Cellulose Acetate–Cellulose Nanowhisker Nanocomposite Immobilized with a DCDHF-Hydrazone Chromophore toward a Smart Test Strip for Colorimetric Detection of Diethyl Chlorophosphate as a Nerve Agent Mimic

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ABSTRACT: Exposure to nerve agents, which are usually colorless and odorless gases, may cause organ failure, paralysis, or even quick death. Diethyl chlorophosphate (DCP) has been recognized as one of the most well-known chemical warfare nerve agent mimics. In the current study, we introduce a simple strategy for the development of a portable and reversible nanocomposite-based microporous strip for naked-eye detection of DCP within a few seconds. A dicyanomethylenedihydrofuran hydrazone (DCDHF-H) chromophore was synthesized by an easy azo-coupling reaction and encapsulated in situ during the preparation of cellulose acetate/cellulose nanowhisker/hydrazone (CA-CNW-H) nanocomposites. These CA-CNW-H nanocomposites displayed a bathochromic shift in the absorption intensity of about 142 nm from 438 to 580 nm with the increase of the DCP concentration. The present CA-CNW-H sensor strip displayed a detection limit for DCP ranging from 25 to 200 ppm. The color change of CA-CNW-H from yellow to purple due to exposure to DCP was detected by CIE Lab analysis. The morphology, fibrous crystallinity, thermal stability, and mechanical properties of the prepared CA-CNW-H sensor strips were investigated.

1. INTRODUCTION

Chemical warfare compounds such as organophosphates, whether in aqueous or gaseous forms, have sparked numerous recent studies. Chemical warfare agents are compounds designed to cause critical organ damage, incapacitation, or even death during military operations owing to their physiological effects.1,2 Agents used in chemical warfare are divided into five categories: nerve, blood, vesicant, incapacitation, and choke agents.3 Nerve agents were created as a consequence of the Second World War’s increasing advancement in chemical warfare weapons. Because of their potential to target the nervous system quickly, they are classified as neurotoxins. Because of their extreme toxicity and ease of production, nerve agents are very dangerous and must be detected using technologies that are both quick and reliable in their detection.4–6 Nerve agents are a class of chemical compounds containing phosphorus that may disrupt the flow of information from the nervous system to various organs. They have gotten a lot of attention because of how quickly and seriously they impact human and animal health.7 A number of different materials, such as gold nanoparticles and fluorescent dyes, have been used in the development of modern organophosphate vapor sensors, which detect a hydrolysis-released functional moiety or quickly detect the organophosphate-containing agent itself. Materials research science has focused on detection devices that help identify chemical warfare agents while using less effort in miniaturizing the sensing tool.8 Analytical applications in actual samples are extremely limited due to the rapid hydrolysis of nerve agent mimics under aqueous conditions. Therefore, nonaqueous systems can be easily used to monitor both absorption and
Scheme 1. Synthesis of the DCDHF-Hydrazone Sensory Chromophore

fluorescence spectral shifts to identify nerve agents.9–11 As a result, simple and efficient methods for detecting nerve agents in aqueous solutions remain highly desirable.

The renewability, biocompatibility, biodegradability, great abundance, and cheapness of celluloseic detectors make them important for environmental and biomedical applications. Cellulose is a hydropphilic biological polymer comprising a β-1, 4-d-glucopyranose moiety bearing a hydroxyl functionality enabling the development of strong H-bonds.12 Nanomaterials have gained popularity for many applications, such as environmental monitoring, medication, sensors, and food processing.13 Although a broad variety of customized nanomaterials were employed to enhance polymer nanocomposites, cellulose nanowhiskers (CNWs) have limited studies in this research field. CNWs are a remarkably promising material for a broad variety of applications, such as packaging, molecular biology, paper manufacturing, and cosmetics.14,15 Acid hydrolysis had been utilized to make CNWs from microcrystalline cellulose to enhance the physical, permeability, and mechanical properties of films. This is because of the enticing qualities of CNWs, such as minimal weight and a high surface area. These physicochemical properties and broad usage have grabbed the attention of both research and industry.16 In order to strengthen and increase the surface area of a cellulose acetate film, CNWs have been employed as a high-quality reinforcement ingredient. Thus, the introduction of CNWs into a cellulose acetate film may greatly enhance the mechanical and thermal properties and porosity and surface area of the developed nanocomposite paper strip.17

