDS and SEM (Figure 1C and sections SV and SVI). Electron micrographs of the MOFcoated fabrics indicated tightly packed MOF-nanorods forming a continuous coating over each fiber. Cross sections of the SOFT-devices indicated conformal coating of the textile by the MOF (see Supporting Information SV). If the swatches remained fully submerged in the reaction solution throughout assembly, the conformity of the MOF assembly was uniform throughout the swatch. Swatches that stuck to the sides of the vial, or remained partially submerged were considered nonfunctional devices, even if the submerged portion displayed conductivity. The elemental composition of the MOF-nanorods matched bulk MOF by EDS (section SVI).

Thermal gravimetric analysis (TGA) of SOFT-devices showed both devices to be stable up to 350 °C under nitrogen

(section SIII). The crystallization of MOF coating did not compromise the thermal stability of the cotton substrate, which is similarly stable up to 350 °C under nitrogen (section SIII). A mass loss around 100 °C corresponding to the loss of trapped or bound water commonly observed in porous materials. A loss of only 1% mass was observed for both devices in this range, suggesting that devices were fully dry after the process of washing and drip drying. These results suggest that conductivity results from the MOF itself, not from trapped water.

Enhanced Porosity. We used Brunauer-Emmett-Teller (BET) measurements to gain insight into the porosity of the SOFT-devices as compared to their MOF and cotton constituents. For Ni₃HHTP₂₁ the BET surface area for the bulk MOF was found to equal 421 m^2/g in argon (77 K), in excellent agreement with reported values $(425 \text{ m}^2/\text{g})$.⁶⁴ Integration of MOFs into SOFT-devices increased the BET surface area from 0.3 m^2/g for bare cotton to 3.6 m^2/g for SOFT-devices, an order of magnitude increase in porosity (section SVII). If all MOF pore openings remained unblocked, and full internal surface area of the MOFs on textiles was available, the BET surface area would be equal to approximately 50 m²/g. The nature of the templation likely caused a certain percentage of MOF surface to be unavailable (the surface that templates on the fiber), leading to a deviation from the theoretical maximum surface area. Ni₃HITP₂ exhibited similar trends, with a surface area of 340 m^2/g for pure MOF and a surface area equal to 6.8 m²/g for the SOFT-device (argon: 77 K)

Functional Performance and Yield. Conductive MOFcoated textiles were classified as functional in this study if they exhibited measurable resistance when probed with a multimeter over a 1 cm distance once fully dried. The crystallization of conformal MOF coatings was found to be an essential feature for the electrical and chemiresistive performance. Control experiments that involved soaking fabric swatches in solutions containing individual starting materials, or repeatedly dipcoating swatches (see section SXI) in suspensions of presynthesized MOFs in varied solvents did not generate a conductive pathway, suggesting that direct crystallization is essential for SOFT-fabrication. As a further control, we soaked swatches of fabric substrate in solutions containing both starting materials, as we would to produce SOFT-devices, but prevented the large-scale crystallization of MOF by limiting the reaction time and keeping the samples at room temperature (5 min soaking with 1 min sonication: see sections SIV for XRD, SV for SEM, and SVI for EDX). This method did not produce a conductive pathway in fabric swatches, implying that crystallization of MOF is required for SOFT fabrication.

Direct solution-phase crystallization of MOFs was capable of generating a large surface area of conductivity, up to 25 cm² of conductive surface (measured diagonally across a 5 cm × 5 cm swatch, largest area tested) for Ni₃HHTP₂ (see section SX). This fabrication method yielded functional swatches with moderate sheet resistance (Ni₃HHTP₂ 2.8 ± 0.5 MΩ/cm², Ni₃HITP₂ 5.6 ± 2 MΩ/cm², Figure 1C) and high yields of functional devices. For each device, we performed a minimum of n = 10 fabrication trials, yielding 94% functional devices for Ni₃HHTP₂ on cotton (n = 30), 87% for Ni₃HHTP₂ on batting (n = 13), and 96% for Ni₃HITP₂ on cotton (n = 23). The small number of nonfunctional devices either failed to display conductivity or did not have a uniform distribution of MOF across the swatch.

