Biosensors and Bioelectronics 98 (2017) 449–456

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

Smartphone-based cyclic voltammetry system with graphene modified screen printed electrodes for glucose detection

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ARTICLE INFO

Keywords:
Cyclic voltammetry
Smartphone
Portable detector
Reduced graphene oxide
Glucose

ABSTRACT

Smartphone-based electrochemical devices have such advantages as the low price, miniaturization, and obtaining the real-time data. As a popular electrochemical method, cyclic voltammetry (CV) has shown its great practicability for quantitative detection and electrodes modification. In this study, a smartphone-based CV system with a simple method of electrode modification was constructed to perform electrochemical detections. The system was composed of these main portions: modified electrodes, portable electrochemical detector and smartphone. Among them, the detector was comprised of an energy transformation module applying the stimuli signals, and a low-cost potentiostat module for CV measurements with a Bluetooth module for transmitting data and commands. With an Application (App), the smartphone was used as the controller and displayer of the system. Through controlling of different scan rates, the smartphone-based system could perform CV detections for redox couples with test errors less than 3.8% compared to that of commercial electrochemical workstation. Also, the reduced graphene oxide (rGO) and sensitive substance could be modified by the system on the screen printed electrodes for detections. As a demonstration, 3-amino phenylboronic acid (APBA) was used as the sensitive substance to fabricate a glucose sensor. Finally, the experimental data of the system were shown the linear, sensitive, and specific responses to glucose at different doses, even in blood serum as low as about 0.026 mM with 3δ/slope calculation. Thus, the system could show great potentials of detection and modification of electrodes in various fields, such as public health, water monitoring, and food quality.

1. Introduction

In recent years, smartphone is one of the most widely used mobile devices. It has been reported that there were over 2.03 billion smartphone users all over the world, and this number will reach to 3.5 billion by 2019 (Sun et al., 2014; Sood et al., 2017). The programmable system, touch screen, high-speed computing, and large data storage have made smartphones much more popular than ever before. Since the smartphone can be used as an integrated platform to receive, analyze, and display data, it plays an irreplaceable role in the portable device, and is considered as the hotspot testing device in the field of biosensor (Nemiroski et al., 2014; Zhang and Liu, 2016; Quesada-González and Merkoçi, 2017). Recently, researchers have attempted to utilize these advantages to design portable and convenient smartphone-based detection systems (Wei et al., 2013; Sun et al., 2016; Guo, 2016). They have taken advantage of high-resolution camera on smartphone to develop the optical detections, such as microscopy imaging, fluorescent, and colorimetric detections (Tseng et al., 2010; Wei et al., 2013; Lee and Yang, 2014). Meanwhile, various electrochemical methods have been combined with smartphones to test the electron-transfer processes and quantitative detections, including the chronoamperometry, square wave voltammetry (SWV), differential pulse voltammetry (DPV), and electrochemical impedance spectroscopy (Lillehoj et al., 2013; Nemiroski et al., 2014; Zhang et al., 2015a; Wang et al., 2017).

As one of the most common electrochemical detection methods, cyclic voltammetry (CV) could be not only used for the surface characterizations of the electrodes and detection, but also used as excellent electrode modification methods (Takahashi and Anzai, 2005; Kaminska et al., 2012; Wang et al., 2013). These advantages of CV could be combined with smartphones to develop multipurpose detectors. Thus, some portable CV systems have been designed for different kinds of detections, such as cortisol detection, hepatitis C core antibody, and water quality monitoring (Cruz et al., 2014; Wang et al.,

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http://dx.doi.org/10.1016/j.bios.2017.07.027
Received 25 March 2017; Received in revised form 7 July 2017; Accepted 10 July 2017
Available online 11 July 2017
0956-5663/

2015; Aronoff-Spencer et al., 2016). In the study of Nemiroski and Sun, mobile phone based CV system was designed for the detection of redox couple (Nemiroski et al., 2014; Sun et al., 2014). The basic and most widely used of CV is also involved in modification and characterization of electrodes in electrochemical measurements. However, there are few reports on smartphone-based systems that can be applied in such applications until now. When a system could modify the electrodes with sensitive material and detect the components momentarily, it was significant to perform smartphone-based detection with the high active electrodes in various fields, such as environment monitoring, food analysis, and healthcare diagnosis.