Because of the portability, reusability, and simplicity, solid-state detection techniques have been critical because they allow for speedy online detection at a low cost.18 Due to the large surface area of cellulose microstructures, analytes such as gases and fluids may be easily absorbed into their surfaces and diffused quickly throughout the mesh, resulting in excellent sensitivity.19 Electrochemical, enzymatic, fluorescence, and surface acoustic wave approaches are some of the detection techniques used for nerve agents. However, these methods were slow to respond, unselective, less sensitive, characterized with a lack of specificity, expensive, and not portable. In addition, they may need the use of highly skilled personnel and specialized electrical and electric components.20–22 In order to enable exact detection of very deadly nerve agent vapors, sensors must respond instantly with high specificity at a low cost. Even these sensors that engage irreversibly with a target vapor have a limitation in that they can only be used once; the benefit of great specificity and quick response time outweighs this disadvantage. A fast-responding sensor for an uncommon event makes the replacement procedure acceptable as long as its chemistry can be trusted to provide accurate results.23 For the identification of a primary hazard or an environmental fluctuation, both colorimetric and fluorescent dye probes have been used as simple and effective techniques of detection. In addition to the lack of electrical or electronic entities, the sensors presented with colorimetric and fluorescent dye probes demonstrated a cheap cost and easy miniaturization technique and the capacity to evaluate the targeted analyte without making physical contact. Additionally, both colorimetric and fluorescent sensor practices do not need the use of highly qualified personnel or a sophisticated apparatus.24,25 Dicyanomethylenedihydrofuran hydrazone (DCDHF-H) chromophores are multistimuli-responsive molecular probes used to monitor hazardous gases, pH, temperature, solvent polarity, and biological substrates. The azo-coupling of dicyanomethylenedihydrofuran with a suitable diazonium salt was all that was required to synthesize such a class of molecular probes.26,27 The thermal, chemical, reversibility, and photo-stability characteristics of DCDHF-H have led to the development of various chromogenic detectors. For halochromic and dangerous gas recognition, they have been used as molecular probes embedded in various polymers. They were utilized as antibacterial substances and as disperse chromophores for coloring hydrophobic textiles.28 Diethyl chlorophosphate (DCP) has been reported as an effective nerve mimic for chemical warfare agents that inhibit acetylcholinesterase (AChE) and cause paralysis and death.29

Herein, microporous sensing technology was provided for colorimetric and onsite detection of nerve agent mimics. We prepared a solid-state colorimetric sensor for nerve agents using biodegradable and renewable microporous cellulose-based nanocomposites with the active sites of the DCDHF-H probe immobilized onto the biocomposite matrix. Selective colorimetric changes together with noticeable naked-eye detection for DCP were detected on the prepared microporous cellulose acetate/cellulose nanowhisker (CA-CNW) nanocomposite matrix immobilized with the DCDHF-H probe. Electric power, electronic components, experienced personnel, and expensive equipment are not required for the present sensor design. This method may provide significant insights into the development of simple, efficient, and inexpensive colorimetric solid-state sensing technologies for the detection of gaseous nerve agents. Moreover, the presented study presents an onsite detection strategy for nerve agents, which is highly significant for protecting human life.
2. RESULTS AND DISCUSSION

2.1. Fabrication of the CA/CNW Sensory Strip. Lower excitation energy that comes with extending the conjugation of a molecular system leads to an electronic molecular system that operates on a push–pull basis. An extended conjugated chemical system derived from para nitro-substituted phenyl-hydrazone conjugated with strong electron-withdrawing DCDHF was demonstrated with DCDHF-H. In comparison to the DCDHF-hydrazone form, the deprotonated DCDHF-H anionic isomers absorbs at a greater wavelength. The acidic hydrazone NH group deprotonates to produce DCDHF-hydrazone anions. Scheme 1 displays a simple procedure for the synthesis of a DCDHF-hydrazone sensory chromophore. DCDHF-hydrazone was synthesized in a reliable procedure for the synthesis of a DCDHF-hydrazone sensory chromophore. FTIR, and DSC were used to investigate the chemical structure of the synthesized DCDHF-hydrazone sensory chromophore.