Two-point conductivity for cotton SOFT-sensors was calculated²⁰ to be 1.6×10^{-4} S/cm for Ni₃HHTP₂ and 2.6 × 10^{-3} S/cm for Ni₃HITP₂. The devices were semiconductive within their usable temperature range (room temperature to ~80 °C, see section SX), as evidenced by their linear increase in conductivity with increasing temperature. Gold-coated pins exhibited Ohmic contacts with the SOFT-sensors in the range from -2.0 to 2.0 V at 0.1 V intervals (see Supporting Information SX).⁶⁹

Mechanical Stability. The SOFT-devices retained the physical properties of the textile and were capable of being bent, twisted, and wrapped around curved surfaces without a significant perturbation or loss of conductivity (Figure 2A).



Figure 2. Selected mechanical and electronic properties of SOFTsensors. (A) Photographs of mechanical manipulation of assynthesized SOFT-devices (4 cm \times 1 cm cotton swatch shown for clarity). SOFT-devices are capable of withstanding twisting, bending, and wrapping around objects without significant changes in resistance, as demonstrated in the plots in parts B and C. (B) Sheet resistance values of cotton SOFT-swatch (2 cm \times 1 cm) upon mechanical manipulation for Ni₃HHTP₂ and (C) Ni₃HITP₂, illustrating their consistent electronic performance under physical stress.

Gentle handling (i.e., installing into custom enclosures, bending) did not cause measurable mass loss of the MOF. Repeated deformation did not impact performance: devices bent or folded up to and beyond 10 cycles (typical handling for multiple sensing experiments) retained consistent conductivity.

The direct bottom-up integration process allows for the coverage of large areas of fabric in different aspect ratios. Squares of material up to 25 cm² displayed conductivity throughout the SOFT-device, including along the diagonal (~5.5 cm). The swatches were cut along the grain, and consequently could be stretched along the diagonal bias. For the large SOFT swatch, stretching deformation did not impact

the resistance greatly: a swatch stretched from 4 to 5 cm (25% increase) showed a resistance change of 0.06–0.05 $M\Omega/cm^2$, respectively (see section SX). The SOFT-devices were stable to washing with water or with organic solvent (acetone) and resistant to disassembly through mechanical handling.

When cut and punctured (e.g., sewing), SOFT-devices lost up to 20% of their mass via fraying of the fabric and some MOF shedding but still retained their conductivity, with no significant change in sheet resistance or chemiresistive performance. Most mass lost was attributable to fraying of the fabric, as the mass of the MOF comprised only 7–8% of the full mass of the device. Fraying occurred primarily during cutting: when the devices were prepared as large swatches $(4.5-25 \text{ cm}^2)$ and then cut into small sections for testing of device properties (i.e., sensing capabilities).

Directed Patterning of Conductive Areas within Devices. The strategy for incorporating conductive nanomaterials into e-textiles through self-assembly makes it possible to fabricate unique device architectures that would be otherwise difficult to achieve. The sensor fabrication was tolerant of an assortment of prepatterned architectures: MOF assembly proceeded on top of and between existing electrodes, including sewn-in conductive threads and painted silver electrodes. Generating patterns of the MOFs on fabrics was accomplished by masking specific areas of the fabric with a hydrophobic barrier (e.g., petroleum jelly). Loading a syringe with petroleum jelly enabled manual patterning of this hydrophobic barrier directly onto the surface of the fabric with reasonable control (± 0.5 cm). Gentle heating (40–50 °C) melted the jelly into the bulk of the textile, and masked the patterned area from MOF assembly in aqueous solution. Isolation of the swatch from the reaction mixture and washing with water, acetone, and with petroleum ether removed any residual petroleum jelly yielding a clean, patterned SOFT-device (section SXII). This approach enabled the preparation of a range of device architectures, including arrays of SOFT-devices mounted on a single swatch, equipped with prepatterned (or sewn) electrodes.

