

Practical and Efficient: A Pocket-Sized Device Enabling Detection of Formaldehyde Adulteration in Vegetables

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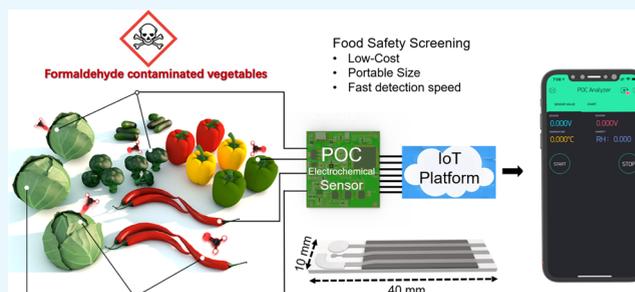


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Supporting Information

ABSTRACT: Formaldehyde, as a carcinogenic substance, is often intentionally used to adulterate vegetables to increase their shelf life, and the adhesive tape used to attach labels can also leave formaldehyde on the surface of vegetables. However, as the “gold” standard, gas chromatography (GC) and high-performance liquid chromatography (HPLC) are expensive for individual tests and confined to the laboratory owing to their size and a suitable detector (low-cost, portable, fast detection speed) to check formaldehyde contamination in vegetables not being available. Here, we tested formaldehyde contamination in vegetables using a low-cost and hand-held detector combined with a screen-printed electrode (SPE) amperometric sensor and an open-sourced potentiostat. The analyzer can detect a concentration of 100 $\mu\text{mol/L}$ formaldehyde and achieve a good linear range between 100 and 1000 $\mu\text{mol/L}$. Furthermore, the detector successfully identified formaldehyde contamination in 53 samples of six different kinds of vegetables even after residual formaldehyde on the surface was evaporated. Most importantly, under the practicability-oriented idea, a cost-effective strategy was implemented for this detector design rather than using other pricey methods (e.g., photolithography, electron-beam evaporation, chemical deposition), which enormously reduces the cost (under $\sim\text{USD } 0.5$ per test) and meets all of the requirements of ASSURED device. We believe this cheap, portable detector could help law-enforcing authorities, healthcare workers, and customers to screen formaldehyde contamination easily. Also, the cost-saving strategy is appropriate for low-income areas, where there is a lack of laboratories, funds, and trained experts.



1. INTRODUCTION

In a country with a large population like China, people consume a gigantic number of fresh vegetables every day. To increase their shelf life, vegetables are often intentionally adulterated with formaldehyde.^{1,2} Formaldehyde is classified by the International Agency for Research on Cancer (IARC) in Group I as being carcinogenic to humans.³ Consuming vegetables or fruit that are contaminated with formaldehyde may cause serious health issues including vomiting, pain, or even coma,⁴ which have a detrimental impact on the health of a population, especially children.⁵ In the European Union, daily exposure to formaldehyde from food of animal and plant origin should be no more than 100 mg/kg, and formalin adulteration is strictly forbidden in China.⁶ Many methods have been investigated to detect formaldehyde, and most of them serve as powerful tools in formaldehyde detection. Chromatography is the “gold” standard for formaldehyde testing,^{7–9} but it is costly (e.g., $\sim\text{USD } 50$ per sample in China) and time-consuming with results being obtained typically after 10 days from the external testing facility. Fourier transform infrared spectroscopy, which requires less detection time and achieves good accuracy, is confined to the laboratory, and trained experts are needed to perform the test. Formaldehyde can be detected based on a colorimetric reaction where sample

distillates are mixed with sulfuric acid yielding a purple color if formaldehyde is present. The colorimetric sensors with a portable size are sensitive to formaldehyde and have proven their efficiency in formaldehyde detection. However, colorimetric sensors prefer ambient relative humidity less than 95%, and the measurement results are sensitive to detection time. Also, because naked eye evaluation of color change is prone to error, spectral detection technology or a digital camera and a flat panel scanner are often employed for color recognition.^{10,11}

Formaldehyde can be also quantified with compact and money-consuming gas sensors, such as metal oxide semiconductor (MOS) sensors that detect formaldehyde in ambient air,^{12–16} but the result can be unreliable owing to its cross-sensitivity and response to changes in ambient humidity.¹⁷ As a method that has found significant success for point-of-care (POC) testing and has become the “gold”

