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# Smartphone-based sensing system using ZnO and graphene modified electrodes for VOCs detection

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ABSTRACT

Volatile organic compounds (VOCs) detection is in high demand for clinic treatment, environment monitoring, and food quality control. Especially, VOCs from human exhaled breath can serve as significant biomarkers of some diseases, such as lung cancer and diabetes. In this study, a smartphone-based sensing system was developed for real-time VOCs monitoring using alternative current (AC) impedance measurement. The interdigital electrodes modified with zinc oxide (ZnO), graphene, and nitrocellulose were used as sensors to produce impedance responses to VOCs. The responses could be detected by a hand-held device, sent out to a smartphone by Bluetooth, and reported with concentration on an android program of the smartphone. The smartphone-based system was demonstrated to detect acetone at concentrations as low as 1.56 ppm, while AC impedance spectroscopy was used to distinguish acetone from other VOCs. Finally, measurements of the exhalations from human being were carried out to obtain the concentration of acetone in exhaled breath before and after exercise. The results proved that the smartphone-based system could be applied on the detection of VOCs in real settings for healthcare diagnosis. Thus, the smartphone-based system for VOCs detection provided a convenient, portable and efficient approach to monitor VOCs in exhaled breath and possibly allowed for early diagnosis of some diseases.

## 1. Introduction

Volatile organic compounds (VOCs), including benzene, alcohol, ketone, alkyl and hydrocarbon, were groups of saturated, unsaturated and oxygenated derivatives, which existed widely in both indoor and outdoor environment (Atkinson, 1997; Kesselmeier and Staudt, 1999). In fact, many VOCs were closely related to environmental evaluation, food quality analysis and diseases diagnosis. For instance, formaldehyde was an important pollutional gas threating human health, while esters played important roles in the perception of odors and flavors in food science (Biasioli et al., 2011; Wieslander et al., 1996). Especially, acetone, alkanes and benzene derivatives had been identified in human exhaled breath from patients with diseases like diabetes and lung cancer (Minh et al., 2012; Phillips et al., 2007, 1999). These VOCs in exhaled breath could reflect the physiological and pathological conditions of human to some degree. A bad apple smell of acetone in human breath accompanied diabetes, while a fishy smell was the result of liver disease and a urine-like smell was related to kidney failure (Di Francesco et al., 2005; Libardoni et al., 2006). Thus, efficient monitoring of VOCs in exhaled breath showed a promising method to obtain human health information. Developments of mature and well-performed gas sensors for the detection of VOCs could be used in clinic practice for the diagnosis of some diseases at its early stage, monitoring the disease progression, and evaluating the diseases recurrence.

Smartphone was becoming more prevalent and widely used in the worldwide because of its strong central processing unit, convenient touch-screen display and large-scale data storage. Utilizing these powerful functions, smartphone had been broadly integrated with sensors, such as ubiquitous test strips, miniature sensor chips and portable hand-held detectors. Recently, smartphone played an increasingly important role in portable sensors for point-of-care test (POCT) as platforms to control, receive, analyze and display sensing signals (Lillehoj et al., 2013; Nemiroski et al., 2014; Vashist et al., 2015). Thus, VOCs monitoring based on smartphone could be developed as a convenient and portable device, which was really useful in some scenes, such as hospitals, indoors, airports and gas stations, for clinic diagnosis and public safety. But until now, there were few reported smartphone-based devices for VOCs monitoring. Therefore, it was

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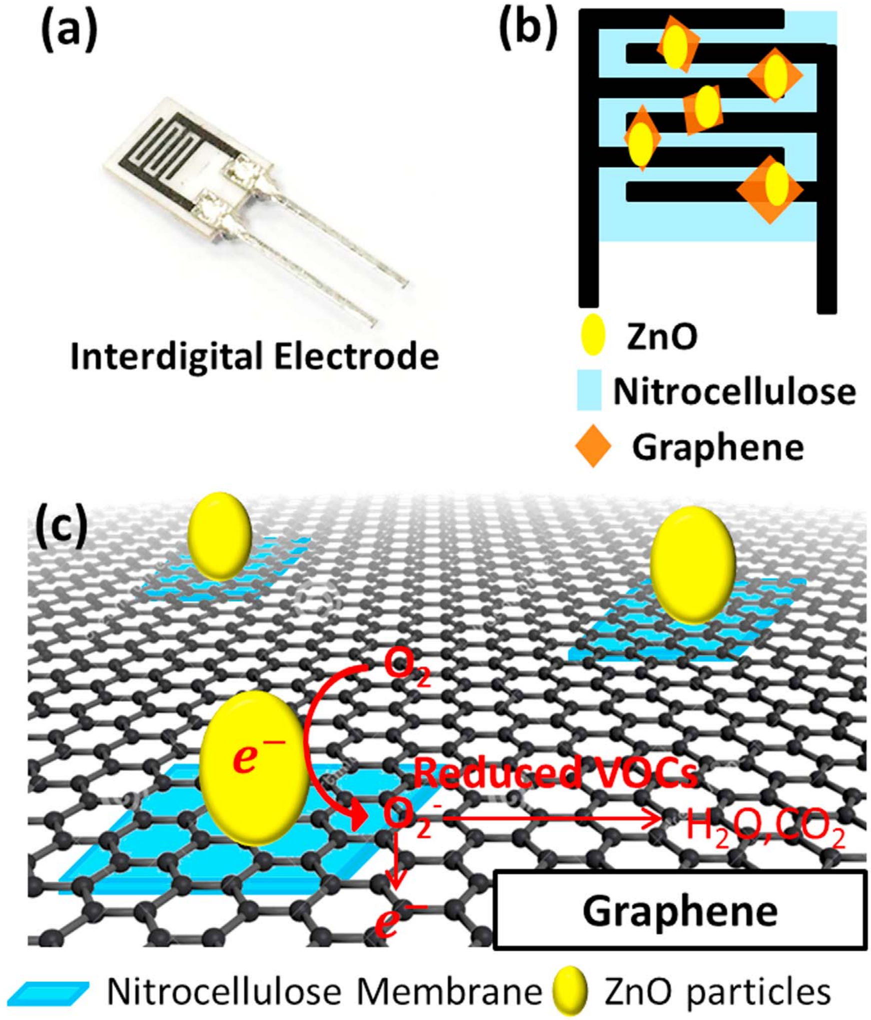


