Portable Nanohybrid Paper-Based Chemiresistive Sensor for Free Chlorine Detection

Yi-Kuang Yen,* Kuan-Yi Lee, Chun-Yi Lin,* Shu-Ting Zhang,* Cheng-Wei Wang,* and Ta-Yu Liu*

ABSTRACT: Detecting the concentration of free chlorine is important for monitoring the quality of water. In this study, we report a nanohybrid paper-based chemiresistive sensor that can be used with smartphones to detect free chlorine ions. The sensor was fabricated using a simple and standardized coating process. The graphene and poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) nanohybrid paper-based sensing device exhibited a more stable and intuitive response to free chlorine than that exhibited by the device using only PEDOT:PSS. The nanohybrid paper-based sensor was sensitive to free chlorine concentrations in a linear range of 0.1–500 ppm, and the limit of detection was 0.18 ppm. The sensor showed specificity for free chloride ions and detection capability in samples. The sensor was integrated as a module with an electric readout system, and the measured signals and results could be displayed in real time on a smartphone. Therefore, the proposed sensing platform is suitable owing to its portability, low cost, ease of use, and capability for on-site water quality measurement.

INTRODUCTION

Monitoring the free chlorine level in water is important because the chlorine level indicates the level of disinfection and the residual chlorine. According to the World Health Organization, the accepted concentration of residual free chlorine in stored household water is 0.2 ppm. In order to not exceed this concentration, the recommended doses of free chlorine to be added in clear and turbid water are approximately 2 and 4 ppm, respectively. The accepted free chlorine concentration in a swimming pool or recreation center is 1.5–2 ppm. Concentrations of free chlorine exceeding these ranges may either lead to inadequate disinfection or adversely affect the human health.

The commonly used methods for the detection and analysis of free chlorine are titration, chemiluminescence, and electrochemical analysis. Particularly, N,N-diethyl-p-phenylenediamine (DPD)-based absorptiometry allows a highly sensitive and precise analysis of free chlorine. However, this method requires expensive optical instruments. Furthermore, iron and manganese alter the outcome of this method; the method also causes the generation of environmentally harmful discharge. Several traditional amperometric electrochemical methods are accurate with a short response time. However, their sensing results are strongly affected by the pH, flow rate, and aging of the electrodes. Moreover, they have a large size, thereby making them difficult to integrate. To address these limitations, microfabricated electrochemical sensors are being developed as alternative approaches owing to their small size, low cost, ease of integration with other components to form integrated detection systems, and their ability to inhibit electrolyte replenishment. Several researchers have used microfabrication technology to fabricate working electrodes of noble metals such as gold and platinum to develop amperometric free chlorine sensors. A boron-doped, diamond electrode-based sensor fabricated using microwave plasma-assisted chemical vapor deposition methods increased the device lifetime. Micromachined electrochemical free chlorine sensors can be developed for miniaturized and cost-effective applications; however, their sensitivity widely varies and the accuracy of these sensors is less than those of conventional sensors. In addition, the shortage of reactivating sensing materials for free chlorine is a major challenge.

Recently, a chemiresistor that differs from conventional amperometric sensors was developed. The device comprised single-wall carbon nanotubes (CNTs) modified by a phenyl-capped aniline tetramer, which can be oxidized by free chlorine and can change the resistivity of the CNTs. This study proposes a new sensor structure and presents an innovative sensing material. Expensive sensing materials such as gold and CNTs as well as the costly micromachining process may hinder researchers from developing a point-of-use, robust, reliable, low-cost, and portable free chlorine sensor. Qin et al. designed a disposable paper-based chemo-resistive amperometric free chlorine sensor that can detect free chlorine in water samples. The free chlorine concentration was detected by measuring the electric resistance of the modified paper. S.-H. Yoon et al. developed a microfluidic paper-based analytical device (μPAD) for the analysis of water quality. The μPAD system was composed of an integrated paper-based interdigitated microelectrode and a planar microchannel for detecting free chlorine ions in water.
reported a paper-based free chlorine sensor fabricated using a hand-drawn poly(3,4-ethylenedioxythiophene):poly-
(styrenesulfonate) (PEDOT:PSS) chemiresistor as the sensing
element. This device was constructed on a low-cost paper
substrate by a simple and cost-efficient fabrication process; the
fabrication can be performed by an untrained personnel. The
sensor provided a wide sensing range (0.5−500 ppm) and
could be reused, making it cost-efficient. Nevertheless, the
hand drawing fabrication method limits the feasibility of mass
production, and the nonstandard production method may also
cause inconsistencies in the performance of each sensor.
Furthermore, the sensor needs a commercial multimeter for
quantitative signal acquisition, which is considerably large in
size to meet the requirements for a portable sensing
application.

