Polyaniline-Functionalized Nanofibers for Colorimetric Detection of HCl Vapor

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ABSTRACT: Hydrogen chloride (HCl) gas is a hazardous byproduct of industrial processes. Colorimetric approaches to facilitate portable and remote detection are especially desirable. We graft polyaniline to the surface of electrospun nylon nanofibers to minimize mass transfer. Using the resulting nanofibers, we demonstrate colorimetric detection of HCl at sub-ppm levels. We investigated the reusability of the fibers and observed a twofold increase in the limit of detection with multiple uses because of dedoping of the PANi indicated by elemental analysis. The limit of detection using visual detection was compared to spectrophotometric analysis. The ΔE from CIE LAB color space analysis via diffuse reflectance spectroscopy enhances the limit of detection by ∼fivefold when compared to visual detection. This analysis is a promising approach for remote detection using simple commercial digital cameras to achieve low limits of detection.

INTRODUCTION

Hydrogen chloride (HCl) gas is a common byproduct of industrial processes. Because it is hazardous, HCl is strictly regulated. An exposure to 5 ppm is considered a workplace hazard. Therefore, portable and remote detection of HCl at the ppm level is necessary. Colorimetric detection that does not require instrumentation is especially desirable.1−6

Optochemical detection of HCl has been reported using thin films of meso-tetra(4-pyridyl)porphyrin, which undergoes a color change upon protonation. Monitoring the change in UV absorbance at 470 nm, the detection limit was 0.01 ppm HCl.5 Similar porphyrins have been incorporated into hydrophobic membranes for sensing. The response rate of the sensor was observed to be diffusion-controlled.7

Electrospun nanofibers are considered promising for improving sensing performance because of their high surface area-to-volume ratio. Porphyrinated polyimide (porphyrins incorporated into the polymer backbone)5 or blends of styrene−ethylene−butylene−styrene triblock copolymer with pH-sensitive, pyridine-based dyes5 has been electrospun for fluorescence-based HCl detection. Improved sensitivity was observed when comparing electrospun nanofibers and drop-cast polymer membranes.

To avoid the need for instrumentation, colorimetric HCl detection using polymer nanofibers has also been considered using polydiacetylenes, a pH-responsive, conjugated polymer that transitions from blue to red upon exposure to HCl because of the formation of quaternary ammonium salts. Visible detection of 2 ppm was reported. However, the nanofibers were not stable upon exposure to HCl, so reuse was not possible.1

Using nylon−polyaniline blend nanofibers, ppb-level detection of HCl was achieved using a quartz crystal microbalance (QCM). The limit of detection was significantly lower than polyvinyl alcohol−polyaniline films (~10 ppm). Frequency shift response curves as a function of time were comparable for three cycles.2 When using a QCM for detection, a color change from blue to green was observed upon exposure to HCl because of the protonation of the polymer backbone.2,8 However, additional studies are required to establish colorimetric HCl detection.
In this work, we demonstrate colorimetric detection of HCl using polyaniline grafted to electrospun nylon-6,6 nanofibers to minimize diffusion limitations. We focus on evaluating the effect of reuse on the limit of detection. We further compare the limit of detection using visual detection to spectrophotometric analysis.

RESULTS AND DISCUSSION

Nanofiber Preparation. Nylon nanofibers were prepared by electrospinning a solution of nylon in formic acid. In a typical experiment, nylon 6,6 was dissolved in formic acid (20 wt %). Electrospinning nylon–formic acid solutions resulted in 290 ± 80 nm nanofibers (Figure 1A). Some netting, that is, the presence of networks of thin nylon nanofibers, was observed. This observation is consistent with recent work using formic acid as a solvent. The formation of the “nanonets” was attributed to phase separation of the polymer during solvent evaporation.

Graft polymerization of polyaniline is initiated from amine groups on the nylon nanofiber. To increase the amine groups available for grafting, the nylon nanofibers were partially hydrolyzed by HCl. Nanofibers were cut into 0.5 in. diameter pieces, then placed in 2.5 M HCl at ambient conditions for 1 h, and finally washed with deionized water until the wash was neutral. Acid treatment of the nylon fibers cleaves the amide groups exposing a carboxylic acid and amine functional group. Polyaniiline was grafted to the nylon fibers via chemical oxidative polymerization at 0 °C based on previous reports. Briefly, the acid-treated fibers were placed in aniline hydrochloride dissolved in HCl. Ammonium persulfate was added dropwise with constant stirring. The reaction proceeded on ice with constant stirring for 2.5 h. The PANi was converted to the emeraldine base form of PANi by exposure to ammonium hydroxide. Upon exposure to ammonium hydroxide, the PANi backbone is deprotonated. There is a corresponding change in optical properties, that is, green to blue (Figure 3A), as can be also be identified by the maximum in % reflectance shifts from ∼540 to ∼475 nm (Figure 3B). The changes in the spectra as a function of pH are comparable to previous reports. Because this change is reversible and can

Figure 1. SEM images of (A) electrospun nylon, (B) acid-treated nylon nanofibers, (C) PANi-grafted to nylon nanofibers exposed to acid and reset with ammonia, and (D) PANi-grafted to nylon reset 15 times with a 3 μm scale bar.