Assessment of SOFT-Devices as Chemiresistive Sensors. We demonstrated the multifunctional utility of SOFT devices in the context of chemiresistive sensing of toxic gases, as well as capture, filtration, and preconcentration of gaseous analytes. The sensing performance of the SOFT devices was tested in the configuration of a chemiresistor against toxic gaseous analytes with low permissible exposure limits (PELs): H_2S (PEL = 10 ppm) and NO (PEL = 25 ppm). As target analytes, H₂S and NO are also relevant for breath analysis, as their relative concentrations in exhalate have implications in endogenous processes related to disease.⁷⁰ Furthermore, H₂S and NO are common toxic emissions from human industry and considered dangerous pollutants.⁷¹ NO, produced primarily in vehicle exhaust, is a reactive compound that contributes to the formation of ozone and smog.^{71,72} H₂S is a corrosive poison released from refineries and animal farms that is acutely dangerous to aquatic life.⁷¹ As such, development of materials and devices capable of maximizing the real-time detection, uptake, or controlled release of NO and H₂S is broadly important in human health and safety,⁷³ environmental remediation,^{71,72} and health monitoring.⁷⁰ As controls, we tested the response of the SOFT devices to water and a range of organic vapors (section SXIII).

General Procedure for Chemiresistive Measurements. SOFT swatches were placed into custom Teflon enclosure equipped with spring-loaded gold pins (serving as electrodes and immobilizing textile swatches) and gas inlet and outlet ports (Figure 3A) and sealed tightly for leak-free gas flow.



Figure 3. Chemiresistive device performance for SOFT-sensors. (A) Custom enclosure for dosing SOFT-sensors with analytes. (B) Representative response for Ni_3HITP_2 (blue) and Ni_3HHTP_2 (red) SOFT-sensors when exposed to (from left to right) NO or H_2S . (C) Slope (*m*) of first 5 min of sensor response versus concentration of analyte, in response to NO (left) and H_2S (right).

Constant voltage was applied across the electrodes using a portable potentiostat (1.0 V). The current was monitored across the exposure (through saturation) and recovery (10 min) cycles of analyte dosing. Gaseous analytes were delivered from custom-ordered tanks containing each analyte at 1% concentration balanced with N_2 , were further diluted in dry nitrogen (N_2), and regulated using a system of dual mass flow controllers.

Characterization of the Sensitivity and Dynamic Range of SOFT-Sensors in N₂. SOFT devices exhibited dosimetric responses to NO and H₂S, detailed in Figure 3B,C and section SXIII, that were contingent upon MOF identity. Percent response is shown in terms of normalized conductance $(-\Delta G/G_o)$, see section SXIII for equation), and compared for SOFT-sensors (1.5 cm × 0.5 cm). While MOFs employing the HHTP organic ligand have been previously used to sense these analytes,²⁹ the study of the chemiresistive responses of HITPbased MOFs to these gases is has not been previously examined.^{27,65} Representative saturation traces for NO and H₂S are shown in Figure 3B. For NO, SOFT-device response decreased with analyte exposure for Ni₃HHTP₂ (saturation = $-49\% \pm 10\%$, n = 3), and increased for Ni₃HITP₂ (saturation = $81\% \pm 6\%$, n = 3), demonstrating the importance of the identity of the heteroatom in the framework cross-linker on sensing ability. When exposed to H₂S, an increase in resistance was observed for both Ni₃HHTP₂ (saturation = $98\% \pm 9\%$, n = 3) and Ni₃HITP₂ (saturation = $97\% \pm 2\%$, n = 3). The density of MOF crystallites in the SOFT-sensors, coupled to the intrinsic porosity of the fabric substrate, likely contributed to enhancing the response sensitivity toward the analyte as compared to previous reports.²⁹ These dosimetric responses were highly reproducible, as evidenced by repeated saturation studies (see section SXIII). For both Ni₃HHTP₂ and Ni₃HITP₂, exposure to H₂S demonstrated >10% variance between batches (80 ppm, n = 3, see section SXIII).