**Fig. 1.** The sensing construction and principle of the graphene and ZnO modified electrodes for VOCs detection. (a) Photo of the interdigital electrodes. (b) Schematic diagram of the electrodes with immobilization of graphene, ZnO and nitrocellulose membrane. (c) The mechanism for detections of VOCs on the modified electrodes. With graphene and ZnO existed on the electrodes, $O_2$ adsorbed on the surface of ZnO and then turned into oxygen adsorbates. In presences of reduced VOCs, electron was freed and transferred to graphene, which caused the impedance of the electrodes changed.

really meaningful to develop a smartphone-based portable device for the detection of VOCs.

Metal oxide nanoparticles such as zinc oxide (ZnO), tin oxide, and tungstic oxide had been extensively developed to respond to VOCs due to their low-cost, large specific surface area, being friendly to the environment and high sensitivity to reduced or oxidizing gases like oxygen (Chatterjee et al., 2015; Li et al., 2004; Zhang et al., 2015b). Tremendous efforts had been devoted to create highly responsive gas sensors by incorporating nanoparticles metal oxide (Bie et al., 2007; Jiaqiang et al., 2006; Lange et al., 2002). However, these sensors had obvious electrical responses only on the premise of a high operating temperature, which resulted in power consumption and obstruction to miniaturization of the sensors. This was undesired in many situations, particularly in the environment with flammable or explosive VOCs. On the other hand, varieties of materials like carbon nanomaterials, inorganic semiconductor and optical fibers had been developed to fabricate gas sensors at room temperature (Bariain et al., 2003; Wang et al., 2013; Zhang et al., 2008). Among them, graphene-based gas sensor had been widely used in VOCs sensors because of its unique atom-thick two-dimensional conjugated structure and excellent electron transfer properties. Graphene was a p-type semiconductor in nature. When graphene was exposed to electron-withdrawing VOCs, it would enhance the doping level of graphene and increase its conductivity. Lots of efforts had been made to fabricate gas sensors using graphene. However, those gas sensors generally had poor selectivity and reversibility due to the indistinctive gas adsorption of graphene by weak van der Waals (Schedin et al., 2007; Yuan and Shi, 2013). Thus, combined with metal oxide and graphene would be a good try to specifically detect VOCs at room temperature (Huang et al., 2012; Li et al., 2015). It would improve the properties of gas sensors in operating temperature and reversibility, which was a promising progress in gas monitoring.

Here, a portable smartphone-based system was developed to measure the impedance change to VOCs on the interdigital electrode. The electrodes were modified by graphene, ZnO and nitrocellulose membrane, and showed high sensitivity to acetone. A hand-held device was developed to detect AC impedance of the electrodes, with the impedance data delivered through Bluetooth and displayed on a smartphone in real time. The smartphone-based device successfully detected acetone as low as 1.56 ppm and distinguished acetone from other VOCs. Finally, the smartphone-based system was used to detect concentrations of acetone in exhaled breath and evaluate its association with the performance of exercise. Combined with smartphones, the system responded to acetone in exhaled breath, which significantly increased after taking stable exercises. Thus, it proved that the system could be used for the detection of VOCs and monitoring the concentration of acetone in exhaled breath from human beings.

## 2. Experimental methods

### 2.1. Chemicals and reagents

In this study, the Graphene was purchased from XFNANO Materials Tech Co., Ltd. (Nanjing, China). The ZnO nanoparticle (99.9% metal bases, 30 ± 10 nm) was from Aladdin and stored in the refrigerator to prevent from being damped. Nitrocellulose membrane (15.6 cm×16.6 cm, 0.45 µm) was purchased from Beyotime. All other chemical regents were of analytical grade and purchased from Sigma-Aldrich.

### 2.2. Design of the interdigital electrode for the detection of VOCs

The interdigital electrode was fabricated with fine pitch and using carbon electrodes as the electron transfer medium. It contained six horizontal carbon electrodes with 4 mm in length and 300 µm in width, while the six carbon electrodes spaced 400 µm with each other. Two vertical carbon electrodes were 500 µm in width and connected with the electrical contact (Fig. 1a and Fig. S1a in Supporting materials). To effectively capture VOCs onto the electrode for an electrical response, the surface of the electrode was modified with graphene, ZnO and nitrocellulose membrane. In this study, 4 mg graphene, 10 mg ZnO and 1 cm×1 cm nitrocellulose membrane were mixed with 2 mL methanol and stirred by lab dancer for 1 min at room temperature, which made each component of the mixed solution become uniformly. The nitrocellulose membrane, dissolved in methanol solution, mixed with graphene and ZnO and helped them be immobilized on the electrodes due to its physical adsorption with the electrodes. To fabricate a sensor with electrical responses to VOCs, 3 µL mixed solution was dropped on the electrode uniformly for two times. The electrodes dried for 1 min after the methanol fully evaporated (Fig. 1b). Then the electrodes could be saved under room temperature, waiting for detections of VOCs. As shown in Fig. S1b (in Supporting materials), it could be found that graphene and ZnO were well immobilized on the electrodes..