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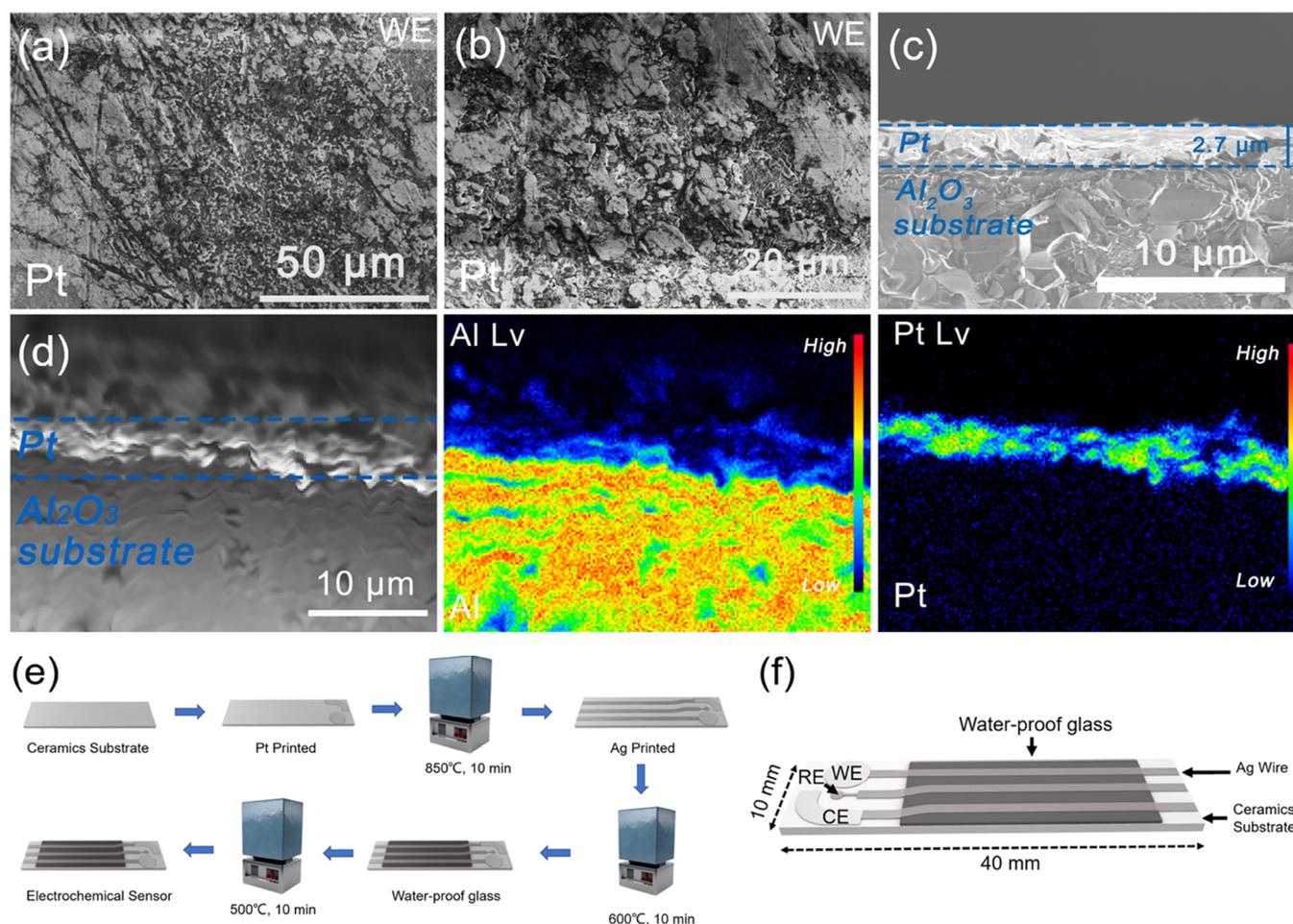


Figure 1. Concept of the amperometric sensor: (a) microstructure of the working electrode, (b) morphology characterization of the platinum working electrode, (c) cross-sectional SEM image of the working electrode; the film thickness of the platinum electrode is around $2.7\ \mu\text{m}$, (d) EPMA elemental (Pt and Al) mapping images of the sensing film, (e) the process used to fabricate sensors, and (f) details of the amperometric sensor with a 4 cm length and a 1 cm width.

standard for monitoring glucose levels in the blood, electrochemical sensors have been widely used in wearable electronics,^{18–21} POC disease screening,^{22,23} and detection of bacterial foodborne pathogens.^{24–26} Complex equipment, such as microlithography-aided manufacture,²⁷ chemical deposition,²⁸ electron-beam evaporator,²⁹ etc., have always been used to manufacture the sensors' sensing part. However, according to the recent evaluation by the United Nations (UN), $\sim 10\%$ of the world's population (700 million) lives below the international poverty line of USD 1.90 per day.³⁰ Therefore, sophisticated instruments in a clean room with trained technicians are unaffordable and less feasible for those below the poverty line. Thus, cost-saving, portable, and easy-to-make formaldehyde detectors are urgently needed by consumers, distributors, and authorities (for example, police and administrators) to screen such toxic vegetables. The World Health Organization (WHO) has set the criterion for evaluating POC devices, and these instruments should contain the following characteristics: affordability, sensitivity, specificity, user-friendliness, rapidity/robustness, equipment-free (portability), and deliverability to end users (ASSURED). Many studies have demonstrated powerful tools in formaldehyde detection,^{31–39} such as chromatography, which has a good low detection limit, and colorimetric sensors and biosensors, which are portable and sensitive to formaldehyde.