Pure cellulose was recovered from rice straw after wax, silica, hemicellulose, lignin, and other soluble components were removed using an alkali solution. The lignin residue was removed, and the white cellulose fibers were revealed when the product was oxidatively bleached. The alkali curing process dissolves and delignifies hemicellulose, causing this effect. The bleaching process of rice straw affected the cellulose accessibility and promoted the acid hydrolysis process, which led to CNW production. The chemical composition of the extracted cellulose showed the cellulosic content (80%), lignin (0.35%), ash (8.15%), and hemicellulose (11.5%). After the noncellulosic components were dissolved, hydrogen bonds were used to connect the dried fibrous cellulose together. Sulfuric acid was used to hydrolyze the remaining pure cellulose content, resulting in the formation of CNWs. To breakdown cellulose polymeric strands into lower molecular weight soluble sugars, the hydrolysis process required 30–45 min to enable sulfuric acid to spread and attack the amorphous cellulose. Because of sulfuric acid, CNWs may be esterified to make cellulose sulfate, which generates negative charges on their surface, allowing for surface esterification. Creating a repulsion force between the CNW’s negative charges helps keep them from undergoing aggregation in an aqueous solution. Solutions of CA-CNW were prepared at various amounts of CNWs. After homogenizing the mixtures, several amounts of DCDHF-H were added to CA-CNW-3, which was monitored as the best-fitting strip. The CA-CNW sensory film was created by drop-casting a homogeneous mixture of the prepared nanocomposites under ambient conditions. As a biomaterial with high porosity, low density, and a large surface area, DCDHF-H was imprinted into the microporous CA-CNW film. The pH-sensory DCDHF-hydrazone chromophore was encapsulated within the bulk of eco-friendly CA-CNW as a hosting matrix to create an easy-to-use and reversible colorimetric sensor. It was found that the CA-CNW-H film had a sponge-like fibrous shape. CA-CNW-H immobilized with a DCDHF-hydrazone sensory chromophore was used to build microporous three-dimensional scaffolds, which facilitate adsorption and diffusion of DCP through the porous bulk to the DCDHF-H spectroscopic probe. The large surface area and extremely porous design results in increased sensitivity to DCP vapors.

2.2. Mechanical Properties. Due to their polar nature, CA and CNWs have both been utilized to make nano-composites with good mechanical characteristics. In both CA and CNW molecules, the majority of the hydroxyl groups form hydrogen bonds that are either intra- or intermolecular in nature. CA’s and CNW’s strong hydrogen bonds make it easy to disperse a variety of substances in the bulk. When it comes to tensile strength and tensile index, tensile strength refers to the greatest stress that a material can withstand before breaking. As can be seen in Figure 1, adding more CNWs to the CA matrix improves the overall strength when compared to using just pure CA. This anticipated that CA and CNWs would be compatible, which improved the interactions between the two molecules. Thus, the best results for the mechanical properties of the prepared CA-CNW film were assigned to CA-CNW-3. The mechanical characteristics were improved by adding the DCDHF-hydrazone sensory chromophore to the CA-CNW films. As a result, it is possible to attribute this to the uniform dispersion of the DCDHF-hydrazone sensory probe across the composite film, together with the creation of hydrogen bonds between the chromophore and the CA and CNW molecules. As shown in Figure 1, increasing the total content of CNWs has a positive effect on the strength compared to using pure CA. This predicted the compatibility between CA and CNWs, which enhanced the interactions between them. Loading the DCDHF-hydrazone sensory probe onto the CA-CNW films resulted in improving the mechanical properties. This could be attributed to the high homogeneous distribution of the DCDHF-hydrazone sensory probe in the nanocomposite film, in addition to the creation of H-bonding between the chromophore and CA-CNW.

2.3. Thermal Properties. Thermogravimetric analysis (TGA) was used to assess the impact of the DCDHF-hydrazone sensory probe on the thermal stability of the CA-CNW films (Figure 2). When the temperature was increased,
there were three primary stages in the thermal breakdown process. The first stage was between 25 and 140 °C, which was assigned to the moisture evaporation at 100 °C. During the second stage, the temperature ranged from 180 to 280 °C, which was assigned to the thermal decomposition of CNWs and CA. The degradation of the cellulosic matrix was identified in the second stage with weight losses of 10, 20, and 30% of the pure sample. The second stage began at a lower temperature with the DCDHF-hydrazone probe added, and weight loss increased. The most weight was lost during the third stage, which was monitored between 325 and 455 °C. S0, S1, and S8 each had a loss rate of 80, 90, and 100% in the third phase, respectively. The inclusion of DCDHF-hydrazone had an impact on weight reduction with increasing the concentration of DCDHF-hydrazone. The CA-CNW-H films with the greatest overall amount of DCDHF-hydrazone lost weight when heated to 470 °C. Thus, the organic DCDHF-hydrazone immobilized in CA-CNW increases the rate of pyrolysis. Due to the greater rate of weight loss of the CA-CNW-H films compared to the pristine CA-CNW film, the thermal stability of the CA-CNW-H films was less than the pristine CA-CNW film’s thermal stability. About 19% of the CA-CNW film’s residual weight was monitored. The thermal stability was shown to be decreased in CA-CNW films when the DCDHF-hydrazone ratio was increased. This delayed the start temperature for the third breakdown stage marginally. The gradual weight loss was attributable to the pyrolysis of more stable residues when the temperature was increased as demonstrated by the TGA curves.

