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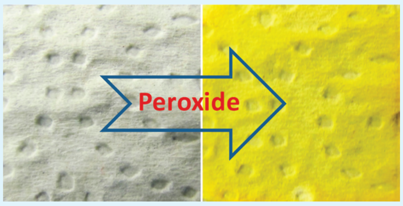
Paper-Based Vapor Detection of Hydrogen Peroxide: Colorimetric Sensing with Tunable Interface

Miao Xu, Benjamin R. Bunes, and Ling Zang*

Department of Materials Science and Engineering, University of Utah, 383 Colorow Dr., Salt Lake City, Utah 84108, United States

Supporting Information

ABSTRACT: Vapor detection of hydrogen peroxide still remains challenging for conventional sensing techniques, though such vapor detection implies important applications in various practical areas, including locating IEDs. We report herein a new colorimetric sensor system that can detect hydrogen peroxide vapor down to parts per billion level. The sensory materials are based on the cellulose microfibril network of paper towels, which provide a tunable interface for modification with Ti(IV) oxo complexes for binding and reacting with H_2O_2. The Ti(IV)-peroxide bond thus formed turns the complex from colorless to bright yellow with an absorption maximum around 400 nm. Such complexation-induced color change is exclusively selective for hydrogen peroxide, with no color change observed in the presence of water, oxygen, common organic reagents or other chelating reagents. This paper-based sensor material is disposable and one-time use, representing a cheap, simple approach to detect peroxide vapors. The reported sensor system also proves the technical feasibility of developing enhanced colorimetric sensing using nanofibril materials that will provide plenty of room to enlarge the surface area (by shrinking the fiber size), so as to enhance the surface interaction with gas phase.



KEYWORDS: vapor detection, hydrogen peroxide, colorimetric sensor, paper-based

Nanofibril-based materials have widely been employed in various electrical, optical, and optoelectronic sensor systems for vapor detection of chemical reagents, mainly because of their large surface area and the interface tunability for strong, highly selective surface binding.[1−15] Compared to the conventional solid films, nanofibers, upon deposition onto a substrate, form a layer of materials through cross-piling of the fibers.[13] This filmlike material possesses continuous three-dimensional porosity, which allows free diffusion of gas molecules throughout the materials matrix, resulting in expedient gas collection and accumulation, and thus fast response for vapor detection of gas analytes. Indeed, fast sensing response in the time range of seconds or even millisecond were previously reported from the nanofibril-based fluorescent materials.[13,16−19] Fast response is crucial for instant, onsite detection of threatening chemicals, particularly the explosives and hazardous gases.

In the past few years, various fluorescent nanofibers were developed for chemical vapor detection through fluorescent emission quenching. These sensor systems have proven to be one of the most sensitive and convenient methods used for expedient detection of nitro-based explosives and organic amines.[13] However, few studies have been performed to extend the nanofibril sensor systems beyond fluorescence quenching to other chemical sensing mechanisms, particularly colorimetric sensing, while still maintaining the superior features of nanofibril materials that are suited for vapor detection, including the large porosity, large surface area, and interface tunability. Colorimetric sensing, relying on chemical binding/complexation induced color change, represents a simple but sensitive detection technique widely used in chemical detection in solution,[20−25] though there are few cases reported for vapor detection, especially with nanofibril materials. We report here, for the first time, a proof-of-concept study of colorimetric vapor detection of hydrogen peroxide using fibril-based sensory materials.