But considering the requirements of the ASSURED device, the process and cost of sensor manufacture still need improvement to fulfill the requirements of low-income areas (Figure 1).

Here, we report a pocket-sized device that enables detection of formaldehyde adulteration in vegetables, which can be fabricated with basic tools and skills through a quick and easy do-it-yourself (DIY) process from cheap, readily available materials. This device is based on the requirements of the ASSURED device. With a formaldehyde concentration detection limit of $100\ \mu\text{mol/L}$, the POC detector in this article makes the immediate analysis and the accurate screening of formaldehyde possible. Furthermore, the easy-to-make and practicability-oriented-idea-based POC detector design and construction ensure the ultralow feedstock cost of $\sim\text{USD } 0.5$ per testing in combination with a reusable open-sourced potentiostat called Openstat costing $\sim\text{USD } 5$. A detailed comparison between our work and several formaldehyde detectors based on requirements of the ASSURED device is shown in Supporting Information I.

2. RESULTS AND DISCUSSION

2.1. Voltammetry Responses to Formalin. Compact-Stat.h (IVIUM, Co., Ltd, the Netherlands) was used to perform cyclic voltammetry (CV) to study the electrochemical behavior of formaldehyde. The performance of the ampero-

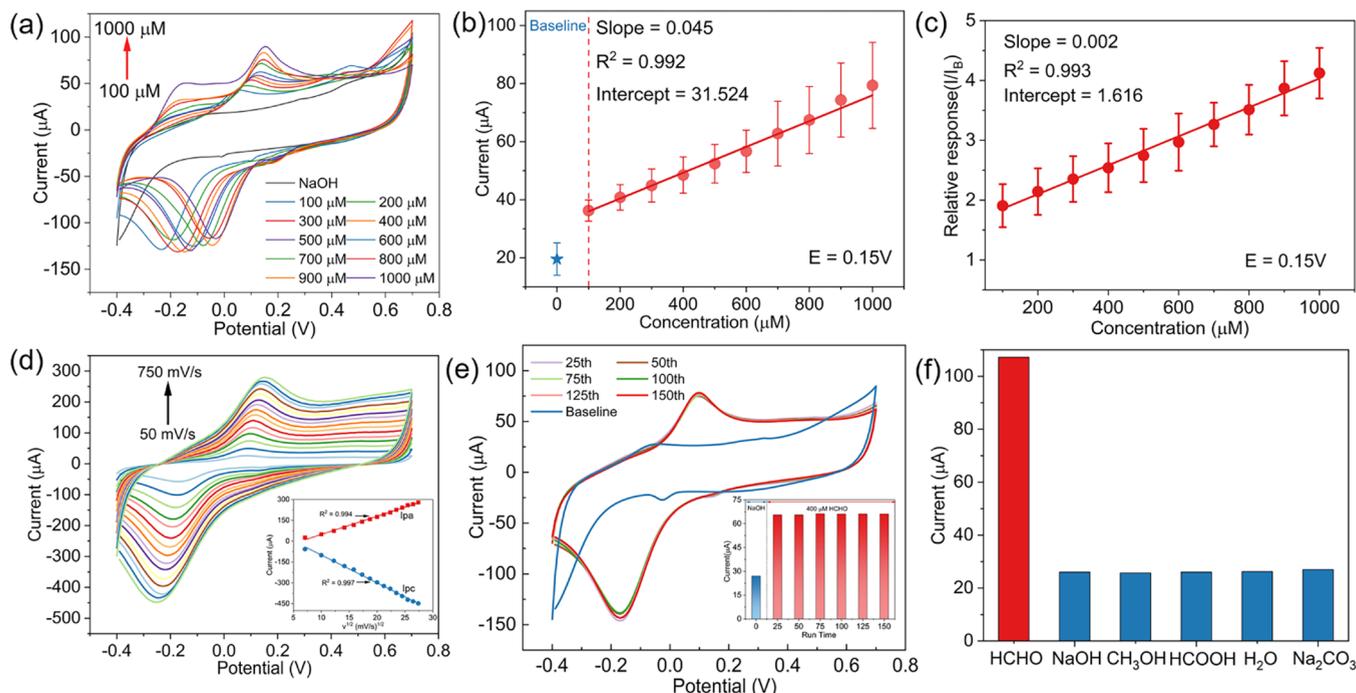
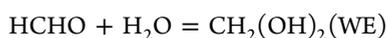
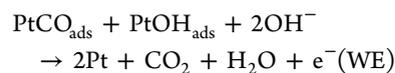
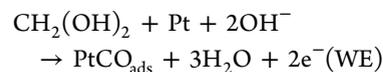