With the efficient immobilization of nitrocellulose membrane, graphene and ZnO could be successfully modified on the interdigital electrode. The sensing structure of the electrodes was shown in Fig. 1c. The modified electrodes could adsorb more gas molecules due to larger specific surface of graphene and ZnO. Gas sensing mechanism of ZnO was based on the premise that adsorption of oxygen on the surface could cause an obvious electrical resistance change. The adsorption of oxygen onto the surface of the electrode could cause electron transfer from the conduction band of the ZnO to oxygen, which turned oxygen into oxygen adsorbates ($O_2^-$, $O^{2-}$ and $O_2^-$). In presences of reduced VOCs gases, such as acetone and formaldehyde, those oxygen adsorbates freed electron and transferred to the surface of graphene. It enhanced the doping level of graphene and transferred more electron to the carbon electrodes, which increased sensors' conductivity (Huang et al., 2012). Generally speaking, graphene, ZnO and nitrocellulose played roles on electron transferring with the electrode, catalytic oxidation and immobilizing film, respectively.

### 2.3. Construction of the gas sample system for VOCs

The gas sample system was designed to adjust the concentration of VOCs. As shown in Fig. 2a, the gas sample system included pure air samples, waste recovery parts, the sensing system and VOCs samples. The pure air samples, including a pure air bottle, could supply pure air as a blank control or mix with VOCs to modulate the concentration. The VOCs samples were contained with liquid VOCs, these VOCs could evaporate at room temperature and then flow through the peristaltic pump into the sensing system. Thus, the concentration of VOCs in the VOCs samples could be calculated in ppm using the following equation (Li et al., 2012; Wang et al., 2012; Zhang et al., 2015b):

$$C = \frac{22.4\rho T V_s}{273MV} \times 1000 \tag{1}$$

where $C$ was the concentration of gaseous VOCs at the room temperature (ppm), $\rho$ was the density of anhydrous liquid VOC (g mL$^{-1}$), $T$ was the testing temperature (K), $V_s$ was the volume of anhydrous liquid VOC (µL), M was the molecular weight of a VOC (g mol$^{-1}$), and $V$ was the volume of the glass container filled with the VOC. In our work, taking acetone as an example and the value of M, $\rho$ and $T$ was 58 g mol$^{-1}$, 0.788 g mL$^{-1}$ and 298 K, respectively. The gas sensing properties tested in a sealed glass container. The electrodes were put into the sealed glass container and the container was cleaned by dry air flow at room temperature in the beginning. The modified electrode of the sensing system could convert chemical reaction to electrical signal, which had a linear correlation to the concentration of VOCs. The electrical signal was then transferred wirelessly to the hand-held device. The waste recovery parts, containing a filled-with-ethanol glass container and a balloon, could dissolve VOCs using ethanol and gather the rest gases.

### 2.4. Impedance monitoring for VOCs based on smartphone

The smartphone-based sensing system was used to record electrical responses of the electrode. As shown in Fig. 2b and c, the smartphone-based system included two devices: a hand-held wireless device and a smartphone, which was further improved from our previous design for impedance measurement at a fixed frequency (Zhang et al., 2015a). The hand-held device, connected with the interdigital electrode, included an impedance converter network analyzer (AD5933, ADF4001 and ADG884 circuit), a microcontroller (Arduino board) and a Bluetooth module (HC-06 shield). Similarly, the Arduino board was employed as a controller unit of the system. First, the Arduino board received control commands from smartphone through the serial port connected with Bluetooth module. These commands included some initial setup about scanning period and frequency of stimuli. Then, $I^2C$ port of the Arduino board would communicate with impedance analyzer chip of AD5933 to let the AD5933 chip send out AC sinusoidal stimuli signals into the electrode and simultaneously received feedback signals from the modified electrode to AD5933 chip. At the same time, the digital port of Arduino board adjusted frequency of stimuli signals by controlling the clock chip of ADF4001 and determined connection states between the sensor and reference resistance by the switch chip of ADG884. Finally, the impedance value could be calculated by the impedance analyzer at a fixed frequency, recorded by Arduino board through $I^2C$ port and delivered to smartphone through Bluetooth.

An Android application program (App) was developed on the smartphone to control the hand-held device, receive real-time data and plot the responses on screen. As shown in Fig. 2c, there were four buttons and one coordinate graph on screen. The coordinate graph was used to display the response change of the electrode in real time. The 'Connect' button was used to search and link the hand-held device with the smartphone through Bluetooth. The 'Frequency' button was set up to choose the frequency of stimuli signals and calibrate the hand-held device with reference resistance. The 'Start' and 'Exit' button had functions to start the measurement with the coordinate graph drawing and terminate the program, respectively. In the measurement, impedance monitoring curve could be plotted in real time. The concentration of VOCs could be shown on the screen of the smartphone.