2.4. Morphological Properties. A recyclable microporous CA-CNW-H strip was developed in order to create a portable solid-state sensor. The test strip made from cellulose acetate and cellulose nanowhisker nanocomposites immobilized with poly(2-vinylpyridine) and the DCDHF-hydrazone chromophore was used to determine the presence of DCP vapors. CA-CNW-H sensors exposed to DCP vapors undergo a quick color shift, which was proved using CIE Lab colorimetric measurements. This change was caused by the transition from the hydrazone chromophore to the phosphoramid form. When DCDHF-hydrazone reacts with DCP, a hydrochloric acid byproduct is released, and the poly(2-vinylpyridine) layer acted as proton-acceptor pyridine active sites to neutralize the released hydrochloric acid byproduct. Thus, even after exposure to DCP vapors, the poly(2-vinylpyridine) layer retains the product’s high reactivity. The methanolic solution of DCP changes the color of the CA-CNW-H sensor strip from yellow to purple, whereas air drying restores the strip’s natural yellow hue. In general, solid-state sensors are easy to use and realistic, while also being affordable, lightweight, and portable. As a portable sensing device, a solid-state detector may be utilized in routine laboratory examinations. As a result, developing a solid-state eco-friendly sensor for nerve agent mimics was critical. A typical cellulose acetate/cellulose nanowhisker nanocomposite substrate has a sponge-like porous structure, is superior in thermal insulation, has strong mechanical properties, and has a large surface area, making it a versatile multipurpose material. ImageJ SEM software measured the pore sizes of the produced CA-CNW-H sensory films and found that they ranged from 5 to 25 μm. These sponge-like structural characteristics are highly significant toward the

Figure 2. TGA of the CA-CNW strips at different ratios of DCDHF-hydrazone.

Figure 3. SEM micrographs of S0 (a−c) and S5 (d−f).
development of ultrasensitive detection tools. No changes were seen in the microporous architecture after adding DCDHF-hydrazone to the cellulose nanocomposite films to indicate that the DCDHF-hydrazone probe was completely incorporated into the bulk of the nanocomposite film. Due to its huge surface area, CA-CNW-H displayed high sensitivity to DCP, helping to diffuse DCP molecules throughout the film matrix. The scanning electron microscopy (SEM) images of CA-CNW-H are shown in Figure 3.

Figure 4 displays the Fourier transform infrared (FT-IR) spectra of the DCDHF-hydrazone-immobilized CA-CNW-blended films. The stretch vibration of OH groups is responsible for the large peak at 3309 cm⁻¹. The aliphatic CH stretch is thought to be responsible for the peak value of 2914 cm⁻¹. The stretching vibration of the pyranose ether bonding is responsible for the spectral bands detected in the 1031–1174 cm⁻¹ range. However, the carbonyl ester (O−C=O; 1718 cm⁻¹) group attributed to cellulose acetate was monitored to disappear with increasing the DCDHF ratio. This could be assigned to the increased DCDHF particles on the paper strip surface blocking the carbonyl group. The cellulose acetate carbonyl group could be blocked also by increasing the ratio of CNWs at different spots on the paper strip surface during the preparation of the CA-CNW-H nanocomposite strips. Similar effects were also monitored for the stretching vibrations of the pyranose ether bonding.