Figure 2. Characterization of the amperometric sensor. (a) Sensor response curves to formalin using cyclic voltammograms at different concentrations, (b) associated linearity curves at $E = 0.15$ V for different concentrations, (c) linear fitting plot with the relative response of sensors; the effect of baseline drift is reduced using the relative response to improve the sensor's consistency, and (d) analysis of SPE at scan rates ranging from 50 to 750 mV/s and linear fits of the oxidized peak current (I_{pa}) and reduced peak current (I_{pc}), indicating that the reaction of the electrode is a diffusion-controlled surface reaction. (e) Reproducibility of each sensor in the presence of HCHO and (f) specificity of the SPE sensor against four interferences in formalin (CH_3OH , HCOOH , H_2O , CO_3^{2-}).

metric sensor was monitored using different analyte solutions. Results show that there is a good distinction between formaldehyde contamination and NaOH solution. Figure 2a shows the representative current responses of formaldehyde in 0–1000 μM solutions. The overall reaction of formaldehyde in alkaline solution has been widely studied.^{40–43} The reaction mechanism of formaldehyde can be complex and depends on many factors, including sensitive materials and the Pt electrode structure, the properties of the electrolyte, and the electrode/electrolyte interface. Figure 2a gives the CV curves of the amperometric sensor of different HCHO concentrations in NaOH. Oxidation and reduction peaks can be clearly observed in the potential range of -0.4 to 0.7 V. During the forward scan, $\text{Pt}-\text{OH}_{\text{ads}}$ was formed and led to a quick increase of current.⁴⁴ Based on the results of the CV study and previous reports,^{45–47} the sensing mechanism of formaldehyde oxidation is presented in detail. Formaldehyde can be oxidized to CO_{ads} (pathway 1). This path involves a reactive intermediate and adsorbed CO_{ads} as a poisoning species, which in turn must be removed by reacting with OH_{ads} . In the other pathway, formaldehyde is oxidized to CO_2 directly (pathway 2).



Pathway 1:



Pathway 2:

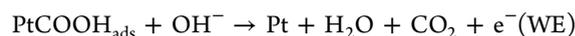
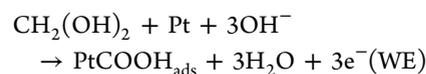


Figure 2d shows that both the oxidation and reduction peak currents at $E = 0.15$ V have a good linear relationship with the square root of the scan rate. This proves that the reaction is a diffusion-controlled process, and this is the linear relationship that we expect. One can easily note that a linear relationship between current and analyte concentrations with a lower detection limit for formaldehyde of 100 μM concentration can be found at potential $E = 0.15$ V as shown in Figure 2b. Also, the relative response shown below was employed to improve the consistency of the amperometric sensor

$$I_R = \frac{I}{I_B}$$

where I_R indicates the relative response, I is the sensor's current in an individual test, and I_B is the baseline of the sensor. Also, it can be found that the sensor current value is