### 2.5. Electrochemical impedance detection for VOCs

Firstly, the electrochemical impedance spectroscopy (EIS) was performed by electrochemical workstation (CHI660E, Chenhua, China) to evaluate frequency-impedance properties of the modified electrode with electrical responses to different VOCs. In the EIS

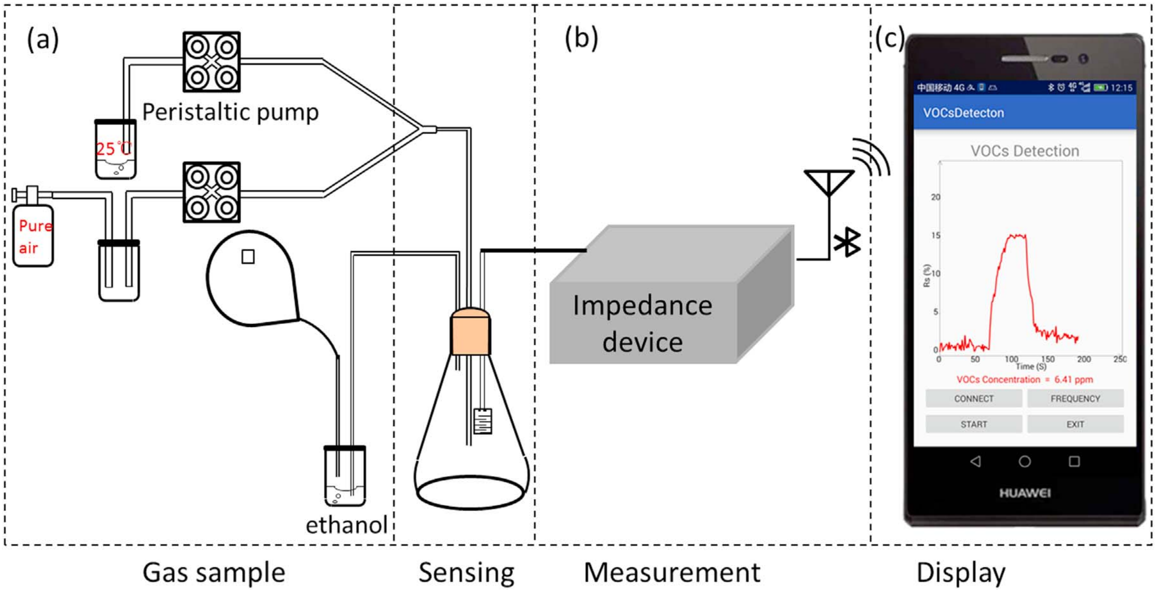


**Fig. 2.** Schematic illustration of the smartphone-based system for VOCs detection. (a) The gas sample system and sensing system. The gas sample system was used to supply different concentration of VOCs and sent VOCs to the electrode of the sensing system to produce impedance changes. (b) The impedance device could detect the impedance change of the electrodes as a response, and then deliver the response to a smartphone in a wireless way. (c) The smartphone screen showed the measurement of acetone in real time and displayed the concentration.

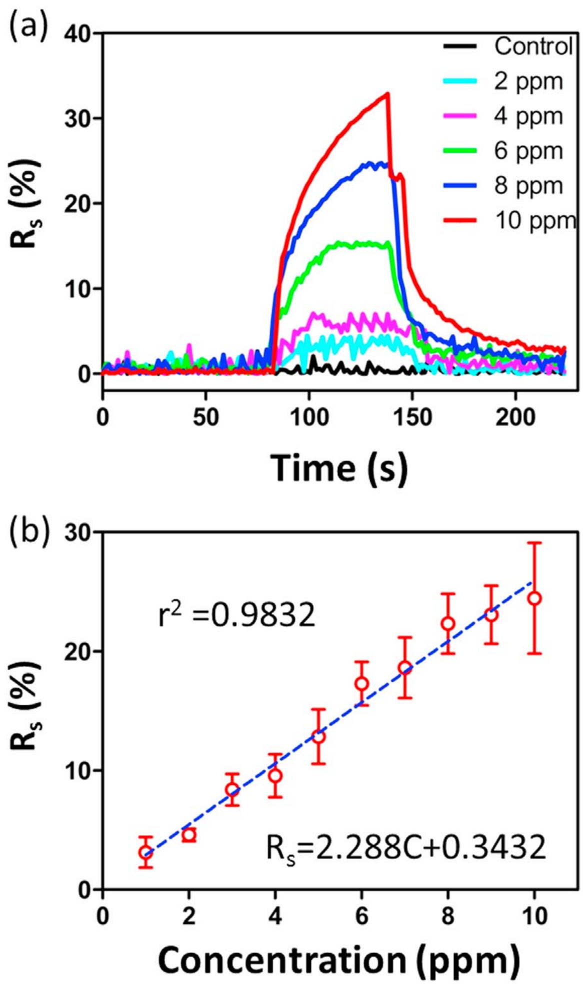


**Fig. 3.** $R_s$ to acetone at different concentrations. (a) Real-time $R_s$ to VOCs of acetone in the ranges from 0 ppm to 10 ppm. (b) Linear dose-dependent fitting curve for $R_s$ versus different concentrations of acetone (mean ± SD, n=5).

measurement, one connected port of the modified electrodes was connected to working electrode of the electrochemical workstation as an input, while another one was connected to reference and counter electrode as an output. The frequency was scanned from 100 Hz to 100 kHz with 200 mV alternating voltage. Different VOCs at 5 ppm were tested by recording the electrochemical impedance spectroscopy, when pure air was used as a blank control. AC impedances at different frequencies were recorded and the change of the impedance was calculated as follow:

$$\Delta R_{VOCs} = R_{VOCs} - R_{air} \tag{2}$$

where $R_{VOCs}$ and $R_{air}$ were impedances of the electrodes with and without VOCs. The characteristic frequencies of different VOCs was at the maximum dip point of $\Delta R_{VOCs}$. The characteristic frequency could be regarded as the inherent property of VOCs to the electrode, which could be used in impedance monitoring based on smartphone at a fixed frequency.