In this study, we developed a portable nanohybrid paper-
based chemiresistor for detecting free chlorine in water. We
considered several advantages of a paper substrate, such as its

Figure 1. SEM images of Whatman no. 1 filter paper at magnifications of 100× and 500×, respectively; (a,b) without modification; (c,d) modified
with PEDOT:PSS; and (e,f) modified with PEDOT:PSS/graphene nanohybrid ink.

Figure 2. (a) Signal responses of PEDOT:PSS-modified paper-based sensors in solutions with different concentrations of free chlorine; (b) analysis
of the linear relationship between the signal response of the sensor (PEDOT:PSS-modified) at different times and the logarithmic concentration of
free chlorine ions; (c) signal response of the nanohybrid ink-modified paper-based sensors in solutions with different concentrations of free
chlorine; and (d) analysis of the linear relationship between the signal response of the sensor (nanohybrid ink) at different times and the
logarithmic concentration of free chlorine ions.
low-cost and porous structures and employed wax printing to form the size and shape of chemiresistors on the paper. PEDOT:PSS or a nanohybrid composite ink of PEDOT:PSS and graphene was utilized as the free chlorine-sensing element. The sensor can detect free chlorine concentrations within the range of 0.1−500 ppm using different calibration curves. The response of the nanohybrid composite paper-based sensor was stable, and the relationship between the concentrations and change in resistance was linear. In addition, with the integrated circuit and the wireless transmission module, the real-time detection signals and the concentration of free chlorine can be viewed on a smartphone for portable and point-of-use applications.

## RESULTS AND DISCUSSION

### Surface Morphology Analysis.

The surface morphologies of the paper-based chemiresistors, fabricated using two kinds of materials, were investigated through scanning electron microscopy (SEM) analysis. Figure 1a,b shows the SEM images (100× and 500× magnification, respectively) of the substrate of Whatman no. 1 filter paper. The cellulose fiber distribution is clearly visible, and its porous structure is suitable for modification with conductive polymers and nanomaterials. Figure 1c,d shows the SEM images of the PEDOT:PSS-modified paper at 100× and 500× magnification, respectively. PEDOT:PSS was absorbed to fill the interstices between the cellulose fibers and formed a conductive network as a sensing element of the chemiresistor. Nonetheless, some interspaces were not occupied, and the paper surface was still rough when observed at a nanoscale. Figure 1e,f shows that the PEDOT:PSS/graphene nanocomposite adheres well to the paper substrate and constitutes a flat conductive sensing surface when compared to the nanohybrid-modified paper.

### Signal Responses and Sensitivity of Free Chlorine Detection.

The PEDOT:PSS paper-based chemiresistor was used to measure free chlorine concentrations in the sample solutions. Figure 2a shows the relative changes in the resistance as a function of time when the sensors were exposed to free chlorine concentrations ranging from 0.1 to 1000 ppm. We observed that the relative resistance changed rapidly, and it increased when the concentrations of free chlorine were high (>50 ppm). Because the thiophene in PEDOT was quickly oxidized by the aqueous hypochlorite to form a structure with a nonsaturated polyol and eliminated sulfur contaminants by forming sodium sulfate, its conductivity likely decreased. The surface morphologies presented in eqs 1 and 2.

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$$\frac{\Delta R}{R_0} = 0.086 \times (0.689 \times \log_{10}(\text{OCl}^{-} \text{conc.}))$$

$$0.1 \text{ ppm} \leq [\text{OCl}^{-} \text{conc.}] \leq 50 \text{ ppm}$$  \hspace{1cm} (1)

$$\frac{\Delta R}{R_0} = 0.002 \times (1.703 \times \log_{10}(\text{OCl}^{-} \text{conc.}))$$

$$50 \text{ ppm} \leq [\text{OCl}^{-} \text{conc.}] \leq 1000 \text{ ppm}$$  \hspace{1cm} (2)