The SOFT-sensors were capable of differentiating certain analyte concentrations semiquantitatively in the first 5 min of exposure (Figure 3C). Plotting the slope (m) of the device trace over the first 5 min of exposure versus the concentration of analyte (5–80 ppm range) provided a linear response for Ni₃HHTP₂ toward decreasing concentrations of NO, and for both devices toward H₂S (summarized in Figure 3C). For Ni₃HITP₂ SOFT-devices exposed to NO, concentrations as low as 10 ppm saturated SOFT-devices at the same rate as higher concentrations.

Detection Limits in N2. The responses of Ni3HITP2 SOFT-devices exposed to NO suggested a low theoretical limit of detection (LOD). We determined the theoretical LODs for each analyte/SOFT-device pair (for full details on calculation, see section SXIII) by exploiting the maximum percent response (within 1 h of exposure) versus concentration of analyte.74 The theoretical LODs of Ni₃HITP₂ and Ni₃HHTP₂ toward NO (0.1-80 ppm) were 0.16 and 1.4 ppm, and those toward H_2S (1-80 ppm) were 0.52 and 0.23 ppm, respectively. For NO, this constitutes one of the best MOF-based sensors.⁷⁵ For H₂S, Eddaoudi and co-workers reported a MOF-based capacitive sensor with an LOD of 5.4 ppb, orders of magnitude lower than our SOFT-devices.⁷⁶ Their system showed a high selectivity for H₂S, while ours is capable of detecting and differentiating NO from H₂S with excellent LODs.

Chemiresistive Responses of SOFT-Sensors in the Presence of Water. The capacity to differentiate the signal corresponding to H_2O from relevant analyte signal is essential for practical applicability. Dosing devices with concentrations of H_2O vapor much higher than the concentrations of analytes (at least 5000 ppm, ~18% relative humidity) caused a decrease in response for Ni₃HITP₂ (-8% ± 2%) and an increase for Ni₃HHTP₂ (26% ± 1%). Principle component analysis (PCA) enabled the straightforward differentiation of sensor response toward H_2O from sensor response toward NO and H_2S (both at 80 ppm diluted in dry N₂) for arrays featuring Ni₃HHTP₂ and Ni₃HITP₂ SOFT-sensors at saturation (Figure 4A).

Encouraged by these results, we tested the ability of the SOFT-devices to detect and differentiate NO and H_2S in a humid environment (18% relative humidity, 5000 ppm). Mixing a humid vapor stream delivered by gas generator with the diluted gaseous stream delivered by mass flow controller upstream of the sensing apparatus produced a humidified analyte stream with controlled concentrations of gas (80 ppm) and water vapor (5000 ppm). Allowing the devices to equilibrate in the presence of H_2O and then dosing with analyte produced signal indistinguishable (within error) from



Figure 4. Performance of SOFT-devices in competition with water. (A) Principle component analysis for arrays of (one each) Ni_3HHTP_2 and Ni_3HITP_2 SOFT-sensors (triangle and diamond each represent single array) at saturation, showing capability for differentiating NO, H_2S , and H_2O . (B) Summarized saturation sensor response for Ni_3HHTP_2 (red) and Ni_3HITP_2 (blue) exposed to analytes (80 ppm of NO and H_2S , left to right) in dry nitrogen (solid bars) and in the presence of 5000 ppm water (with water droplet), demonstrating consistent function between dry and humid (18% RH) environments.

dosing in dry N_2 (Figure 4B, section SXIII). Many chemiresistors can be sensitive or unstable to the presence of water. However, in one example, a related MOF-based chemiresistor isoreticular to those used in our SOFT-sensors (Cu₃HITP₂) was shown to detect NH₃ in humidity levels up to 60% RH.²⁸ This work is the first example of using Ni₃HITP₂ and Ni₃HHTP₂ to detect NO and H₂S in the presence of humidity, and our results appear consistent with the promising precedent for related systems. Due to limitations of the gas delivery apparatus (see section SXIII for details), sensing of analytes in environments with higher humidity was not examined.