The driving force behind this work is 2-fold; one reason is to expand the fundamental science of colorimetric sensing to fibril mesostructured materials for vapor detection and the other is more practically driven, to develop a methodology for vapor detection of hydrogen peroxide, which still remains challenging for the current sensing techniques.[26] Particularly, the fibril sensory materials employed in this study were fabricated from common paper towels, which compose cellulose fibril network (Figure 1) suited for interface engineering to enable efficient vapor sensing. Although the fiber size is in the range of micrometers (not as essentially as small as nanometers), this fibril network structure is ideal as a test to prove the feasibility of using colorimetric sensing for vapor detection, for which the bleached paper possesses a bright, high-contrast background for color change reading. Moreover, toward practical application, development of sensor systems based on papers represents a simple, cheap approach that may lead to manufacturing of portable, disposable devices as evidenced by the works of Whitesides and others.[27−30]

Vapor detection of hydrogen peroxide not only implies practical applications in industrial and biorelated monitoring, but will provide a new way to detect the peroxide explosives such as triacetone triperoxide (TATP), from which hydrogen peroxide can be identified as a signature compound.[31−33] Peroxide

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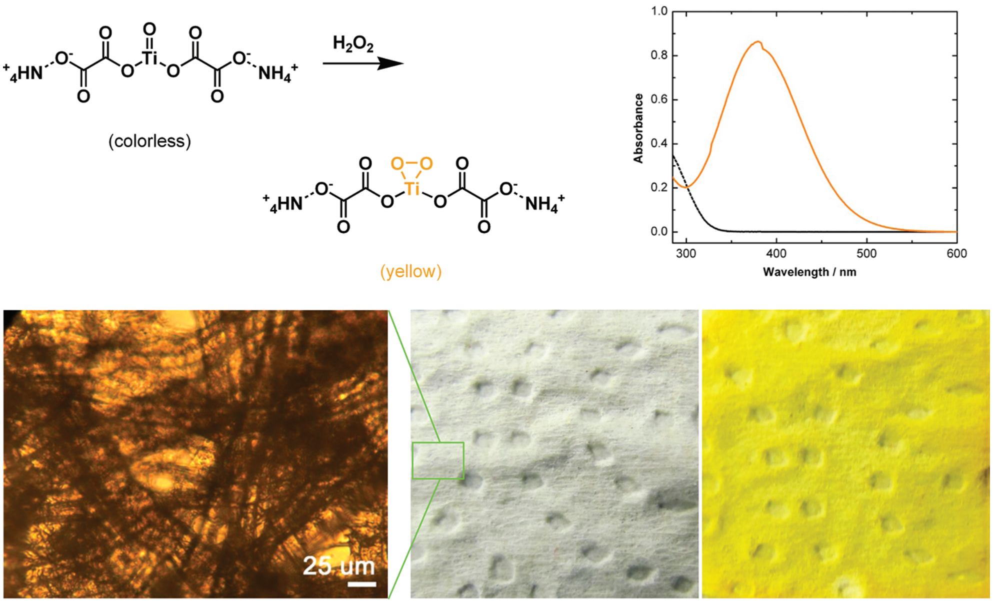

Figure 1. (Top) Colorimetric sensing based on peroxide complexation with Ti(IV) oxo moiety (>Ti═O). The UV−vis absorption spectra were obtained for a water solution of titanyl oxalate (1.0×10^{-3} M) before (black) and after (red) addition of 0.04 wt % H_2O_2. (Bottom) Yellow color formation as photographed over a piece of paper towel (2 × 2 cm^2, loaded with 0.1 mmol titanyl oxalate) upon exposure to the vapor of 35 wt % H_2O_2 solution. Also shown is an optical microscope photograph of the paper towel, revealing the cellulose fibril network.

explosives are essentially as deadly as conventional high explosives, but can be manufactured cheaply and easily at home from off-the-shelf ingredients, and therefore are often used for making improvised explosives devices (IEDs). Moreover, detection of these explosives through direct sensing of the peroxide compounds remains difficult for fluorescence sensing and conventional electronic detection systems.[34−37] To this end, hydrogen peroxide, which is often leaked from the organic peroxides as synthetic impurities or can be generated from the chemical decomposition of peroxide explosives,[37,38] particularly under UV irradiation,[31−33] is generally considered as a signature compound for detecting the peroxide explosives. However, the development of vapor sensing of hydrogen peroxide is not as advanced as the solution-based approach, for which various molecular probes have been developed.[22,26,39−48] This is mainly because of the lack of appropriate sensory materials that can not only demonstrate sensitive, selective response to the adsorption of hydrogen peroxide, but also provide fast collection and accumulation of hydrogen peroxide in the vapor phase, particularly in an open atmosphere.