The coefficients of determination in eqs 1 and 2 are 0.99 and 0.96, respectively. The limit of detection (LOD) is defined as triple the signal response in a blank solution ($\Delta R/R_0 \equiv 0.013$). Hence, the LOD of the PEDOT:PSS-based free chlorine sensor is 0.07 ppm ($\Delta R/R_0 \equiv 0.039$) for a duration of 300 s. During practical application, the sample solution was added dropwise on the sensor, and the measurement was conducted for 15 s. When the signal response $\Delta R/R_0$ at the 15th second was larger than 0.04, eq 2 was adopted to calculate the concentration of free chlorine. Otherwise, when the response was less than 0.04, measurement by the sensor continued until the 300th second and eq 1 was used to calculate the free chlorine concentration.

The same measurement procedures were used for the free chlorine detection tests of nanohybrid conductive composite paper-based chemiresistors. Figure 2c shows the relative change in resistance as a function of time when the sensors were exposed to free chlorine concentrations ranging from 0.1 to 500 ppm. The response of nanohybrid conductive composite paper-based chemiresistors to free chlorine was different from that of the PEDOT:PSS-modified paper-based chemiresistor. The relative change in resistance increased significantly when the sensor responded to free chlorine regardless of the concentration level. Figure 2d shows the calibration curves of the relative change in resistance upon exposure of the sensor to free chlorine for various durations (15, 120, 180, and 300 s). The sensor response to the concentration of free chlorine could not be differentiated at the measuring time of 15 s. From the regression analysis of the data, the signal response showed a better linear relationship with the concentration of free chlorine at the measuring time of 300 s than at other measuring times. However, the slope of calibration curves was the same for low concentrations (0.1−50 ppm). Compared with the measured results, the response signals of nanohybrid paper-based sensors stabilized faster than those of the PEDOT:PSS-paper-based sensors. This may be due to the stability of the nanohybrid composite, which led to less intense redox reactions between the high-concentration free chloride and PEDOT:PSS. The sensitivity of the nanohybrid paper-based sensor can be expressed as

$$\frac{\Delta R}{R_0} = 0.2899 \log_{10}([\text{OCl}^{-} \text{conc.}]) + 0.3476,$$

$$0.1 \text{ ppm} \leq [\text{OCl}^{-} \text{conc.}] \leq 500 \text{ ppm}$$  \hspace{1cm} (3)

where the coefficient of determination is 0.99. The LOD is taken as triple the signal response in a blank solution ($\Delta R/R_0 \equiv 0.03$), and the LOD of the hybrid conductive composite-based free chlorine sensor is 0.13 ppm ($\Delta R/R_0 \equiv 0.09$) for the measuring duration of 300 s. During application, 15 μL of the sample solution was placed on the sensor and measurement was conducted for 300 s. Subsequently, to determine the free
chlorine concentration, the signal response $\Delta R/R_0$ at 300 s was substituted into eq 3.

**Selectivity.** We evaluated the selectivity of the sensor by considering environmental interferences as its practical application for monitoring water quality. For this, 1000 ppm testing solutions were prepared with other ions capable of causing interference. A drop of these solutions was applied to the sensors and measurements were performed for 5 min at room temperature (27.5 °C). The responses of the sensors (Figure 3) clearly showed high selectivity toward free chlorine over other ions. The responses for most interfering ions were lower than 0.05, which is less than the response of 1 ppm obtained for free chlorine. Aside from the response to free chlorine, the response to hydroxides was the only one higher than 0.1. However, the concentrations of interfering ions are generally below 1000 ppm in real water samples, which may not significantly affect the sensor response.

**Portable Sensing Platform.** For portability, the paper-based sensor was integrated with a signal-capturing system and wireless module that displays the measured result on a smartphone. The signals can be viewed in two modes: one is the terminal mode that shows the final measured free chlorine concentration in ppm, whereas the other is the graphic mode that illustrates the real-time measured signal plots in ppm and by the resistance change (shown in Figure S1) or all in ppm (shown in Figure S2). In the initial test experiments, we observed irregular noise in the signals on the mobile device. This issue may lead to an inaccurate blank signal. To solve this problem, we switched to a more stable input power and used magnets to strengthen the contact between the electrode and the signal acquisition line. We also modified the signal-capturing program, changing the signal value that was originally taken for the 60th second to the average value of 60 s as the reference value. We also replaced the resistors of the system with carbon films and ceramic resistors, which reduce noise.