Influence of Applied Voltage on Device Performance. The chemiresistive performance of devices was not affected by applied voltage: SOFT-devices performed indistinguishably at 1.0 V versus 0.1 V applied voltage (section SXIV). Since the measurements of current resulted in reliably and conveniently measurable numbers (\sim 0.5–1.0 μ A for Ni₃HHTP₂ and 0.1–1.0 mA for Ni₃HITP₂) when 1.0 V was applied, chemiresistive sensing experiments were performed at an applied voltage of 1.0 V. Devices maintained their Ohmic character in the range of –2.0 to 2.0 V while saturated with gaseous analytes (section SXIV).

Device Recovery and Long-Term Stability. Despite exhibiting dosimetric responses toward NO and H_2S , the SOFT-devices were fully recoverable postsaturation by washing. A simple wash step with water (suspending devices in deionized

 H_2O for 5 min), followed by complete drying in air (12 h) fully restored the function of the devices within error (see section SXIV). Heating the swatches was less effective: after exposure to H_2S , gentle heating of the swatch in air (70 °C, 1 h) partially restored the performance of the sensors to >60% recovery for Ni₃HHTP₂ and >70% for Ni₃HITP₂ (see section SXIV).

The nature of the observed recovery by washing suggests that the host–guest interaction of metal to analyte is consistent with a Lewis acid binding site at the metal center. It is possible that axial water ligands bound to the metal center (shown to be present in an isoreticular MOF crystal structure)⁶⁴ are displaced by more favorable binding with incoming analyte molecules upon analyte dosing. Displacement of adsorbed oxygen on the surface is also plausible. The electron donation provided by the bidentate chelation of catecholate or imino moieties to the metal center is known to increase the lability of the interaction between axial ligands and the metal center in octahedral Ni(II) complexes.⁷⁷ We hypothesize that soaking of the analytesaturated device in water can release the bound analyte through ligand displacement in water and restore the sensing ability of the SOFT-device.

SOFT-devices also displayed very good shelf lives. After standing exposed to ambient air for over a month (50 days), the resistance of the devices increased by 32% (average sheet resistance L = 5 cm, fresh = 0.81 M Ω /cm², aged = 1.1 M Ω / cm²). However, the chemiresistive sensing performances of the devices did not diminish with time, in spite of the increase in resistance (See section SXIII).

Summarized Fundamental Insight and Performance Advances from Chemiresistive Devices. The sensing results summarized in Figures 3 and 4 highlight the novelty in the performances of these devices and shed light on fundamental advances in understanding the charge transport properties and host/guest interactions of conductive MOFs. Important differences in the direction of the chemiresistive response were observed for Ni₂HHTP₂ and Ni₂HITP₂ in response to NO: a critical observation in elucidating ligandspecific differences in the fundamental sensing mechanisms for charge perturbation in structurally similar MOFs. We propose that the chemiresistive responses for devices equilibrated in dry and humid N₂ suggest that Ni₃HHTP₂ behaves as a p-type semiconductor, while Ni_3HITP_2 could be a mixed-type (p/n)semiconductor.⁷⁸ However, the charge transport mechanisms of these materials are highly complex, and ligand-specific differences in MOF structure, defects, host-guest interactions, and charge transfer kinetics may exist. It is possible that the ligandspecific responses we observe are consequences of these differences.