We report herein a new colorimetric sensor system that can be used for efficient vapor detection of hydrogen peroxide. As shown in Figure 1, the colorimetric sensing employed in this study relies on the peroxide complexation to the Ti(IV) oxo complex (>Ti═O), which is intrinsically colorless (i.e., with no absorption in the visible region), but turns to bright yellow upon complexation with hydrogen peroxide through formation of the Ti(IV)-peroxide bond (with absorption maximum around 400 nm).[22,39,49,50] Such complexation-induced color change is exclusively selective for hydrogen peroxide, with no color change observed in the presence of water, oxygen, or common organic reagents such as alcohols, hexane, acetone, etc. The Ti(IV)-peroxide colorimetric complexation was previously employed for the spectrophotometry detection of hydrogen peroxide in solutions.[22,39,41,42,44,49−52] To adapt the colorimetric sensing from solution phase to a solid state suitable for vapor detection, the Ti(IV) species must be well-dispersed throughout the supporting matrix to maximize exposure to gases, while maintaining its chemical activity (for complexation with hydrogen peroxide) and stability (against hydrolysis into the inactive oxides, e.g., TiO_2).

In this study, we used paper towel as the template materials, wherein the cellulose microfibril networks provide a large interface to be modified with the Ti(IV) oxo species to facilitate efficient colorimetric sensing of hydrogen peroxide. These paper-based sensory materials thus prepared possess the unique features that are desirable for vapor sampling and detection, including (1) continuous pore channels, allowing for efficient diffusion of gaseous molecules throughout the film matrix, making it possible to fabricate a thick film to increase the optical density and thus enhance the sensing accuracy; (2) a three-dimensional microscopic structure that allows for maximal distribution of the Ti(IV) oxo moiety on the surface, thus enabling maximal exposure to the gaseous analytes; (3) a colorless background in the pristine state (i.e., before exposure to hydrogen peroxide) allowing for high contrast measurement of the color formation.

Ammonium titanyl oxalate (structure shown in Figure 1) was chosen for this study because of its colorless background and robust stability against hydrolysis, as well as its high solubility in water (significantly higher than its potassium salt). Another colorless Ti(IV) oxo complex, titanium(IV) oxysulfate, was also tested initially, though it was not chosen for the following sensor investigations because of its limited aqueous solubility. To confirm the stoichiometric colorimetric reaction between the titanyl salt and hydrogen peroxide, we performed a titration experiment over a solution of ammonium titanyl oxalate solution (1.2×10^{-4} mol/L) with the addition of hydrogen peroxide at various molar ratios, shown in Figure S1 in the Supporting Information; the color formation (due to production of titanium-peroxide, Figure 1) was monitored by measuring the UV−vis absorption spectra of the solution. A plot of the absorbance at the