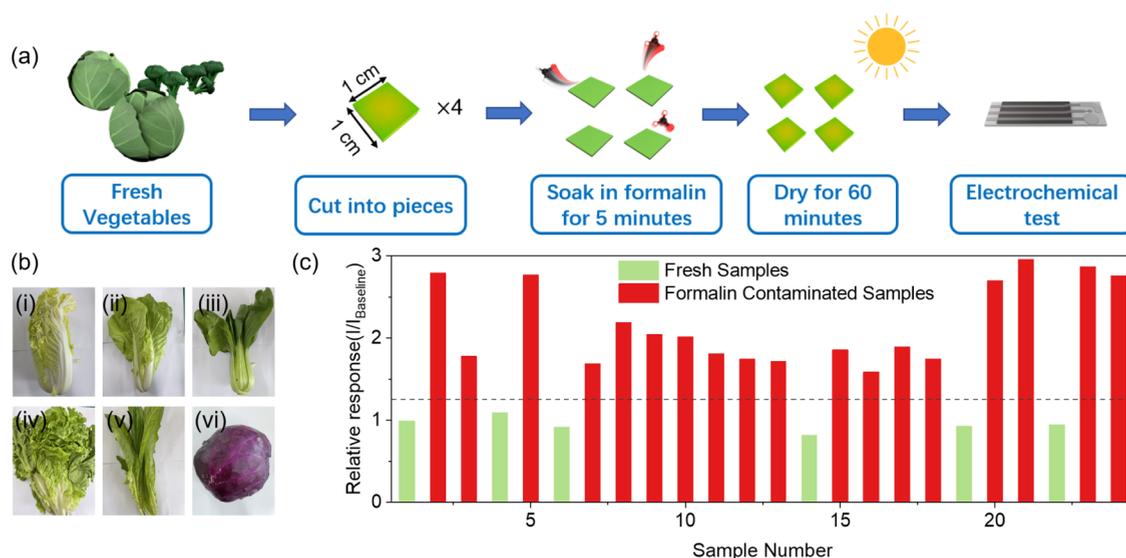


Figure 3. Performance in real contaminated vegetable samples. (a) Process of preparing contaminated vegetable samples: first, fresh vegetables were cut into 1 cm² pieces, four pieces were taken as a group and each group was soaked in formalin for 5 min, each set of samples was allowed to dry for 60 min to simulate the use of formaldehyde in the market to keep fresh vegetables, and then electrochemical sensors that we fabricated were used to detect these vegetable samples. (b) Vegetable samples used in the test: (i) cabbage, (ii) Chinese cabbage, (iii) rapeseed, (iv) lettuce, (v) leaf lettuce, and (vi) purple cabbage. (c) Bar diagram showing the relative responses of the sensor for 24 vegetable samples, and the dashed line shows the threshold (1.25 times larger than the baseline current).

slightly larger (1.5–2.5 times greater) than those without formaldehyde. According to this behavior, one can accurately tell whether the solution contains formaldehyde.

The selectivity of amperometric sensors is crucial because various chemicals in formalin may influence the accuracy of the sensor readings. Figure 2f shows that the presence of other interferences in formalin causes negligible interference to the response of the sensor, which maintains the excellent selectivity of formaldehyde. Also, the interface from the vegetables itself also has been studied. We compared the current value between clean vegetable samples and samples after formaldehyde treatment, as shown in Supporting Information Figures S11 and S12. Six vegetables without formalin adulteration are examined (12 samples in total). One can easily see that the current of samples without formalin treatment is similar to the current in the blank electrolyte solution as a relative response close to 1. As we know, some vegetables contain natural formaldehyde, for example, some kinds of mushrooms.⁴⁸ However, we focus on the detection of formaldehyde itself because we believe it is harmful to human health. Users can also employ our sensor to detect whether a specific kind of vegetable contains natural formaldehyde or not.

The reproducibility and stability of sensors were also characterized as shown in Figure 2e. A short-term 120 min repeatability measurement with 150 times successive transient response to formaldehyde (400 μM) was performed as shown in Figure 2. One can note that the response of the sensor was steady with all of the CV curves almost coinciding. It can be found that the sensor response presented a standard deviation (SD) of 0.327 μA and a relative standard deviation (RSD) of 0.496% over 150 cycles at $E = 0.15$ V. The kinetics of the electrode was investigated by analyzing the effects of the scan rate on the peak of the redox current. The electrochemical performance was tested in a 400 μM formaldehyde ferricyanide solution, with scan rates ranging from 50 to 750 mV/s. Maximal current values of the redox (I_{pa} and I_{pc}) reaction increased linearly with $R^2 = 0.99$ on increasing the scan rate. In

addition, the voltage width between redox peaks became wider and wider (Figure 2d). Based on these results, a linear fit was performed about the oxidation peak (I_{pa}) and reduction (I_{pc}) peak currents related to the square root of the scan rate ($v^{1/2}$). The ultimate linear equations were determined to be $I_{pa} = 13.41v^{1/2} - 87.74$ and $I_{pc} = -20.24v^{1/2} + 104.12$ (Figure 2d). The results from this linear fit demonstrate that the electrochemical signal was the result of a diffusion-controlled surface reaction.

2.2. Design of Openstat and Validation of the Formaldehyde Detector from Vegetable Samples. As shown above, at a potential of 0.15 V (vs Ag), the current value of the sensor in response to a formaldehyde-contaminated solution is usually 1.5–2.5 times higher than the baseline. The threshold of formaldehyde adulteration is whether the relative response of the sensor can achieve current 1.25 times larger than that in the NaOH solution at potential $E = 0.15$ V. Oxidation and reduction peaks can be easily observed in the CV plot if the sample is contaminated with formaldehyde (as shown in Figure 2a). Thus, we found that at potential $E = 0.15$ V, the response current of the sensor can achieve good linearity. When the current of the sensor is 1.25 times higher than the average of the baseline current, it can be considered as formaldehyde-adulterated. The current value and the alert of adulteration are displayed on the app. Meanwhile, a light-emitting diode (LED) on the circuit board of Openstat lights up.