Secondly, the time-impedance scanning was obtained from smartphone-based system at a fixed frequency. VOCs with given concentration flowed stably into the sensing system, adsorbed on the electrode and caused the change of the electrical resistance of the electrode. The electrical information was received by impedance network analyzer and calculated to the electrical impedance of the electrode by chip of AD5933. The gas sensing properties could be assessed through their responses of the sensors ($R_s$), which were defined using the following equation:

$$R_s = \frac{R_{air} - R_{gas}}{R_{air}} \times 100\% \tag{3}$$

where $R_{air}$ and $R_{gas}$ stood for the electrical impedance of the electrode in the pure air and in the VOCs, respectively. Thus, the reaction information of VOCs on the modified electrode could be reflected through the $R_s$.

## 3. Results

### 3.1. Gas sensing properties of ZnO and graphene modified electrodes

To verify whether the electrode had responses to VOCs, $R_s$ change was monitored by the smartphone-based system at different concentrations of VOCs. Fig. 3a showed the $R_s$ change recorded by the system with acetone at different concentrations. The whole $R_s$ monitoring lasted for 220 s. Acetone was added into the sensing container at 90 s from the beginning. The $R_s$ were observed to increase rapidly into a high plateau phase and kept stable for a period of time. After 150 s, acetone was removed, and pure air was added into the sensing container again. Then, the $R_s$ could decrease quickly and returned to the initial base line. It suggested that the modified electrode showed a good response and reversibility in the detection of acetone. Thus, it could be used to detect acetone in real time. Meanwhile, a trend was found that the peak of the response increased along with the increasing of the concentration of acetone. The results demonstrated that the $R_s$ change had dose-dependent characteristics.

To further explore the relationship between concentrations of acetone and $R_s$, $R_s$ were calculated from average value of recorded points in the high plateau phase and plotted with the concentration (Fig. 3b). Then, the $R_s$ to acetone were in a dose-dependent manner, and the curve could be fitted with $R_s$ to acetone at different concentrations using the following equation:

$$R_s = 2.288C + 0.3432 \tag{4}$$

where $C$ represents the concentration of acetone. The curve showed a linear correlation between $R_s$ and the concentration of acetone from 0 ppm to 10 ppm. According to the curve, the detection limits of acetone could reach as low as 1.56 ppm using 3δ/slope calculation for the dose-dependent fitting curve. It proved that the modified electrode could be used as gas sensors for the detection of VOCs, such as acetone, realizing quantification for VOCs.

### *3.2. Distinguish different VOCs using impedance spectroscopy*

Different kinds of common VOCs, such as ethanol, acetic acid, formaldehyde and mixing samples, were used to test the specificity of the smartphone-based system. The $R_s$ to these VOCs were obtained in the same procedure as that in the previous detection of acetone, and results were shown in Fig. 4a. It was obvious that the maximum change of $R_s$ elicited by acetone was significantly larger than those of ethanol and acetic acid did, which almost had no $R_s$ changes. However, the system also showed large $R_s$ about 11.3485% to formaldehyde, which might be related to formaldehyde sharing similar polar structure with acetone (Li et al., 2015). Moreover, the electrodes with pure graphene modification showed low responses to ethanol, acetic acid and formaldehyde, while acetone had almost 10% $R_s$. However, the pure graphene modified electrode did not have reversibility to acetone, the thermal energy at room temperature was not enough to overcome the activation energy needed for molecular desorption (Yavari and Koratkar, 2012; Yuan and Shi, 2013). It meant that the pure graphene modified electrode would be inaccessible to perform continuous detection in the measurement.

As shown in Fig. 4b, the electrodes had strong responses to mixing samples like ethanol and acetone, compared with single sample of acetone or ethanol. Therefore, we could select those mixing VOCs according to the comparison between responses to sole VOC and mixing samples. To sum up, compared with electrodes with pure graphene modification, modification with graphene and ZnO effectively enhanced the response and reversibility of the sensing system to acetone. Meanwhile, it indicated that graphene and ZnO modified electrode only had responses to some kinds of VOCs like acetone and formaldehyde.