**Real Sample Measurements.** The sensing platform was further employed to measure samples collected from different sources, including tap water and water collected from a swimming pool. The measured results were compared with the reference concentrations acquired from a commercial DPD-based colorimetric sensor (Milwaukee, MW-10, Taiwan), as shown in Table 1. We observe that the measured concentrations of free chlorine were consistent for both methods with a variation of less than 11%.

Thus, the proposed sensors present several advantages as follows: (1) A simple and inexpensive fabrication process, with the total cost of the device estimated as $0.03. The fabrication process can also be standardized for mass production and disposable usage. (2) Capability to be integrated as a portable platform suitable for on-site inspection and real-time measurement. The measurement process is easy and the interface is user-friendly. (3) A wide concentration range can be measured, making the sensor applicable for different purposes. (4) The amount of sample required for the measurement is very small (microliter level) and there is no need for pre-processing.

**CONCLUSIONS**

In this study, we developed a portable, low-cost, and easy-to-use free chlorine sensor using a nanohybrid conductive paper-based chemiresistor. The fabrication process of the paper-based sensing device is simple and cost-effective and can be standardized. The graphene and PEDOT:PSS nanohybrid paper provides a more stable and direct sensing mechanism than the one modified with PEDOT:PSS. The measured results can be captured, processed with an integrated circuit, and displayed on a mobile phone in real time. The sensor was proved to possess specificity and capability to detect free chlorine ions in water samples. The sample volume needed was 15 μL, and the process did not require professional knowledge. The sensing platform has the potential to be applied in the daily monitoring of water quality, especially in less-developed or resource-limited areas.

**EXPERIMENTAL SECTION**

**Chemicals and Reagents.** Most chemicals were purchased from Sigma-Aldrich. PEDOT:PSS (1.3 wt %, 483095)

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**Table 1. Free Chlorine Detection of Real Water Samples**

| Sample          | Measured by the proposed sensor (ppm) | Measured by the DPD-based colorimetric sensor (ppm) |
|-----------------|--------------------------------------|-----------------------------------------------|
| Tap water       | 0.26 ± 0.15 (n = 5)                  | 0.25 ± 0.05 (n = 5)                           |
| Swimming pool   | 1.87 ± 0.42 (n = 5)                  | 2.10 ± 0.25 (n = 5)                           |

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**Figure 4.** (a) Printing of the design pattern on the qualitative filter paper (Whatman no. 1); (b) placement of the paper on the hotplate to melt the wax; (c) distribution of the PEDOT:PSS or the nanohybrid conductive ink as a sensing layer; (d) application of the conductive silver paint as the electrodes; and (e,f) design and fabrication of a 3D-printed case for electric readout system integration.
stock solution was diluted to 0.65 wt % with deionized water (DIW, DQ3, Millipore) for fabricating the sensor. To produce a conductive composite ink, 2 g of graphene ink (I-MS18, Enerage) was added to 15 mL of isopropyl alcohol (W292907) and placed in an ultrasonicator to disperse for 15 min. Subsequently, the graphene ink solution was stirred for 48 h to be fully dispersed before further usage. Finally, the composite ink was produced by mixing the 1.3 wt % PEDOT:PSS solution with graphene solution in a proportion of 7:3. This mixed ratio is chosen because the sensor obtained with this ratio has a stronger response signal to free chlorine (Figure S3). The average conductivity of nanohybrid ink sensing layer was 1.7 S cm⁻¹. Solutions containing 1000 ppm of sodium chloride (NaCl, S7653), sodium hydroxide (NaOH, S8045), sodium hydrogen carbonate (NaHCO₃, 401676), calcium chloride (CaCl₂, C1016), potassium standard solution (1000 mg/L, KNO₃, 170230), and aluminum sulfate [Al₂(SO₄)₃, 202614] were prepared for control measurements. Sodium hypochlorite (NaOCl, 5% available chlorine, 9416-01), purchased from Avantor J.T.Baker, was used as the main hypochlorite (NaOCl, 5% available chlorine, 9416-01), purchased from Avantor J.T.Baker, was used as the main