To verify the reliability of our sensor in an actual-use scenario, 24 vegetable samples from six different kinds of vegetables, lettuce, leaf lettuce, cabbage, Chinese cabbage, rapeseed, and purple cabbage, were obtained. Figure 3a,b illustrates the sample preparation process and different vegetables used in this study. Briefly, 18 groups of samples were randomly adulterated with formaldehyde using this method, and the remaining six groups are blank control groups. As shown in Supporting Information Figure S6, high-performance liquid chromatography (HPLC) was employed to

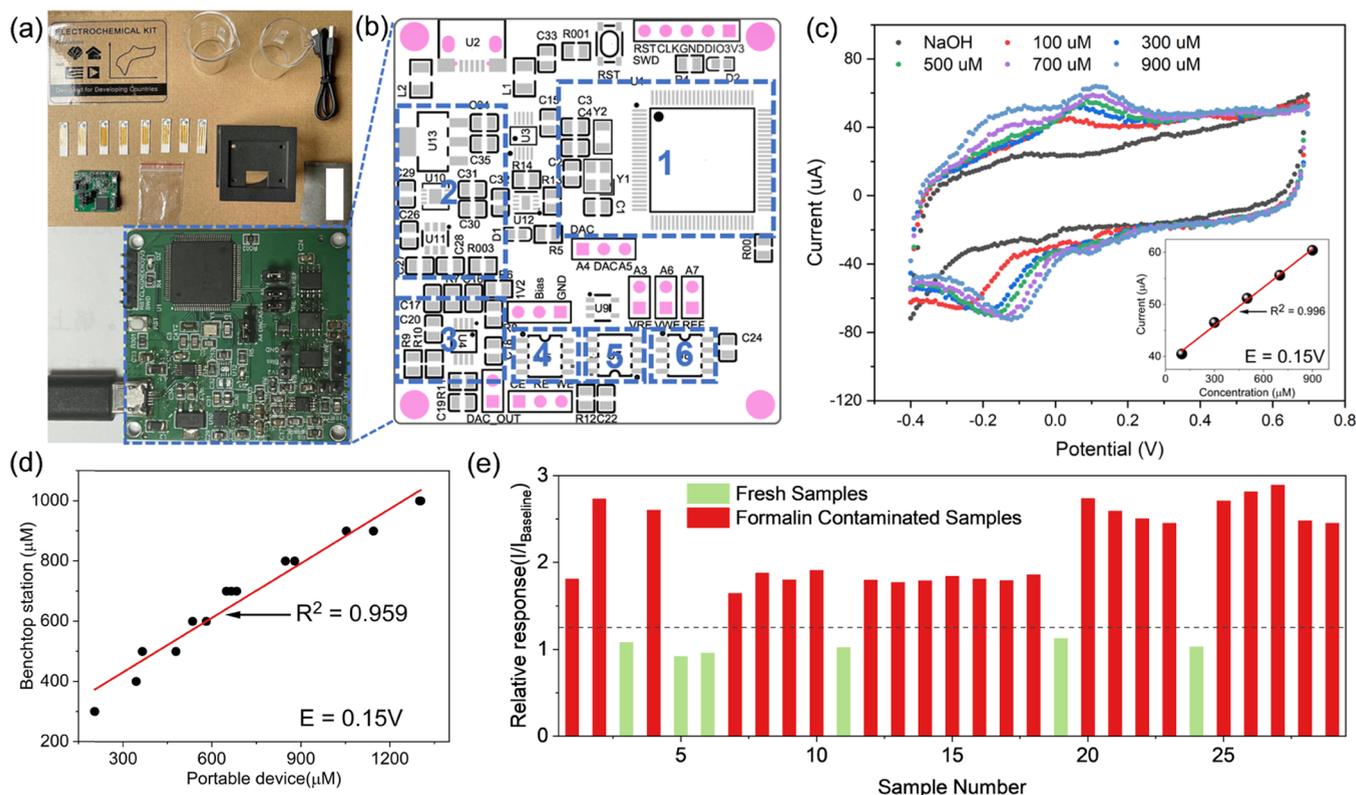


Figure 4. Characterization of the portable device. (a) Photograph of the whole POC sensor package and (b) the labeled PCB diagram of the device used for formalin contamination analysis: (1) multipoint control unit (MCU) for signal produce and data process, (2) power supplies provide 1.2 and 3.3 V voltage, (3) low-pass digital filter, (4) operational amplifier, (6) control amplifier, and (5) transimpedance amplifier. (c) Cyclic voltammograms and the linear fitting plot (inset) at different concentrations using the portable device. (d) Validation of the portable device: the linear correlation between the concentrations of formalin detected by the portable device and benchtop station. (e) Relative responses of the sensor with the portable device for 29 vegetable samples (six fresh, 23 contaminated); the dashed line shows the threshold (1.25 times larger than the baseline current).