### *3.3. A frequency spectroscopy-based method to distinguish different VOCs*

Although it was difficult to distinguish acetone and formaldehyde with the graphene and ZnO modified electrodes, impedance readout in sensing cases was often frequency-dependent due to part phase

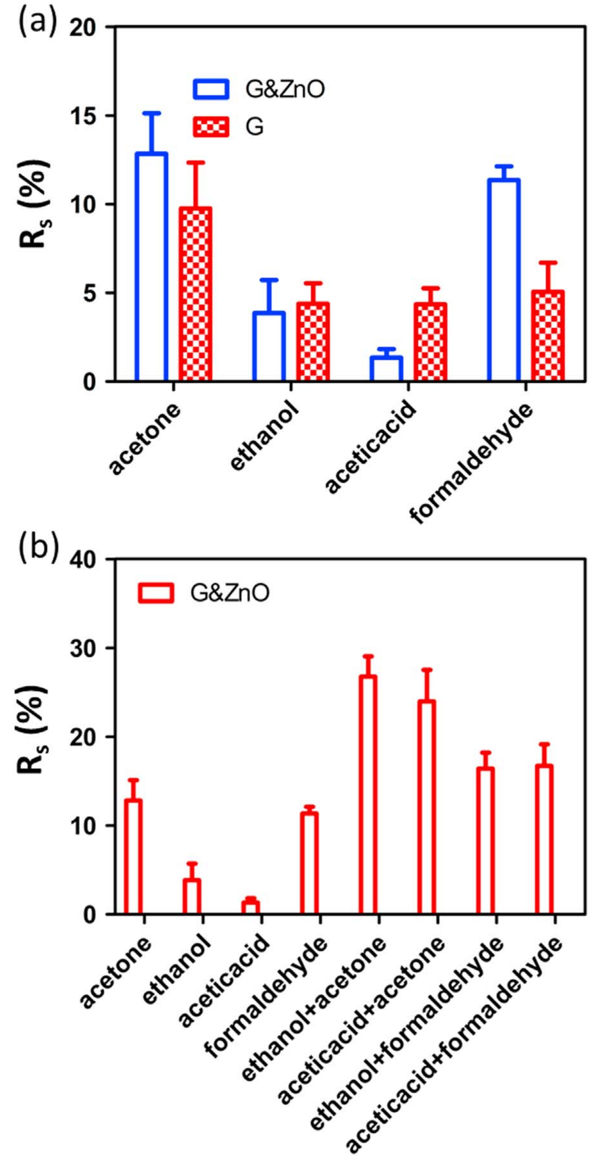


**Fig. 4.** The selectivity of modified electrodes with different VOCs and mixing gases. (a) Responses of graphene and ZnO modified electrodes and pure graphene modified electrodes to different VOCs by smartphone-based system. (b) Responses of graphene and ZnO modified electrodes with sole and mixing gases. The concentration of acetone, acetic acid, ethanol, formaldehyde and mixing gases were all fixed at 5 ppm (mean ± SD, n=5).

properties of the sensors. Therefore, the AC impedance measurement for different VOCs was measured by the electrochemical workstation to verify the relationship between AC impedance change of the electrode and frequency. The frequency-dependent impedance properties of the ZnO and graphene modified electrode for acetone and formaldehyde could be observed in Fig. 5a. It was found that the AC impedance change caused by acetone had the most significant dip at around 2.1 kHz in the whole frequency range of 100 Hz–100 kHz, while that of formaldehyde had maximum change at around 19.9 kHz. Visibly, AC impedance change of the modified electrodes showed different characteristic frequencies for different VOCs, which proved that the sensors had obvious frequency-sensitive characteristics. Thus, different characteristic frequencies in the impedance spectroscopy of different VOCs could be used in fixed frequency impedance monitoring based on smartphone. As shown in Fig. S2 (in Supporting materials), responses measured by smartphone-based system were similar with that of

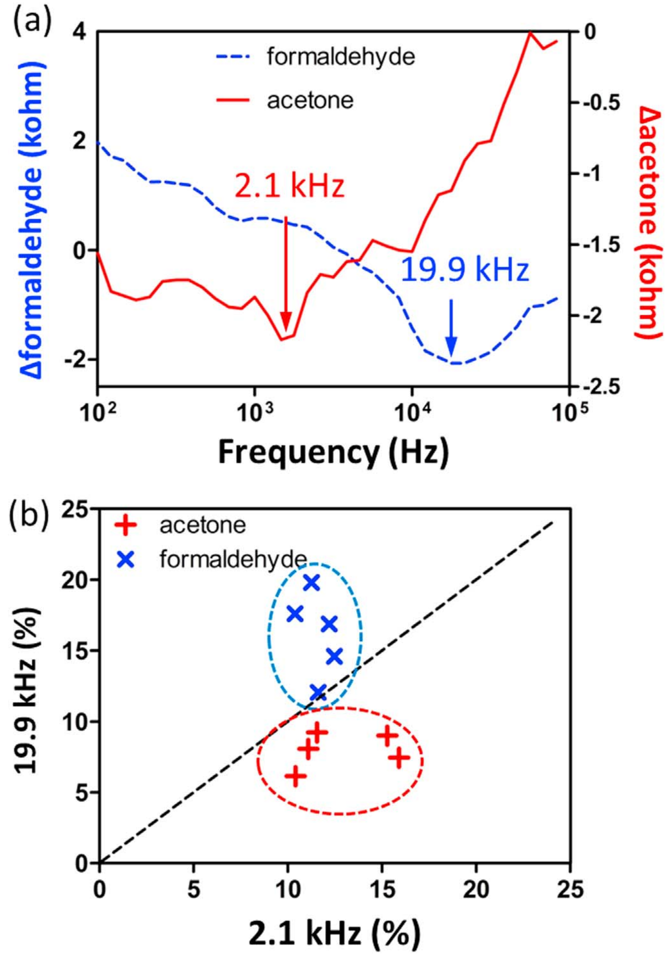


**Fig. 5.** The frequency properties of the modified electrode for acetone and formaldehyde. (a) Impedance spectroscopy of the electrodes for acetone and formaldehyde, whose frequency ranges from 100 Hz to 100 kHz. The characteristic frequencies of AC impedance change for acetone and formaldehyde was 2.1 kHz and 19.9 kHz, respectively. (b) Distinguish acetone and formaldehyde on 2.1 kHz and 19.9 kHz by using smartphone-based device. The $R_s$ measured at 2.1 kHz was used as horizontal axis, while that at 19.9 kHz was used as vertical axis. The acetone points lie on the bottom region of the dotted line, while formaldehyde points lie on the top region of the dotted line.