2.5. Colorimetric Sensing of DCP. Over the past several decades, a wide range of chemical warfare chemicals have been prepared. Chemical warfare agents are some of the most destructive and deadliest weapons employed in combat. A variety of organophosphates have been studied for use as military nerve gas and agricultural pesticide formulations. The development of innovative and improved methods to detect highly reactive organophosphonates, such as sarin, tabun, and soman, is still required despite the advances in research made over the previous few decades. These organophosphonate-based nerve agents function as strong inhibitors of AChE that is critical for nerve function. The current detector’s architecture has the ability to undergo a bathochromic shift when exposed to reactive phosphate esters. These findings provide a straightforward procedure for creating a DCDHF-H-immobilized reversible sensing nanocomposite strip. The solid-state microporous detector’s sensitivity to DCP solution in methanol may be increased because of the increased surface area. Upon exposure to a 1 M methanolic DCP solution, CA-CNW-H changes color from yellow to purple (pH 6.8). The molecular switching activity of the DCDHF-H active sites allowed the detection of nerve agents. The current colorimetric probe uses an irreversible interaction between DCDHF-H and phosphoryl halide to identify the presence of an organophosphonate-based nerve agent. There is a maximum absorption wavelength of 438 nm assigned to the DCDHF-hydrazone protonated isomer. However, the DCDHF-hydrazone deprotonated anion isomer exhibits a maximum absorption wavelength of 580 nm. The conjugation of the hydrazone anion fragment with the electron-acceptor DCDHF moiety creates a donor−acceptor structure (Scheme 2). There is acidic N−H in the phenylhydrazone unit that is beneficial for the anion generation and improves the electron donation ability of the hydrazone moiety.

The colorimetric analysis of the sensor strip was explored at different ratios of DCDHF-H, as given in Table 1. The microporous cellulose film’s sensitivity was tested while the concentration of DCDHF-hydrazone was increased. The DCDHF-hydrazone ratio was observed to affect the sensitivity of the microporous cellulose dipstick. Increasing the DCDHF-hydrazone ratio higher than S₅ resulted in lower sensitivity. No colorimetric changes were detected with the decrease of the DCDHF-hydrazone ratio to less than S₃. Thus, the best colorimetric detection results were assigned to S₅.

Scheme 2. Suggested Reaction Mechanism of DCDHF-Hydrazone with DCP

![Scheme 2](https://doi.org/10.1021/acsomega.1c07198)
When the concentration of DCDHF-hydrazone was increased from $S_1$ to $S_5$, the color strength increased significantly. However, the quantity of DCDHF-hydrazone increasing from $S_5$ to $S_0$ was associated with a very small increase in color strength. As a consequence, the $S_5$ sample was monitored with the best colorimetric data. When the concentration of DCP is increased from 25 to 200 ppm, the absorbance wavelength maxima increased from 438 to 580 nm. Before and after exposure to DCP vapors, the three-dimensional colorimetric space parameters ($L^*, a^*, b^*$) were explored. When DCDHF-hydrazone interacts with DCP, the maximum absorption changes to a longer wavelength, demonstrating a bathochromic shift. Thus, it is possible to use DCDHF-H⁺ spectral property to identify organophosphonates. DCP was identified at concentrations between 25 and 200 ppm (Figure 5). As the concentration of DCP was increased, the absorbance intensity at 438 nm (hydrazone form) steadily increased, approaching 580 nm (hydrazone anion form). Infrared and proton NMR spectral profiles of DCDHF-hydrazone in the presence and absence of DCP confirmed the deprotonated hydrazone anion’s existence. In the infrared spectrum of DCDHF-hydrazone recovered from a mixture of DCP and DCDHF-hydrazone in acetonitrile, the typical secondary NH band (at 3257 cm⁻¹) was found to vanish (Figure 3S). A little quantity of DCP was added to a DMSO-$d_6$ solution of DCDHF-hydrazone to see whether the results were different from those of the control. The N=H signal (at 12.09 ppm) of the DCDHF-hydrazone $^1$H NMR spectrum was monitored to progressively vanish as the DCP concentration increased (Figure 4S). This suggests the presence of a quinoid form generated between the hydrazone NH nitrogen lone pair of electrons and 4-nitrophenyl.$^{34,35}$ After abstracting a proton from the NH moiety driven by DCP, the DCDHF-hydrazone anion exhibits an improved resonating activity due to the negative charge interacting more strongly with the DCDHF acceptor, leading to an extended conjugation. Figure 6 displays a color change of the paper strip from yellow to orange, red, and purple depending on the DCP concentration (0–200 ppm). Based on the above-mentioned results, an intramolecular charge transfer shift in the DCDHF-H active sites is most likely to be responsible for these colorimetric changes. Because of the reversible deprotonation/protonation process of DCDHF-H, this reversible colorimetric shift in response to DCP exposure may be attributed to the delocalization of charges on the generated deprotonated hydrazone anion. In order to recognize DCP, the hydrazone NH proton is displaced with DCP, which is made possible by the strongly electron-withdrawing nitro group on the hydrazone moiety and the strong DCDHF fragment. $S_5$ was tested for reversibility by exposure to DCP vapors to result in a rapid shift in colorimetry from yellow to purple. After a few seconds of removing the DCP vapor source, the sensor returns to its original yellow hue, demonstrating a high degree of reusability. After a few repetitions of this operation, it was determined that the reversibility was not fatigued. As a result, the sensor’s matrix may be reused several times with gaseous organophosphate nerve agents without degrading. Figure 7 shows the maximum value of absorbance intensity at 438 and 580 nm after each cycle in the absence and presence of DCP vapors.