verify the formaldehyde in vegetables. In the presence of formaldehyde, the current value of the amperometric sensor is 1.25 times higher than its baseline (at $E = 0.15$ V); therefore, with a threshold of 1.25 (relative response), our sensor successfully detected all contaminated vegetables even when there was no residual liquid on the surface of the vegetables, making it an effective tool in market supervision and large-scale screening.

The result in Figure 3c is performed by an electrochemical workstation (CompactStat.h), which is also confined to the laboratory and expensive. To further reduce the cost of each test and improve on-site inspection capabilities, an open-sourced potentiostat was developed to perform the test. Figure 4a,b illustrates the system-level overview of the signal transduction, conditioning, and processing paths to facilitate measurements. With a printed circuit board (PCB) of size 5 cm \times 4 cm, the signal conditioning path for the amperometric sensor is implemented with analog circuits and in relation to the corresponding transduced signal. The circuits are configured to ensure that the final analog output of the amperometric sensor in the formaldehyde test is finely resolved while staying within the input voltage range of the analog-to-digital converter (ADC). Also, a square wave was generated by the digital-to-analog converter (DAC) to perform the CV test, and a low-pass digital filter was used to improve the quality of this signal. Furthermore, the microcontroller's computational and serial communication capabilities are used to compensate and relay the conditioned signals to a PC. The data of each test

can be analyzed on a PC, and an LED is used to indicate the presence of formaldehyde in the test sample. To validate the reliability of Openstat, cyclic voltammetry of 100–1000 μ M formaldehyde solution was performed by Openstat, as shown in Figure 4c, and good linearity ($R^2 = 0.99$) can be found at a potential of $E = 0.15$ V. Further, we directly calibrate the formaldehyde concentration determined by Openstat and a benchtop workstation (CompactStat.h) on the same set of samples with unknown formaldehyde solutions with concentrations ranging from 100 to 1000 μ M. As shown in Figure 4d, two sets of formaldehyde concentrations were well correlated, with $R^2 = 0.956$ at $E = 0.15$ V (vs Ag). These results validated the reliability and applicability of Openstat as a portable electrochemical analyzer. Finally, 29 vegetable samples from the six different vegetables mentioned above were obtained, with a detection threshold of 1.25 (relative response). Our POC formaldehyde detector composed of amperometric sensors and Openstat successfully detected all samples contaminated with formalin. The formaldehyde detector price is the main factor when assessing its applicability for the potential mass screening of vegetables. By following a simplicity- and practicability-oriented strategy (screen printing, large-equipment-free, easy manufacture), rather than any costly method (e.g., photolithography/electron-beam evaporation), the feedstock cost per detector was enormously reduced and became affordable in low-income areas. The feedstock cost for each examination (i.e., one amperometric sensor) and one reusable Openstat is \sim USD 0.08 and \sim USD 2.47, respectively,

demonstrating an ultralow price for large-scale screening and quality control by police and administrators, as well as high suitability for resource-poor conditions where there is a lack of sophisticated instruments, clean rooms, funds, and highly trained technicians.

3. CONCLUSIONS

In conclusion, we present an easy-to-make, low-cost, simple-to-use, and reliable formaldehyde detector that can be readily used by consumers, distillers, and law-enforcing authorities for easy formaldehyde contamination screening. This modular design could also be applied for electrochemical education and other uses. Affordable detectors are particularly attractive for widely distributed use, especially in low-income economies where food safety is a concern. In the next step, we will further lower system costs, improve the detector's sensitivity and reliability, reduce the size of the detector using microfluidic chips and modified electrodes, and perform larger-scale tests in actual-use environments.