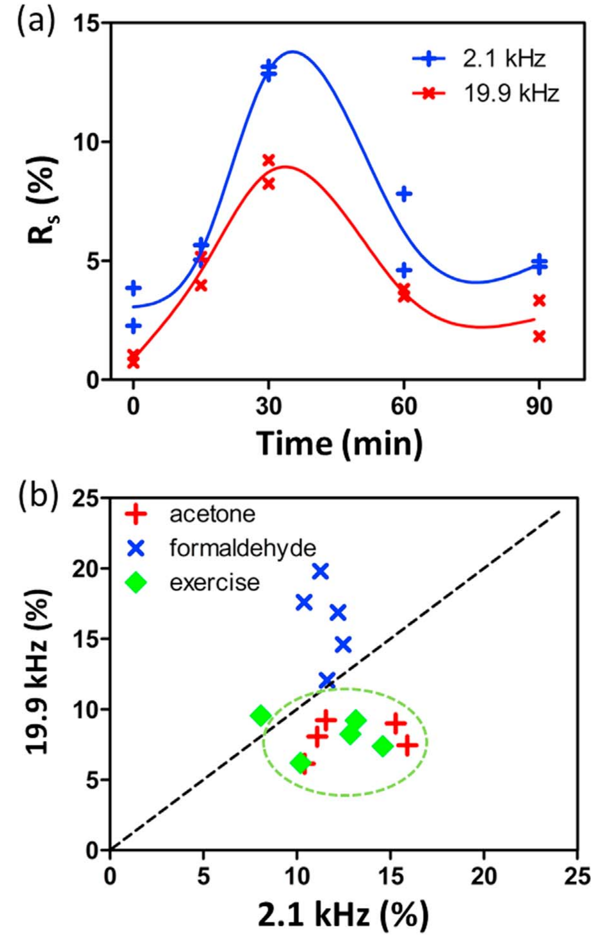


**Fig. 6.** Responses of the smartphone-based system to exhaled breath during exercise. (a) The real-time $R_s$ to exhaled breath before, during and after exercise measured at 2.1 kHz and 19.9 kHz. The $R_s$ increased after a stable exercise and then decreased after stopping exercise. (b) The $R_s$ to exhaled breath after 30-min exercise measured at 2.1 kHz and 19.9 kHz. The AC impedance change to exhaled breath at 2.1 kHz was larger than that at 19.9 kHz, which showed those exhaled breath points after 30-min exercise located on the bottom region of the dotted line.

electrochemical workstation. Meanwhile, the responses to acetone measured at around 2.1 kHz were larger than that at other frequency point. The narrow graph showed the similar responses to acetone at 5 ppm measured by smartphone-based system and electrochemical workstation, which showed that the smartphone-based system had good reliability.

Utilizing this property, the smartphone-based sensing system could distinguish acetone and formaldehyde. The AC impedance changes to these two kinds of VOCs were measured at 2.1 kHz and 19.9 kHz. It could be found that $\Delta R_{VOCs}$ to acetone by the smartphone-based system at 2.1 kHz were larger than that at 19.9 kHz, while $\Delta R_{VOCs}$ to formaldehyde measured at 2.1 kHz were smaller than that at 19.9 kHz. Thus, it was obvious that acetone and formaldehyde could be distinguished in a way as locating in the different region of a two-dimensional plane coordinate. Fig. 5b showed that those points of acetone lied on the bottom of the dotted line, while the points of formaldehyde lied on the top of the dotted line. According to the characteristic of frequency points of acetone and formaldehyde, responses of the sensing system to two kinds of VOCs measured at different frequency obviously located in the different region. Therefore, the smartphone-based system could further distinguish different VOCs using both their $R_s$ and their characteristic frequencies, which successfully solved the difficulty of selectivity.

### 3.4. Human exhaled breath test using smartphone-based system

Acetone was one of typical VOCs in exhaled breath of human beings. It had been reported that the concentration of acetone in exhaled breath was closely related to some diseases and exercise condition. Especially, the biological intensive exercise could elicit lipolysis, produce acetone in blood and significantly increase the concentration of acetone in exhaled breath. Thus, the smartphone-based sensing device was used to assess human metabolism by measuring acetone in exhaled breath. Fig. 6a showed a dynamic change of $R_s$ to exhaled breath before, during and after a stable exercise measured at 2.1 kHz and 19.9 kHz, respectively. At the beginning of exercise, the responses could be observed to increase and reach peak at around 30 min (subjects only exercised for 30 min, which not meant this $R_s$ was the maximum during exercise). After stopping exercise and resting about 90 min, the responses decreased back to steady states again. It could be found that the smartphone-based sensing system had responses to the exhaled breath and could be detected by the system. Meanwhile, responses to exhaled breath measured at 2.1 kHz were larger than that measured at 19.9 kHz in the same time points.