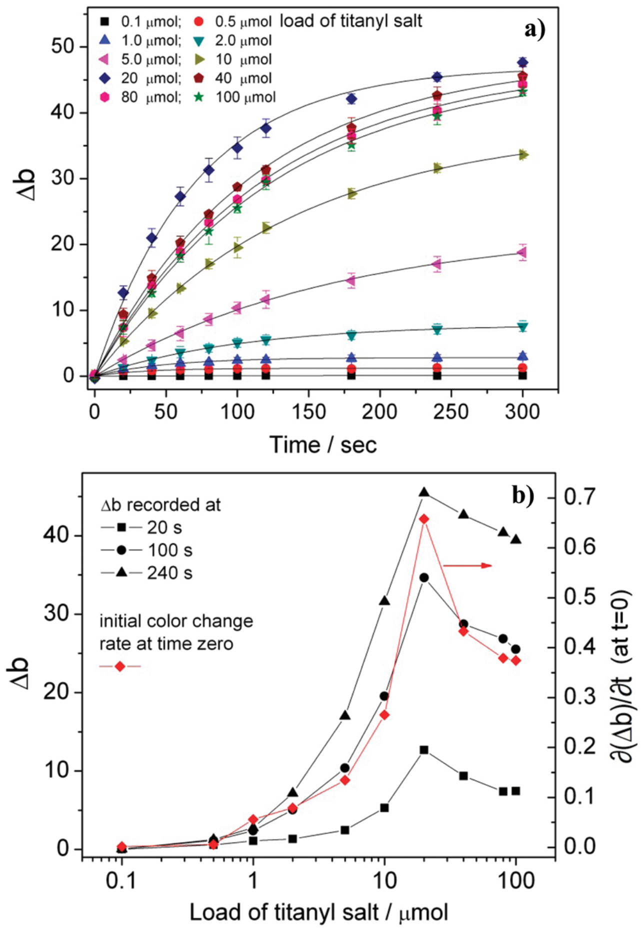

Figure 2. (a) Time course of the yellow color formation measured over a piece of paper towel (2.5 × 2.5 cm^2 size) loaded with titanyl oxalate salt. The color change was recorded using a CR-10 color reader (from Konica Minolta), and the value Δb refers to the color change between yellow and blue as defined in the CIELAB color space system. Shown in the figure are the series of measurements performed over the paper towels loaded with varying amounts (μmol) of the titanyl salt upon exposure to a saturated vapor of 35 wt % aqueous solution of H_2O_2. The error bars are standard deviations of the data. (b) Δb recorded at three time intervals (20, 100, 240 s) are plotted as a function of the molar amount of titanyl salt loaded. Plotted in the same figure (right axis) are the initial color change rates $\partial(\Delta b)/\partial t = K'K$ (deduced from the fitting of panel a) with the loading amount of titanyl salt.

maximum (378 nm) as a function of the molar ratio of H_2O_2/Ti(IV) indicates that the color formation saturates at a molar ratio of 1:1, proving the 1:1 stoichiometric reaction between H_2O_2 and Ti(IV) salt as illustrated in Figure 1.

As detailed in the Experimental Methods section, titanyl oxalate was coated onto the cellulose fibrils by drop-casting a fixed volume of water solution of the salt onto a small piece of paper towel. By changing the concentration of titanyl oxalate, the loading amount within the paper matrix can be adjusted as needed. This drop-casting method proved effective for producing a homogeneous distribution of titanyl salt among the cellulose fibril networks of the paper towel (see Figure S2 in the Supporting Information). These paper-based sensor materials demonstrated bright yellow color formation upon exposure to the vapor of hydrogen peroxide (Figure 1), whereas no response was observed to other common liquids or solid chemicals, proving extreme selectivity toward hydrogen peroxide. To prove the selectivity of titanyl oxalate salt toward hydrogen peroxide, we performed UV–vis absorption spectral measurements for the colorimetric reaction between H_2O_2 and Ti(IV) salt (deposited on a quartz slide as a thin film), and compared to various other common solvents by exposing the same Ti(IV) salt film to these vapors, As shown in Figure S4 in the Supporting Information, despite the much higher vapor pressure of the solvents, the titanyl oxalate film demonstrated negligible colorimetric response to these solvents, i.e., minimal absorbance was detected at the same maximum wavelength after 600 s of vapor exposure. In contrast, upon exposure to the saturated vapor of 35 wt % H_2O_2 solution, the same film demonstrated intense color formation as measured at 386 nm.

Generally, the higher the load of the titanyl oxalate species, the more hydrogen peroxide can be captured and complexed within a certain time, thus leading to increased sensing efficiency. However, a further increase in the salt loading would restrain the porosity, causing a decrease in vapor accessibility. Such a trade-off is clearly shown by the data in Figure 2a, where initially the color change (defined as Δb, the color change between yellow and blue in the CIELAB color space system) increases with the loading amount of titanyl salt. After passing the loading level of 20 μmol (for a 2.5 × 2.5 cm^2 paper towel), a continuous increase of titanyl salt led to a decrease in the color change, indicative of a shrinking of surface area. Figure 2b shows the values of Δb recorded at three time intervals (20, 100, 240 s) plotted as a function of the molar amount of titanyl salt loaded. All the three plots show the same trend of change, yielding an optimal loading level of titanyl salt, 20 μmol.