In terms of performance, the magnitude of device responses greatly exceeds the best previously reported results for this class of materials.²⁹ Moreover, the direction of device response allows for facile differentiation of analytes, and finally, the capacity for the devices to detect analytes in the presence of H_2O is highly desirable,⁷⁹ since many chemiresistive devices are either sensitive to H_2O^{80} or sensitive to pretreatment conditions in the presence of $H_2O.^{81}$

Analyte Breakthrough in Flow-Through SOFT-Devi-ces. The intrinsic porosity of cloth is one of the notable advantages to utilizing fabric as a substrate in e-textiles.^{8,9} The capacity for chemical adsorption of gases hierarchically within the fabric and the integrated porous material^{42,82} offers an opportunity for preconcentration of analytes and simultaneous filtering and detection of gases. Related flexible systems, such as

mixed matrix membranes (MMMs)^{83,84} or hybrid MOF/ polymer composites,⁵² are effective functional components in gas sequestration and separations.^{50–52,54–56} These systems, however, have not yet been developed into effective, electrically accessible sensors that detect capture and breakthrough. Since porous MOF-based membranes are widely known as functional systems capable of gas separation and sequestration,⁸⁵ our SOFT-devices are excellent candidates for integration into an electronic sensor with filtration properties.

We performed breakthrough studies employing two SOFTsensors layered in a custom enclosure, shown in Figure 5A.



Figure 5. Breakthrough studies for simultaneous detection and capture of analytes. (A) Custom Teflon enclosure used to determine membrane breakthrough for SOFT-devices. Two devices are loaded such that the diameter of the inner bore for gas flow is completely covered by SOFT-devices. Spring loaded gold pins immobilize the sensors and serve as electrodes. The enclosure is then completely sealed for leak-free flow. (B) Representative breakthrough sensing traces for SOFT-devices. The first device exposed to analyte is represented by a solid line, the second device by a dashed line. The delayed response of the second device reflects gas capture by the first device.

This experiment demonstrated potential for quantitative realtime detection and filtration of NO and H_2S (Figure 5B, section SXVI) using SOFT-devices. The experiment was prepared such that the pressurized gas stream (gas flow = ~0.5 L/min) must pass through a first SOFT-sensor, followed by free space (~0.20 cm³), then a second SOFT-sensor (Figure 5A). The chemiresistive response for each sensor was monitored continuously, and the devices were allowed to equilibrate in N₂ until a stable baseline current was observed. Devices were monitored for 10 min in dry N₂, then dosed with analyte for a span of 60 min before recovering in N₂. To ensure that any capture of analyte was specific to the SOFT-device, and not to the cotton, we performed experiments wherein the first SOFT-device was replaced by unmodified cotton fabric. In these control experiments, breakthrough of analytes to the second membrane (SOFT-device) was not significantly attenuated upon dosing (See section SXVI).

For breakthrough systems with two identical sensors (i.e., Ni₃HHTP₂/Ni₃HHTP₂ or Ni₃HITP₂/Ni₃HITP₂), analyte breakthrough showed attenuated response between the first and second sensor. For the sake of quantitative comparison, breakthrough responses at 10 min of analyte exposure were considered, and full representative traces are shown in Figure 5B. At 10 min of exposure to NO (10 ppm), Ni₃HITP₂/ Ni₃HITP₂ increased in response by 11% for the first sensor, and only 2% for the second, corresponding to uptake of 0.4 mmol of NO (~12.9 mmol of NO/mg of Ni₃HITP₂) before breakthrough (accounting for the volume of exposed SOFTdevice). For Ni₃HHTP₂/Ni₃HHTP₂, 10 min of exposure to NO (20 ppm) caused a decrease in resistance of -3% for the first sensor and -1% for the second, equivalent to uptake of 0.8 mmol of NO (~22.9 mmol of NO/mg of Ni₃HHTP₂). With exposure to H_2S (10 ppm), Ni_3HITP_2/Ni_3HITP_2 devices increased in the response measured by the first sensor by 65%, and 16% for the second, corresponding to an estimated uptake of 0.4 mmol of H_2S before breakthrough, equivalent to ~12.3 mmol of H₂S/mg of Ni₃HITP₂. For Ni₃HHTP₂/Ni₃HHTP₂ exposed to H_2S (20 ppm), an increase in response of 7% for the first sensor and 2% for the second was recorded after 10 min of exposure: an estimated uptake of 0.7 mmol of H₂S before breakthrough ($\sim 23.8 \text{ mmol of } H_2S/mg \text{ of } Ni_3HHTP_2$).