Only negligible changes in the colorimetric CIE Lab measurements were detected upon exposure to vapors of various solvents and acids, such as acetic acid, formic acid, hydrochloric acid, methanol, ethanol, tetrahydrofururan, n-hexane, dimethyl sulfoxide, acetonitrile, dichloromethane, chloroform, toluene, and deionized water. Thus, no interference to the detection performance of the sensor strip were observed by these solvents or acids. However, the sensor strip was observed to respond to the vapors of aliphatic amines. The less-basic aryl amines were undetectable. Relying on the amine alkaline strength, a selectivity was observed for the different aliphatic amines ($2° > 1° > 3°$), as illustrated in Table 2.

Table 1. Colorimetric Properties of CA-CNW-H Strips at Different Ratios of DCDHF-Hydrazone Before ($A_1$) and After ($A_2$) Exposure to DCP Vapors

| strip | $L^*$ | $a^*$ | $b^*$ | $K/S$ |
|-------|-------|-------|-------|-------|
| $S_0$ | 91.24 | 91.51 | −0.63 | −0.45 | 1.31 | 1.46 | 0.74 | 0.81 |
| $S_1$ | 85.78 | 72.04 | −13.91 | 14.53 | 17.97 | −5.67 | 1.05 | 2.62 |
| $S_2$ | 83.56 | 70.28 | −13.54 | 15.28 | 18.61 | −6.55 | 1.83 | 3.78 |
| $S_3$ | 82.79 | 69.34 | −12.00 | 18.67 | 20.53 | −8.02 | 2.44 | 4.66 |
| $S_4$ | 80.85 | 67.07 | −10.75 | 20.35 | 22.84 | −10.41 | 4.59 | 6.58 |
| $S_5$ | 77.26 | 62.12 | −7.38 | 23.70 | 25.90 | −13.63 | 7.32 | 9.41 |
| $S_6$ | 76.00 | 61.53 | −6.42 | 24.81 | 26.91 | −14.91 | 8.50 | 9.90 |
| $S_7$ | 75.82 | 60.12 | −5.17 | 24.52 | 27.00 | −14.80 | 9.31 | 10.20 |
| $S_8$ | 75.31 | 59.40 | −5.64 | 24.14 | 28.08 | −15.07 | 9.62 | 10.71 |

Figure 5. UV–vis absorption spectral profiles of $S_5$ as a function of the DCP concentration.
Temperature

Vapors Released by Heating the Alkyl Amine to its Boiling

Exposure to Vapors of DCP in the absence and presence of DCP vapors. The concentration range of 25 ppm of S5 in the absence and presence of DCP vapors. A hydrazone-type DCDHF-based chromophore was immobilized onto polymer nanocomposite strips based on CA-CNW. Exposure of CA-CNW-H to DCP vapor changes the hue from yellow to orange, red, and purple, relying on the amount of DCP. High sensitivity and selectivity were shown by the microstructured CA-CNW-H detector. SEM, FT-IR, and thermogravimetric analysis were utilized to examine the films' morphological and structural properties. Comparing the present colorimetric detector, which contains an environmentally benign CA-CNW biopolymer-based nanocomposite, to earlier sensors that usually necessitate complicated electronic parts and difficult processing, the former has simple, portable, cheap, rapid, reversible, sensitive, and selective performance for onsite detection of hazardous organophosphorus vapors.

3. CONCLUSIONS

A hydrazone-type DCDHF-based chromophore was immobilized onto polymer nanocomposite strips based on CA-CNW. The concentration range of 25–200 ppm of a reactive DCP nerve agent simulant causes them to change color in less than a second. After exposure to DCP aqueous or vapor phases, the hydrazone-immobilized CA-CNW sensor showed a reversible colorimetric change, which was recognized by CIE Lab analysis. Selective responses to DCP vapors make these CA-CNW-H nanocomposite sensor strips appropriate for quick analysis. Selective responses to DCP vapors make these CA-CNW-H nanocomposite sensor strips appropriate for quick analysis. Selective responses to DCP vapors make these CA-CNW-H nanocomposite sensor strips appropriate for quick analysis. Selective responses to DCP vapors make these CA-CNW-H nanocomposite sensor strips appropriate for quick analysis. Selective responses to DCP vapors make these CA-CNW-H nanocomposite sensor strips appropriate for quick analysis.