The data presented in Figure 2a can be fitted following the reaction kinetics equation,

$$\Delta b = K'(1 - e^{-Kt}) \tag{1}$$

where K and K' are constants with K related to the given vapor pressure of H_2O_2 and the total load of titanyl salt and K' referred to as the ratio of the color density to the molar amount of surface complexed hydrogen peroxide. Derivation of this equation is based on the surface adsorption kinetics, i.e,. rate of absorption is proportional to the surface density of the unreacted Ti(IV) sites . From eq 1, we can get the color change rate

$$\partial(\Delta b)/\partial \mathrm{t} = K'Ke^{-Kt} \tag{2}$$

At time zero ($t = 0$), we have the initial color change rate $\partial(\Delta b)/\partial t = K'K$. Because both K and K' can be deduced from the fitting shown in Figure 2a, the initial color change rates were thus obtained for the different loading levels of titanyl salt. Plotting these initial rates as a function of the molar load of titanyl salt (right axis of Figure 2b) gives the same trend of change as plotted for the absolute color change at different time intervals (left axis of Figure 2b), indicating the same optimal loading of 20 μmol. The color change rate represents a parameter that directly relates to the response speed of a sensor material, whereas the absolute value of color change recorded at a given time is usually used for evaluating the sensitivity or detection limit. Interestingly, plots regarding both parameters (as shown in Figure 2b) produce the same optimal value for the load of titanyl salt. In the following experiments, all paper towels were kept at the same size of 2.5 × 2.5 cm^2 and loaded with titanyl salt at a fixed amount of 20 μmol, with the aim to detect hydrogen peroxide at various diluted vapor pressures.

