DetectsVX: Organophosphate-Sensing Hydrogel Platform

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ABSTRACT

Materials that selectively actuate in response to chemicals in the environment can serve as the foundation for new sensing platforms that take advantage of innate chemical reactivities to provide low-power, selective sensing of chemical agents. A Johns Hopkins University Applied Physics Laboratory (APL) team designed an organophosphate-sensing platform, called DetectsVX, that uses a hydrogel. Initial demonstrations of sensors based on this selectively actuating material have been successful, and the team is currently pursuing innovations in both hydrogel chemistry and sensing mode.

New materials that selectively actuate (swell) based on chemicals in the environment can serve as the basis for next-generation low-profile, low-power sensing platforms. In 2017, Gkikas et al. published[1] a report on a hydrogel that actuates in response to exposure to a simulant for VX (venomous agent X), an extremely toxic organophosphate nerve agent. The hydrogel was designed with two reactive components that work in concert to produce the actuation: an oxime-functionalized monomer and a disulfide diacrylate cross-linker. The oxime reacts selectively with organophosphates and liberates a sulfide from V-agent simulants. The resulting sulfide reacts with the disulfide to open the diacrylate cross-links, causing the hydrogel to swell (Figure 1). The material was used to coat fibers, creating a reactive fabric that could be used for protection against chemical exposure. Our team at APL recognized that we could use a similar strategy to build unique, selective, low-power sensors.
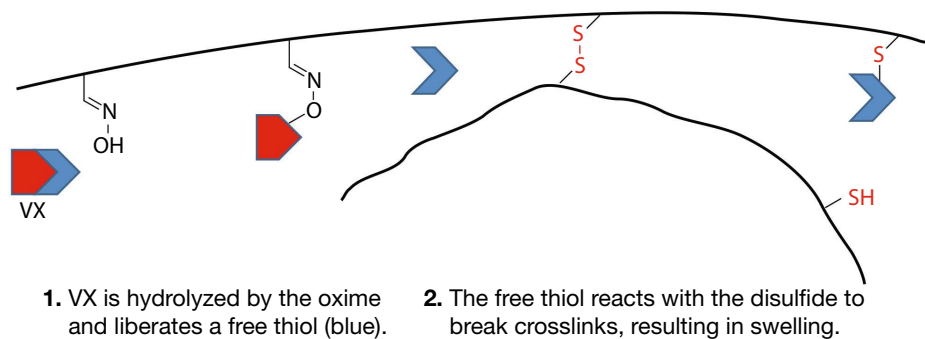

1. VX is hydrolyzed by the oxime and liberates a free thiol (blue).

2. The free thiol reacts with the disulfide to break crosslinks, resulting in swelling.

Figure 1. Schematic of swelling process (actuation). In the first step, VX is hydrolyzed by the tethered oxime, liberating the thiol substituent (blue). In the second step, the thiol breaks the disulfide cross-linker, which results in swelling.
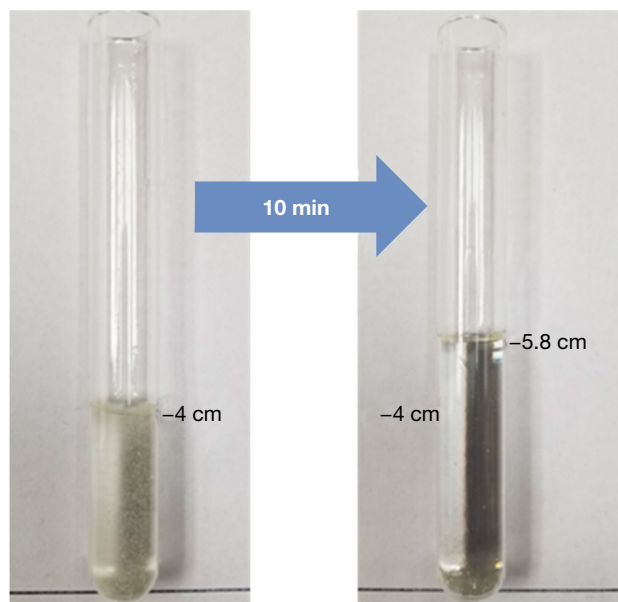
Figure 2. DetectsVX gel swelling. The hydrogel actuated 10 min after exposure to malaoxon, a common VX simulant (left).

Figure 3. M8 paper, commonly used in the field for chemical agent detection. Shown are the standard M8 paper color key (left) and false positive results of M8 paper with common chemicals (right).

Following published protocols,[1] we synthesized the base monomers and prepared the cross-linked hydrogel. We investigated the effect of common interferents on gel volume to ensure that any potential sensor would be specific to the desired analyte(s). For the current hydrogel, the only chemical that induced swelling of the material was malaoxon, a commonly used simulant for VX (Figure 2). Most of our chosen interferents, including water, sodium hydroxide, DMSO (dimethylsulfoxide), hydrochloric acid, chloroform and diesel, had no effect. Several organic solvents (acetone, ethanol, and toluene) degraded the gel but did not induce swelling (so would not result in a false positive).

In contrast, M8 paper, a color-changing indicator commonly used in the field for chemical agent detection, is well known for its poor selectivity and high percentage of false positives. Many of the interferents we tested produced a false positive result on M8 paper. For example, the solvent DMSO gives false positive for VX, sodium hydroxide in water registers as a G-agent, and the common solvent toluene registers as blister agent (Figure 3). In addition, when we tested solutions of malaoxon in solvents, the color change was typically dominated not by the dissolved analyte, but by the carrier solvent, which may include water, toluene, or acetone

(registering as no result, blister agent, and G-type nerve agent, respectively). For this reason, M8 paper users are instructed to use the color indicator to test only neat chemicals—an extremely limiting requirement. A sensor based on the selectively actuating hydrogel would not suffer from the same limitations.

Initial demonstrations of sensors based on this selectively actuating material have been very successful. Thin films of the hydrogel were cast on interdigitated electrodes and exposed to the VX simulant malaoxon. Using the electrodes, a >50% increase in capacitance was measured after exposure.

The team is currently pursuing innovations in both hydrogel chemistry and sensing mode. Chemistry efforts include general improvements to the current hydrogel, with goals of improving material robustness and reaction time, as well as the design and synthesis of novel cross-linkers, with goals of creating hydrogels that will react to different target analytes. We are also working to optimize different sensing modes and form factors, aiming for configurations that do not require continuous power for operation. We envision that this technology could be the foundation of a new sensing platform that takes advantage of innate chemical reactivities to provide low-power, selective chemical sensing of a wide range of chemical agents.

REFERENCE

[1]M. Gkikas, R. K. Avery, C. E. Mills, R. Nagarajan, E. Wilusz, and B. D. Olsen, "Hydrogels that actuate selectively in response to organophosphates," *Adv. Funct. Mater.*, vol. 27, no. 6, 1602784, pp. 1–10, 2017, https://doi.org/10.1002/adfm.201602784.

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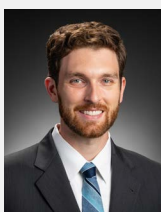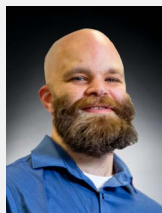
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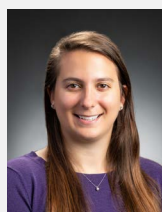
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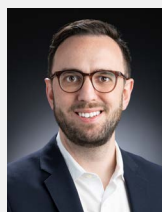
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