4. EXPERIMENTAL SECTION

4.1. Materials and Reagents. CA (Mn = 30 000; acetylation composition of ~39.8 wt %, Aldrich), polyethylene glycol (PEG 3350; plasticizer, Merck), sulfuric acid (H2SO4, Sigma-Aldrich), poly(2-vinylpyridine) (Sigma-Aldrich), hydrogen peroxide (H2O2, Merck), DCP (Sigma-Aldrich), and organic solvents (spectroscopic grade, Aldrich) were acquired from commercial sources (Egypt). The compounds utilized in the synthesis of DCDHF and DCDHF-H were purchased from Sigma-Aldrich, including 2, 4-dinitroaniline, 3-hydroxy-3-methyl-butan-2-one, and dicyanomethane. Dicyanomethane and 3-hydroxy-3-methyl-butan-2-one were used according to a prior procedure to synthesize DCDHF 1 with a yield of 58%.30,36 DCDHF-H 3 was synthesized using DCDHF as a starting intermediate employing a previously reported literature method.31,37

4.2. Preparation Methods. 4.2.1. Synthesis of DCDHF 1. Sodium methoxide (300 mg), 3-hydroxy-3-methyl-butan-2-one (9 g), and dicyanomethane (12 g) were admixed in absolute ethanol (20 mL) by magnetic stirring. The admixture was refluxed for two hours. To get off-white crystals, the mixture was chilled to 0–5 °C, and the precipitate was filtered under vacuum and washed with cold absolute ethanol; mp 201–203 °C; 1H NMR (CDCl3, 400 MHz): 2.37 (s, 3 H), 1.64 (s, 6 H).

4.2.2. Synthesis of DCDHF-H 3. A solution of 2, 4-dinitroaniline (400 mg, 2.2 mmol), HCl (1.5 mL) and deionized water (1.0 mL) was chilled in an ice bath at 0–5 °C while stirring. Sodium nitrite (aqueous; 2.5 mmol) was slowly added to the above-prepared solution to generate the diazonium salt, which was stirred for 15 min at 0–5 °C. DCDHF (400 mg, 2.0 mmol) was mixed with CH3COOH (2.0 mL) and CH3COONa (2.5 g) in acetone (15.0 mL) and cooled to 0–5 °C. The chilled diazonium salt was poured slowly in the DCDHF solution while vigorously stirring at 0–5 °C. The crude solid was filtered under vacuum, rinsed with deionized water (5 × 10 mL), crystallized from n-propanol/chloroform, and then allowed to air-dry to get a reddish solid (552 mg; 64%); m.p. 233–235 °C; 1H NMR (400 MHz, DMSO-d6, 400 MHz): 2.47 (s, 3 H), 1.64 (s, 6 H).

Table 2. Changes in CIE Lab of the Paper Strip (S5) upon Exposure to Vapors of Different Aliphatic Amines; the Vapors Released by Heating the Alkyl Amine to its Boiling Temperature

| amine       | L*  | a*  | b*  |
|-------------|-----|-----|-----|
| blank       | 77.26 | −7.38 | 25.90 |
| piperidine  | 65.04 | 14.90 | −11.72 |
| diethylamine| 68.51 | 12.57 | −9.63 |
| n-butylamine| 69.62 | 11.87 | −8.04 |
| ethylamine  | 71.05 | 9.63  | −6.53 |
| triethylamine| 73.05 | 8.90  | −5.73 |
| tributylamine| 74.74 | 5.23  | −4.81 |

Figure 6. Color change of the paper strip (S5) depending on the DCP concentration; 0 ppm (a), 25 ppm (b), 0 ppm (c), 50 ppm (d), 100 ppm (e), and 200 ppm (f).

Figure 7. Maximum value of the absorption intensity at 438 and 580 nm of S5 in the absence and presence of DCP vapors.

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| tributylamine| 74.74 | 5.23  | −4.81 |
DMSO-d$_6$): 12.09 (s-broad, 1 H), 8.57 (s, 1 H), 8.38 (d, 1 H), 8.22 (dd, 1H), 7.64 (d, 1H), 1.80 (s, 6H); IR (v/cm$^{-1}$): 3258 (N–H), 2226 (CN), 1579 (C≡N), 1512 and 1327 (NO$_2$).