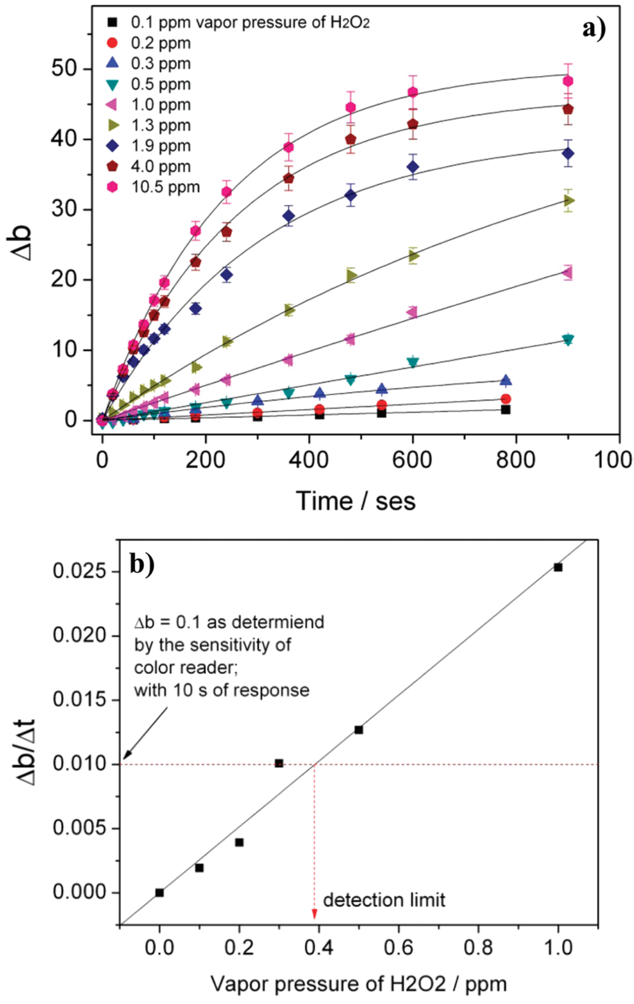

Figure 3. (a) Time course of the yellow color formation measured over the paper towel (2.5 × 2.5 cm^2) loaded with a fixed amount of titanyl oxalate salt (20 μmol) upon exposure to the saturated vapor of aqueous solution of H_2O_2 at various diluted concentrations. The data fitting was based on eq 1. For the data obtained under low vapor pressures of H_2O_2 (0.1, 0.2, 0.3, 0.5, and 1.0 ppm), Δb is linearly dependent on time, following the equation $\Delta b = K'Kt$. The slope ($\Delta b/\Delta t$) thus extracted can be replotted as a function of the vapor pressure of H_2O_2, as shown in (b), which yields a linear relationship with a fitting correlation coefficient of 0.99. The error bars are the standard deviations.

We expected that the wide interface and large porosity of the cellulose fibril networks would make the paper towel ideal for fast vapor response. To compare, we investigated the time course of the colorimetric reaction between the H_2O_2 vapor and the solid thin film of Ti(IV) salt, shown in Figure S3 in the Supporting Information. The thin film was made by drop-casting 130 μL of 0.1 M aqueous solution of ammonium titanyl oxalate onto a quartz slide to make a film of an area of ca. 4 cm^2, so that the molar amount of Ti(IV) salt per unit area is approximately the same as the amount of 20 μmol loaded onto a 2.5 × 2.5 cm^2 size of paper towel as shown in Figure 2. The UV−vis absorption spectrum of the film (with bare quartz slide as reference) was measured at various time intervals after exposure to the saturated vapor of 35 wt % H_2O_2 solution (225.4 ppm), shown in Figure S3a in the Supporting Information. The color formation saturates after about 600 s of vapor exposure (see Figure S3b in the Supporting Information), about four times slower than the paper towel sample, for which the same amount of titanyl salt saturates around 150 s (Figure 2).

Shown in Figure 3a are the values of Δb as a function of exposure time, measured under a series of equilibrium vapor pressures of H_2O_2, which were obtained by diluting the 35 wt % aqueous solution with water. All data fit very well to eq 1. It can be clearly seen from Figure 3a that the higher the vapor pressure of hydrogen peroxide, the faster the color forms. This is consistent with the surface adsorption kinetics as discussed above. When the vapor pressure of H_2O_2 was low, i.e., around or below 1.0 ppm, it took much longer to reach the equilibrium plateau, and more interestingly, within the early time regime (e.g., 900 s as investigated in our study here) Δb changes almost linearly with time. This is not surprising, if considering the small value of Kt, which allows the kinetics eq 1 to be simplified to a linear dependence on time,

$$\Delta b = K'Kt \tag{3}$$

Therefore, for low vapor pressures of H_2O_2, we have the slope $\Delta b/\Delta t = K'K$. Because K is proportional to the vapor pressure, it is expected that $\Delta b/\Delta t$ will be linearly dependent on the vapor pressure of H_2O_2. This linear relationship is indeed shown in Figure 3b, where for the low vapor pressures (0.1, 0.2, 0.3, 0.5, and 1.0 ppm) the slopes ($\Delta b/\Delta t$) as extracted from the plots in Figure 3a are replotted as a function of the vapor pressure of H_2O_2. Considering the measurement sensitivity of the color reader ($\Delta b = 0.1$), and if allowing for a detection response time of 10 s, we have $\Delta b/\Delta t = 0.01$, which corresponds to a vapor pressure of 0.4 ppm as indicated in Figure 3b. This value (corresponding to 250 times dilution of the commercial 35 wt % H_2O_2 solution) can be roughly considered as the detection limit for the vapor of hydrogen peroxide under the current measurement conditions. Upon further improvement and optimization of the measuring system, particularly by integration into a closed detector system (for maximized vapor sampling), the detection limit is expected to be improved down to the lower ppb range.