Figure 2. FTIR-ATR spectra of nylon and PANi-grafted to nylon nanofibers normalized and baseline-corrected. Upon grafting, new peaks at ∼820 and ∼1495 cm⁻¹ are observed because of the presence of PANi.
We performed elemental analysis of the fibers after 15 resets for comparison to the initial nanofibers (Table 1). Comparison using XPS indicates a decrease in the chlorine content with multiple resets. This dedoping has been observed previously and attributed to the diffusion of the small anion dopants out of the PANi. In previous reports, dedoping affects the PANi backbone oxidation state and reduces the conductivity of PANi. The change in the oxidation state affects the colorimetric detection, and as the dopant level decreases, the amount of HCl required to induce a change in color increases. Given that the dopant level is 0% after 15 resets, no further decrease in the limit of detection is expected with further reuse. A consistent response would be expected in a practical setting, provided an appropriate pretreatment to dedope the fabrics.

Limit of Detection Comparison: Visual Detection Versus Spectrophotometric Analysis. The sub-ppm limit of detection is promising, and colorimetric detection offers an equipment-free method of analysis. With visual detection, we expect there to be a trade-off between the ease of use and limit of detection. Therefore, we compared the limit of detection using visual determination with diffuse reflectance spectroscopy after 15 resets. Using visual determination, a color change was observed at a concentration of 0.2 ppm. Using diffuse reflectance spectroscopy, we used two metrics to define the color change: (1) an increase in the wavelength at which the maximum reflectance occurred of 20 nm or (2) a ΔE of 5 in the CIE LAB color space from the diffuse reflectance spectroscopy measurement. The CIE L*A*B* space was defined by the International Commission on Illumination, abbreviated CIE. It uses three axes to define color, lightness (L), A-axis to differentiate red and green, and B-axis to differentiate blue and yellow. The L*A*B* space was selected because it is strongly correlated with human visual perception. The limit of detection using the CIE L*A*B* color space was 0.04 ppm, whereas the limit using the shift in the wavelength was 0.08. As expected, spectrophotometric analysis decreased the limit of detection by ~fivefold. Interestingly, the changes in the CIE L*A*B* color space were ~twofold more sensitive than monitoring changes in the reflectance spectra. The use of the CIE L*A*B* color space to define a color change can be adapted to commercial cameras to facilitate remote monitoring as a future direction.

Overall, the focus of this work was the visual detection of HCl using PANi-modified polymer nanofibers. PANi is a useful platform for evaluating visual detection and has been used for the detection of other compounds such as NH4, H2S, etc. Because the mechanism of the color change is due to the protonation of the PANi backbone, this approach is not specific to HCl. Selective detection of HCl may be possible by doping PANi with iron and aluminum and will be the objective of future studies.

Table 1. XPS Elemental Analysis of PANi (Emeraldine Base Form)-Containing Fibers Initially and after 15 Resets

| Resets | CI (at. %) |
|--------|------------|
| 0      | 0.09 ± 0.02 |
| 15     | 0.00 ± 0.00 |

Figure 3. (A) Photograph of PANi-grafted nanofibers in the emeraldine base form (blue, bottom) and emeraldine salt form (green, top). (B) Analysis of the different forms of PANi by diffuse reflectance spectroscopy.

Figure 4. Minimum amount of HCl detected visually within 5 min initially and after being reset multiple times. The minimum amount of HCl increases after 2 and 6 resets but remains consistent from 6 to 15 resets (p < 0.05).

HCl vapor that could be detected visually within 5 min increased from 0.09 to 0.16 ppm. The concentration of HCl vapor that could be detected visually after 15 resets was comparable to 6 resets (Figure 4).