The results shown in Figure 5B reflect a remarkable capacity for SOFT-devices to simultaneously detect and capture analytes below their permissible exposure limits. The practical implications of such results are highly promising with respect to applications of SOFT-sensors in novel portable filtering and sensing technology. A gas mask that employed one or more layers of SOFT-sensor would allow for a warning to be transduced before user exposure to toxins, with a predetermined breakthrough rate based on analyte concentration.

CONCLUSION

This paper describes the first example of flexible, textilesupported chemiresistive sensors employing conductive metal organic frameworks (MOFs) as functional materials. The use of direct assembly produces robust e-textiles over large areas, and their preparation from direct assembly of monomers to produce conformal coatings of conductive material at the fiber level is efficient, straightforward, and requires no specialized equipment. The SOFT-device arrays represent a novel class of smart fabric sensors that are mechanically robust and capable of simultaneous, quantitative detection, uptake, and differentiation of hazardous gases.

The SOFT-devices reported herein serve as the first example of e-textiles employing MOFs as the functional component and possess at least three unique performance characteristics of broad potential utility in gas detection and capture. First, Ni₃HITP₂ and Ni₃HHTP₂ SOFT-devices serve as the first single-platform e-textile sensor capable of detecting both NO (LOD = 0.16 and 1.4 ppm, respectively, 0.1–80 ppm) and H₂S (LOD = 0.52 and 0.23 ppm, respectively, 1–80 ppm) and constitute the best MOF-based chemiresistors for NO and H₂S detection. Second, these devices retain their performance in 18% humidity and are fully recoverable and washable. Third, a single SOFT-device effectively sequesters NO or H₂S in simultaneous uptake and detection step, providing predictable rates of breakthrough based on analyte concentration. While these systems are robust, they may lose mass upon handling that involves cutting or puncturing of the fabric due to fraying or MOF shedding. This limitation could be overcome by the introduction of a porous polymeric coating, which would add long-term stability to the device but still be permeable enough to allow perfusion of gaseous analytes or water to the SOFT swatch. Technical optimization of factors influencing wearability, long-term stability, and performance in the presence of high humidity and in complex sensing environments that include mixtures of potentially interfering gases will need to be addressed before practical application of SOFTdevices in the state-of-the-art wearable systems.

The behavior of SOFT-devices provides fundamental insight on properties of this class of conductive MOFs, including mechanistic details of analyte interaction and change transport. The dosimetric responses of SOFT-devices to analytes are entirely recoverable by washing, which suggests metal-analyte binding interactions that are consistent with labile Lewis acid site coordination. The direction of the dosimetric responses implies that Ni3HITP2 is a mixed semiconductor, while Ni₃HHTP₂ may be primarily p-type in nature. We believe that these SOFT-devices have the potential to help elucidate further fundamental properties of conductive MOFs. In the future, this technology may have broad utility in sensing applications ranging from real-time gas detection in wearable systems, to electronically accessible adsorbant layers in protective equipment like gas masks. Finally, our fabrication method has the potential to be extended into other systems, producing a range of novel, multifunctional e-textiles with highly tunable properties, and a host of unprecedented applications in wearable and portable devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b08840.

Experimental methods, characterization of MOFs and devices, electronic characteristics, mechanical properties, and customization of SOFT-devices, comprehensive chemiresistive sensing performance and recovery of SOFT-devices, and breakthrough control experiments (PDF)

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Notes

The authors declare no competing financial interest.

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