In conclusion, we have developed an efficient colorimetric sensing system for the vapor detection of hydrogen peroxide. The sensory materials are based on the cellulose fibril network of paper towels, which provides a tunable interface for modification with Ti(IV) oxo complexes for binding and reaction with H_2O_2. This one time use paper-based sensor material can provide a simple and economic method for peroxide vapor detection. Prospectively, the reported vapor sensor system proves the technical feasibility of developing enhanced colorimetric sensing using nanofibril materials that will be fabricated from building-block molecules functionalized with a Ti(IV) oxo moiety. Such a "bottom-up" approach will provide plenty of opportunities to enlarge the surface area (by shrinking the fiber size), enhancing the surface interaction with gas phase. Research along this line is underway.

■ EXPERIMENTAL METHODS

UV−vis absorption spectra were measured on a PerkinElmer Lambda 25 spectrophotometer. Optical microscopy imaging was performed with a Leica DMI4000B inverted microscope equipped with a high-resolution CCD camera. The color reader model CR-10, was purchased from Konica Minolta Sensing Americas, Inc. (minus value 0.1). The mini fan used for vapor exposure was purchased from Radio Shack (40 mm, 12V DC, 6500 rpm). Ammonium titanyl oxalate monohydrate and other chemicals were purchased from Fisher and used as received. The paper towels were purchased from SAFECHEM (Tork Advanced perforated Towel (white), HB9201).

Paper sample preparation: 100 μL of water solution of ammonium titanyl oxalate was drop-cast onto a piece of paper towel (2.5×2.5 cm^2 size), followed by drying in vacuum at room temperature for 1 h. To adjust the molar amount of titanyl salt loading (as marked in Figure 2a), various concentrations of stock solutions of titanyl oxalate were prepared and used: 0.001, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.4, 0.8, and 1.0 mol/L. Because of the bulk homogeneity of the fibril structure of the paper towel, a small droplet of water can be absorbed instantly and spread throughout the matrix of paper. For a small size of paper (2.5×2.5 cm^2), 100 μL of water solution was equally drop-cast at multiple points (3×3) atop the paper, thus a producing homogeneous distribution of the titanyl salt within the whole area, shown by the uniform color density upon exposure to the hydrogen peroxide vapor (see Figure S2 in the Supporting Information).

Vapor sensing test: For the measurements at a fixed vapor pressure of H_2O_2 (presented in Figure 2), the test was performed by hanging the loaded paper towel in the saturated vapor (225.4 ppm), above 10 mL 35 wt % H_2O_2 solution contained in a sealed 50 mL vial. The yellow color thus evolved at different time intervals was measured by the CR-10 color reader. For the measurements at a fixed load of titanyl salt (as presented in Figure 3), approximately 1 L of H_2O_2 solution (diluted down to various concentrations) was put in a 10 L container and sealed for 12 h to reach the equilibrium vapor pressure. The equilibrium vapor pressure corresponding to a specific diluted concentration of H_2O_2 solution was deduced from the literature.[53] The sensing test was performed by putting the loaded paper towel facing close ($\sim$ 0.5 cm) to the center of the fan, which was hung in the vapor contained in the sealed container (about 20 cm above the solution surface). The vapor was blown onto each sample (12 V, 6500 rpm) for various time intervals (shown in Figure 3) before taken out for color reading. In this study, the various low concentrations of H_2O_2 solution were obtained by diluting the commercial 35 wt % solution with pure water by 1000, 500, 300, 200, 100, 75, 50, 25, and 10 times, producing various saturated (equilibrium) vapor pressures, correspondingly, 0.1, 0.2, 0.3, 0.5, 1.0, 1.3, 1.9, 4.0, and 10.5 ppm.[53]

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Photograph showing the homogeneous distribution of titanyl salt via drop-casting, UV−vis absorption titration between titanyl salt solution and H_2O_2, time course of color formation monitored by UV−vis absorption, and selectivity test against potential interferences (PDF). This material is available free of charge via the Internet at http://pubs.acs.org/.

AUTHOR INFORMATION

Corresponding Author

*E-mail: LZANG@eng.utah.edu.

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