In contrast with our experiments, when PANi deposited on a filter paper was used for the colorimetric detection of ammonia, no change in the limit of detection was noted for up to 50 cycles. To understand the observed decreased limit of detection of HCl vapor, we further analyzed the initial samples and the reset samples using X-ray photoelectron spectroscopy (XPS).
■ CONCLUSIONS

Overall, we have demonstrated the use of PANi-grafted nylon nanofibers for the colorimetric detection of HCl. Sub-ppm levels of HCl were detected visually within 5 min. We investigated the reusability of the fibers, and the limit of detection increased by ~50% with multiple uses. We attribute this increase in the limit of detection to dedoping of the PANi indicated by elemental analysis. After an initial decrease in the dopant level, the limit of detection remains consistent, which is important for practical applications. Complete dedoping is observed after 15 resets, yet no further decrease in the limit of detection is expected with additional uses. Finally, we quantify the trade-off between the ease of use and limit of detection by comparing visual detection to spectrophotometric analysis. The limit of detection improved by ~50% using the ΔE from the CIEL*a*b* color space analysis. This analytical approach is promising for remote detection using commercial digital cameras to achieve low limits of detection with simple equipment.

■ METHODS

Materials. Nylon-6 pellets (Ultramid B40 01, viscosity average MW = 63 kDa) were obtained from BASF Corporation (Michigan, USA). NMP and ammonium hydroxide were obtained from Fisher Scientific (Wood Dale, IL, and Arlington, TX, respectively). Aniline hydrochloride, ammonium persulfate, formic acid, and hydrochloric acid were obtained from Sigma (St. Louis, MO). All chemicals were used as received.

Electrospinning. Nylon nanofibers were prepared by electrospinning a solution of nylon in formic acid. In a typical experiment, nylon 6,6 was dissolved in formic acid (20 wt %). The mixture was stirred for 3–4 h at 60 °C and cooled at an ambient temperature for 1 h without stirring to minimize air bubbles. The solution was then electrospun onto aluminum foil using a point-plate configuration composed of a precision syringe pump (New Era NE-300) and a high-voltage power supply (Matsusada Precision Inc., model AU-40R0.75) with positive polarity. Typical electrospinning parameters were a flow rate of 0.15 mL/h, tip-to-collector distance of 12 cm, 22-kV output rate of 0.15 mL/h, tip-to-collector distance of 12 cm, 22-kV. Polyaniline was grafted to the nylon via chemical oxidative polymerization at 0 °C based on previous reports.11 Briefly, the acid-treated fibers were placed in 10 mL of 0.150 M aniline hydrochloride dissolved in 1.2 M HCl and placed on ice. Ammonium persulfate (0.150 M in 1.2 M HCl) was cooled to 0 °C and 10 mL was added dropwise with constant stirring. The reaction proceeded on ice with constant stirring for 2.5 h. The PANi–nylon samples were placed in 0.1 M ammonium hydroxide and sonicated for 30 min to convert the PANi to the emeraldine base form. Because the emeraldine base form is soluble in NMP, the fabrics were placed in NMP and sonicated for 30 min to remove PANi not covalently attached to the surface.12,13 The NMP washes were continued until the solvent remained colorless after sonication. Finally, the fabrics were rinsed with deionized water and dried at ambient conditions before further use.

Sample Characterization. The samples were sputter-coated with gold, and the fiber morphology was examined with SEM using Hitachi SU-70 FE-SEM (accelerating voltage of 2 kV). The average fiber size and standard deviation were determined by measuring the diameter of 100 fibers using ImageJ software developed by US NIH. Nylon nanofibers and PANi-grafted samples were analyzed by attenuated total reflection (ATR) infrared spectroscopy (Thermo Scientific Nicolet iS10). Spectra were recorded from 400 to 4000 cm⁻¹ averaging 64 scans. Diffuse reflectance spectra (350–1200 nm) of the samples were obtained with an Ocean Optics Flame spectrometer (FLAME-S-VIS-NIR-ES) equipped a tungsten–halogen light source (HL-2000-HP-FHSA, 20 W output) with a diffuse reflectance probe (RPH-1) at room temperature using poly(tetrafluoroethylene) as a standard.27 Elemental analysis was performed using a ThermoFisher ESCALAB 250 X-ray photoelectron spectrometer with a monochromated aluminum X-ray source, survey and high-resolution spectra were recorded by 1 and 0.1 eV steps, respectively similar to previous reports.28 Data were fit and analyzed using CasaXPS 2.3.16 V and NIST standard reference database 20, version 4.1. The dopant concentration was determined from the high-resolution spectra measuring three locations per sample.

Colorimetric Detection of HCl. Colorimetric responses to HCl vapor were carried out by visual inspection. In a sealed container, nanofibers with PANi were suspended over aqueous HCl solutions of increasing concentration until a visual color change was observed within 5 min. The HCl in the vapor phase was calculated from tabulated data.29 Afterward, the fabric was reset by submersion in an ammonium hydroxide solution (5 mL, 0.1 M) for 1 min, dried at ambient conditions, and the colorimetric response was remeasured. To examine reusability, the colorimetric responses for up to 15 resets were measured for at least 6 samples.

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Notes
The authors declare no competing financial interest.

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