In fact, $R_s$ changed after exercise because the composition of exhaled breath changed. According to the characteristic frequency of acetone, several human exhaled breath tests were measured using the smartphone-based device at 2.1 kHz and 19.9 kHz. As shown in Fig. 6b, for all of the subjects exercised 30 min, most of response points were on the bottom of the dotted line. Combined with the fact that the concentration of acetone in exhaled breath increased during exercise, VOCs existed in exhaled breath during exercise could mainly be regarded as acetone. It proved that the smartphone-based system could be used to monitor the concentration of acetone in exhaled breath.

## 4. Discussion

### 4.1. Performance of the smartphone-based device for VOCs

For VOCs detection, two vital factors were efficient capture of VOCs on the electrode and accurate record of the electrical signals by hand-held device. Firstly, graphene and ZnO were widely used to fabricate gas sensors due to their excellent structural properties (Li et al., 2015; Wang et al., 2014, 2006). In this study, graphene was used as electron transferring carrier, while ZnO played the role as catalytic oxidation and the interdigital electrodes were employed as an impedance transducer. Thus, efficient electron transferring on graphene decreased the difficulty of catalytic oxidation on ZnO, which reduced the reaction condition from high temperature to room temperature. Secondly, EIS of the electrode reflected changes of the electrical properties, which arose from adsorbing events at surfaces of electrodes. AC impedance changes often could be measured as the results of gas molecules adsorbing on the electrode surfaces (Alizadeh and Soltani, 2013; Liu et al., 2013). Therefore, EIS measurement could successfully quantify VOCs adsorption on the surface of the modified electrode. In fact, the interdigital electrodes were small in size, low-cost and easy-to-use. The sensing system for VOCs detection could be developed into portability and reutilization due to its good reversibility to VOCs gas molecules. It was improved on the basis of our previous work, which detected explosive gas molecule like 2,4,6-trinitrotoluene (TNT) in solution samples (Zhang et al., 2015a). Thus, the electrodes could be used for POCT of VOCs detection in clinic due to its quick response to VOCs. It really provided a low-cost, portable and real-time-detective approach for detection of VOCs.

Furthermore, using the modified electrodes as a sensor, the smartphone-based system showed good performance in the detection of VOCs. For sensitivity, the smartphone-based system successfully detected acetone, while its detection limits reached as low as 1.56 ppm. It could satisfy discrimination between the exhaled breath acetone concentration of healthy human ( $<$ 900 ppb) and diabetic patients ( $>$ 1.8 ppm) (Righettoni and Tricoli, 2011; Toyooka et al., 2013). For selectivity, it could be observed in experiments that various VOCs had different characteristic frequencies in impedance spectroscopy. Different characteristic frequencies might be supposed from different adsorption enthalpies between various VOCs molecules and graphene, which was reported by the theoretical and experimental investigations about organic molecules on graphene (Fattah et al., 2014; Lazar et al., 2013). Thus, the characteristic frequency could be used as a distinctive parameter to distinguish different VOCs. Finally, a test by monitoring acetone in exhaled breath during exercise was conducted. The sensing system showed good reversibility to exhaled breath, which could realize real-time, long-term and continuous detection. This proof of concept demonstrated that the smartphone-based system for VOCs detection could be used to monitor acetone in exhaled breath from human beings and applied to early diagnosis for diabetic patients.

### 4.2. Potential applications of the smartphone-based system

In recent years, lots of portable sensing devices were developed with smartphone for different POCT applications, such as glucose analysis in blood, urine detection and bacteria monitoring (Jang et al., 2015; Liu et al., 2014). However, those POCT applications were difficult to widely use due to sampling difficulty and physical invasion. Compared with the blood and urine sample, it was simple and non-invasive for POCT applications to obtain VOCs in exhaled breath. Thus, our smartphone-based system for acetone detection could benefit early diagnosis in home healthcare and primary care for diabetes. In fact, many other VOCs in human exhaled breath could also reflect people's physiological and pathological condition to some degree (Bajtarevic et al., 2009; Buszewski et al., 2007; Fabian et al., 2008). Nowadays, there were more than 200 kinds of VOCs being found in human exhaled breath. Especially, most of them could be used as the main biomarkers, which in return help human know what's wrong with their body. Major VOCs presented in exhaled breath included isoprene, acetone, ethanol, methanol, alkyl and other alcohol. For instance, alkanes and benzene derivatives were closely related to lung cancer, while heptanal and isopropyl myristate were breath biomarkers of breast cancer (Bajtarevic et al., 2009; Phillips et al., 2006, 1999). Similar to acetone, those VOCs also could adsorb on the surface of the graphene and metal oxide modified electrode and then elicit impedance response change (Huo et al., 2013; Robinson et al., 2008). Thus, our portable sensing devices, integrated with miniaturized sensors, portable circuits and ubiquitous smartphone, could meet higher request for mobility and convenience of POCT for many important diseases, such as cancers, in home healthcare services.

## 5. Conclusions

Overall, the design, fabrication and test of a smartphone-based impedance monitoring system were presented to detect and distinguish VOCs. The interdigital electrodes were modified with graphene and ZnO as sensors for VOCs detection. The smartphone-based system could detect acetone as low as 1.56 ppm in real time by combining hand-held impedance monitoring device and smartphone. The selectivity of the system was also tested by characteristic frequencies of VOCs. Thus, the smartphone-based sensing system was a low-cost, portable, real-time and efficient platform to detect VOCs, such as acetone and formaldehyde.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.bios.2016.09.084.

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