4. EXPERIMENTAL SECTION

4.1. Synthesis of the Amperometric Sensor. To fit all of the conditions of the ASSURED device, the sensor was designed from the point of the most convenient manufacturing that is cost-effective, can be made from common materials, and the sintering furnace is the only equipment needed to manufacture this sensor. Also, the cost of each sensor is less than USD0.5, which makes it more practical to use in low-income countries. Figure 1 explains the concept of the amperometric sensor and its fabrication process. Platinum (Pt) and silver (Ag) were screen-printed onto the ceramic substrate. A typical process is shown in Figure 1e: first, the ceramic substrate was cut into a small size, as shown in Figure 1f, then Pt is used to print the working electrode (WE) and counter electrode (CE) on the substrate and annealed in air at 850 °C for 10 min. Next, printed Ag is used as the reference electrode (RE) and conductor. Finally, the waterproof glass is printed onto the Ag wire and heated via calcination at 500 °C for 10 min. After overnight curing at room temperature, fine emery paper was used to abrade the top surface of the three electrodes, removing the oxide layer formed during sintering. The scanning electron microscopy (SEM) images of the surface and cross-sectional view of the working electrode are shown in Figure 1. The surface morphology of the working electrode and the counter electrode is presented (check Supporting Information Figure S1 for the SEM image of the reference electrode), and according to the X-ray diffraction (XRD) pattern (in Supporting Information Figure S2), the major phases of the WE are metallic Pt (PDF # 87-0646) and α -Al₂O₃ (PDF # 82-1399), which is the main constituent of ceramic substrates. Diffraction peaks of the material are relatively sharp, which indicates that the crystallinity of the prepared material is relatively high. The diffraction peaks appearing at 39.95, 46.41, and 67.67° are the same as those of Pt (PDF # 87-0646), and peaks at 39.796, 46.283, and 67.53° are consistent with those of α -Al₂O₃ (PDF # 82-1399). The cross-sectional scanning electron microscopy (SEM) image of the amperometric sensor shows the Pt sensing film (thickness: 2.7 μ m) (Figure 1c). The thicknesses of the sensing layer in all of the sensors were similar. The electron probe microanalysis (EPMA) elemental mapping results show that the Pt component is uniformly distributed throughout the Al₂O₃

substrate, whereas the components are located only in the overlayer. The amperometric sensor can be fabricated by a quick and easy three-step method. The details of the sintering furnace, conductive metal paste, the layout of electrodes, and equipment for performing SEM and XRD are provided in the Supporting Information.

4.2. Sample Preparation. To demonstrate our sensor design, amperometric sensor prototypes were fabricated and the sensing performances were characterized. First, the performance of detecting formaldehyde concentration in water was verified. Sodium hydroxide (NaOH) was added to the water as an electrolyte material, 2 mL of NaOH solution (2 mol/L) was mixed with 38 mL of deionized water to dilute to a 0.1 mol/L NaOH solution. Different concentrations of formaldehyde were added into the sodium hydroxide solution using a pipette. Second, as shown in Figure 3a,b, six common vegetables (cabbage, rapeseed, lettuce, Chinese cabbage, leaf lettuce, and purple cabbage) were bought from Wumei Supermarket (Beichen district Tianjin, China), and each was cleaned under running water. Next, the six vegetables were cut into small pieces with a 1 cm \times 1 cm size to make sure each set of samples had a similar surface area. Four pieces from the same vegetable were taken as a group, and each group was sprayed with different concentrations of formaldehyde (0.01 and 0.05 mol/L). It should be noticed that the sample preparation process in laboratory tests is complicated because a control variable method is employed to make sure that the response is caused by formaldehyde and has nothing to do with the shape or size of the vegetables. In a large-scale screening scenario, if the user does not have to accurately measure the concentration of formaldehyde in vegetables, any size or shape can be cut for measurement. Then, the procedure of sample preparation and test could be greatly simplified for practical use. After that, each group was placed in a fume cupboard for 60 min (ensuring that all of the liquid on the surface of the vegetables evaporates) to simulate the process of unscrupulous vendors intentionally adulterating using formaldehyde. For the electrochemical test, the samples were placed in a beaker with 40 mL of 0.1 mol/L NaOH solution. A holder (see Supporting Information G for details) containing the amperometric sensor and our open-sourced low-cost potentiostat Openstat was placed above the beaker to make sure that the amperometric sensor was inserted vertically into the solution, keeping the solution just submerged through the electrode region for electrochemical analysis. Before each test, calibration was executed. First, the sensor's sensing electrode was placed in the NaOH solution, and cyclic voltammetry (CV) measurement was performed to obtain the baseline value. Then, the vegetable sample was placed in the beaker, and the CV measurement was performed again. The relative response was calculated with two results. The measurement of baseline current can be seen as a calibration procedure. Thus, zero calibration was performed before each test, and for practical usage, a screen of formaldehyde is acceptable. Cyclic voltammetry (CV) was performed during the test with a scan rate of 50 mV/s ranging from -0.4 to 0.7 V. All of the data was sent to a PC through a universal serial bus (USB) cable and simultaneously transferred to a mobile app through an IoT platform known as Blynk (detailed information can be found in Supporting Information K: Schematic review of Openstat).

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c04229>.

Reagents and apparatus used in this study; material characterization of sensing materials; vegetable samples used in this study; results of high-performance liquid chromatography; and design of the data acquisition system (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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