4.2.3. Preparation of CNWs. Rice straw was provided from Egypt’s Kafr El-Sheikh agriculture fields. According to the previous literature protocol,$^3_2$ a fine white cellulose powder was prepared. Crushing, rinsing, and air drying processes were first applied to prepare rice straw dry stems. In a planetary ball mill, the resultant substrate was ground to a fine powder over 30 min. NaOH$_{aq}$ (10% w/w; pH 10.5) was added to the given powder (100 g) and stirred for 4 h at 100 °C. To ensure that all traces of alkali had been removed, the mixture was then subjected to several washes with distilled water, air-dried, and ground. At 95 °C, the mixture was bleached by stirring with Na$_2$SiO$_3$ (3 g L$^{-1}$) and H$_2$O$_2$(aq) (5 g L$^{-1}$) at a ratio of 1:20 for 30 min. In order to obtain a fine white cellulose powder, the product was grinded for 60 min in a planetary ball mill. The extracted cellulose’s chemical composition was determined using the TAPPI standard procedure. Both cellulose and hemicellulose were evaluated using TAPPI/(T-222)OS83, TAPPI/(T-203)OS74, and hemicellulose were evaluated using TAPPI/(T-203)OS74. The previous literature protocol (see ref$^{33}$) was used to prepare the CNWs, in which the isolated cellulose powder was hydrolyzed in H$_2$SO$_4$ (65%; 1:8.75 w/v) at 45 °C for 30 min. Diluted with pure water, the suspension was centrifuged for 10 min at 8000 rpm. In order to obtain the CNWs, the gel was homogenized (25 kHz) for 20 min in an ice bath, filtered, washed with deionized water, and dialyzed to reach a pH of 7.

4.2.4. Preparation of CA-CNW-H Nanocomposite Strips. CA (15 g) was dissolved in acetone (300 mL) to produce a clear solution, and then, PEG 3350 (1.5% w/w) was added. Poly(2-vinylpyridine) (0.5% w/w) was added to the above-prepared solution, and then, CNW was added at different ratios, including 0, 1, 3, and 5% w/w, abbreviated by CA-CNW-0, CA-CNW-1, CA-CNW-3, and CA-CNW-5, respectively. CA-CNW-3 was monitored as the best concentration of DCDHF-H, the sensor strips were treated with DCDHF-H at various concentrations, including 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, and 1.4% w/w. The mixtures were homogenized for 5 min, stirred for 30 min, decanted onto a Petri plate, and allowed to air-dry. Depending on the concentrations of DCDHF-H, the sensor strips were abbreviated by S$_0$, S$_1$, S$_2$, S$_3$, S$_4$, S$_5$, and S$_6$.

4.3. Characterization Methods. A differential scan calorimeter (DSC; Instruments TA2920) was utilized to study the thermal properties of the synthesized DCDHF-H chromophore. A BRUKER AVANCE 400 MHz NMR spectrometer was used to study the NMR spectra of the synthesized DCDHF-H probe. A Beckman Coulter pH1340 was employed to determine the pH readings. A Shimadzu 8400S was used to measure the Fourier transform infrared spectroscopic data. The strip microstructure morphological was studied using a Quanta 250-FEG (Czech Republic) scanning electron microscope (SEM). A Lloyd instrument (U.K.) was employed to determine the pH readings. A Shimadzu 8400S was used to measure the Fourier transform infrared spectroscopic data. A Beckman Coulter pHi340 spectrometer was used to study the NMR spectra of the synthesized DCDHF-H probe. A Beckman Coulter pHi340 spectrometer was used to determine the pH readings. A Shimadzu 8400S was used to measure the Fourier transform infrared spectroscopic data.

4.4. Detection of DCP. To explore the reversibility of the CA-CNW-H nanocomposite strip, a 10 mL test tube containing a methanolic solution of DCP (5 mL; pH 6.8) was used to investigate the sensor strip’s activity. The sensor strip (S$_1$) was placed close to the test tube’s rim at 45 °C to show an immediate colorimetric shift in response to inhalation of the evaporated DCP gas. At room temperature, the absorption intensity of S$_1$ at 438 and 580 nm was examined to determine the reversibility. While measuring the absorption maxima’s intensity, K/S, and CIE Lab for each reversible cycle, the absorption spectra were repeatedly between 438 and 580 nm in the absence and presence of DCP vapors. On the other hand, the CA-CNW-H paper strip was immersed in methanolic solutions with different concentrations of DCP to explore its detection limit.
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