Fabrication of the Sensor. A schematic of the fabrication process of the paper-based free chlorine sensor is shown in Figure 4. Wax printing was first conducted to form the shape of the sensors (3 × 8 array) on a piece of filter paper (type 1, Whatman). Second, the printed paper was placed on a hotplate at 100 °C for melting wax as the barrier. Subsequently, 15 μL of PEDOT:PSS or nanohybrid conductive ink (PEDOT:PSS/graphene) was distributed on the center circle area of the sensor. After the ink was dried at 80 °C, a film was formed, which served as the sensing element of the chemiresistor. Then, a conductive silver paint (CSIP-998) was drawn on both sides of the resistor as electrodes. Finally, a protective layer (Vaseline Jelly Original) was applied to both junctions to prevent contact between the electrodes and liquid. A 3D-printed electrical readout case was designed and fabricated for easy measurement and usage, as shown in Figure 4e,f. Currents were measured before and after depositing the PEDOT:PSS or nanohybrid conductive ink on the sensors to confirm their operability and characterize their preliminary electrical properties. The measured results are shown in Figure S4.

Measurement System and the Procedure. The signal of the sensor can be measured using a source meter (Keithley 2400, Tektronix, Beaverton, OR, USA). LabVIEW software was used to control the source meter and record measurements. Moreover, to achieve portability, the measurement system was designed for miniaturization and wireless transmission. The signal measurement system is illustrated in Figure 5. A designed circuit was used to capture the sensor signal and convert the resistance signal into voltage. The voltage signal was amplified by an operational amplifier and input to an electronics platform (Arduino Uno Rev3 SMD). The built-in analog-to-digital converter (ATmega328) on the platform converted the analog signal into digital signal. The signal was read and further processed through program coding using Arduino software (IDE). Finally, the processed signal was transmitted to a mobile phone (ASUS ZenFone 5 T00P, Taiwan) through a bluetooth module (HC-05). The surface morphology of both paper-based chemiresistors was characterized via SEM (JSM-7610F, JEOL, Tokyo, Japan).

The process flow of the system for quantitative analysis of the free chlorine concentration was as follows: First, the system detected whether the sensor was connected to the measure-
ment system, as well as if the sensor had failed. The user may adjust the position of the sensor or change the sensor. Second, the system measured the signals for 60 s, and the average value was used to determine whether the signal was steady ($\Delta R/R_0 \geq 0$). After confirming that the signal was steady, a "Drop!" indicator appeared on the screen of the mobile phone, and the sample solution (15 $\mu$L) could be applied to the sensor using a pipette. The system continuously measured signals for 300 s and displayed the signal on the smartphone. Meanwhile, the system calculated and determined the free chlorine concentration from the signals through calibration curves within a given range, and the concentration is displayed in ppm on the smartphone. All the measuring processes were programmed (the code is available in the Supporting Information) on an android smartphone.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03366.

Real-time measurements through smartphone; signal response of sensors made with different mixed ratios of nanohybrid ink solutions; current measurements of the sensor before and after depositing sensing layer; and app code of android smartphone (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Yi-Kuang Yen — Department of Mechanical Engineering and Institute of Mechatronic Engineering, National Taipei University of Technology, Taipei 10608, Taiwan; orcid.org/0000-0002-2570-5707; Email: ykyen@ntut.edu.tw

**Authors**

Kuan-Yi Lee — Department of Mechanical Engineering, National Taipei University of Technology, Taipei 10608, Taiwan

Chun-Yi Lin — Department of Mechanical Engineering, National Taipei University of Technology, Taipei 10608, Taiwan

Shu-Ting Zhang — Department of Mechanical Engineering, National Taipei University of Technology, Taipei 10608, Taiwan

Cheng-Wei Wang — Department of Mechanical Engineering, National Taipei University of Technology, Taipei 10608, Taiwan

Ta-Yu Liu — Department of Mechanical Engineering, National Taipei University of Technology, Taipei 10608, Taiwan

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.0c03366

**Author Contributions**

$^{8}$K.-Y.L., C.-Y.L., S.-T.Z., C.-W.W., and T.-Y.L. contributed equally. The manuscript was written through contributions of all authors. Y.-K.Y. conceived the idea and designed the experiments. K.-Y.L., and S.-T.Z. carried out the design and fabrication of the sensor. C.-Y.L., C.-W.W., and T.-Y.L. software and validation.

**Notes**

The authors declare no competing financial interest.

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