Smartphone-based detection means that the testing was not only performed by the pocketsize system, but the sensors and their modification were also convenient and effective. Thus, it was in high demand for miniaturization of sensors and method of modification needed to be as simple as possible. The size of sensors in electrochemical analysis has become increasingly smaller and more portable than before (Zhang et al., 2015a; Bouchaala et al., 2016; Guo and Ma, 2017). The sensors can be fabricated on planar substrate with tiny size, such as interdigital electrodes and screen printed electrodes (SPE) (Li et al., 2015; Yang et al., 2016; Barton et al., 2016). Among them, SPE have such advantages as small size, light weight, and low cost, which are more disposable than other traditional electrodes. Thus, they could be widely used for smartphone-based detection in various fields from environment monitoring to biomarker testing. Moreover, as a kind of emerging two-dimensional carbon nanomaterial, graphene oxide (GO) can be combined with miniature sensors for biosensor detections. Since it contains oxygen-containing groups such as hydroxyl groups (–OH), carboxyl groups (–COOH), and epoxy groups on graphene single sheets, these groups can combine with biomolecules, such as protein, amino acid, and antigen-antibody by amide bond formation with amine groups (Zhu et al., 2010b; Zhang et al., 2015b). According to this character, GO and sensitive substance can be easily modified on the electrodes by electrochemical methods. Through the CV performed, the GO that composed with sensitive substance could be gradually reduced as the reduced graphene ox ide (rGO), and deposited on miniature sensors. Since its strong conductivity and large surface area, the rGO could be used to improve electrochemical properties for smartphone-based detection (Kaminska et al., 2012; Yang et al., 2017).

In this paper, a smartphone-based CV system was designed and a convenient way of electrode modification based on the system was used for portable detection. The system contained these main parts: the smartphone, hand-held detector, and modified electrodes with substance sensitive. The smartphone was used to control the system, process data, and display results in real time through an application (App). The hand-held detector was developed to perform CV for electrode modification and detection, as well as to transmit the obtained data to the smartphone. By testing various concentrations of redox couple, the smartphone-based system could be demonstrated proper functioning at different scan rates. As a demonstration, the method of medication with the system was used for glucose detection. Through modifying the rGO and 3-amino phenylboronic acid nanocomposites (rGO/APBA) by the smartphone-based CV system, the SPE was used as disposable sensors for glucose detection. Therefore, the smartphone-based system was performed for varied functions of CV, such as modification and characterization of the electrode and further quantitative detection.

2. Materials and methods

2.1. The Design of the hand-held CV detector and the App

The hand-held CV detector was used to test and transmit electronic information to the smartphone. There were several main modules in it: energy transformation module, the low-cost potentiostat module (AD8608, ADI) for CV measurements, and the Bluetooth module (HC-06, Fig. S1, in the Supplement material) for transferring data and command. The energy transformation module was composed of a power unit and digital-to-analog converter (DAC, DAC8552, TI). The power units contained two power supply chips, TPS79933 and TPS79901, which offered 5 V and 3.3 V voltages for the hand-held CV detector, respectively. C8051f005 was used as the microcontroller unit (MCU) of the detector to control the DAC to output the excitation signals on the sensors and used to convert the measured analog signal into digital signals. A 2.1 × 3.3 in. printed circuit board (PCB) prototype was used for certificating the functions of the three blocks and the performance of the CV test.

An App was developed to connect smartphone with hand-held CV detector via Bluetooth, so that to control CV measurement, process the real-time data, and plot the cyclic voltammogram.

2.2. The design of smartphone-based CV system

The smartphone-based CV system was consisted of the sensor, the hand-held CV detector, and the smartphone. The sensors, including three-electrode and SPE, were modified by the functional components and then used to convert chemical molecular reactions into measurable analog signals, which were recorded and converted into digital signals by the hand-held CV detector. Then, they were transmitted to the smartphone on the CV detector. According to these data, the CV curve was recorded and plotted on the smartphone.

2.3. Performance test of the smartphone-based CV system

The aqueous solution of ferricyanide/ferrocyanide (1 mL, 5 mM, 1:1) was chosen as the redox couple to prove the accuracy and stability of system. The system was tested by different scan rates and measured redox couple solutions at different concentrations. Gold electrodes, platinum electrodes, and Ag/AgCl electrodes were used as working electrode (WE), counter electrode (CE), and reference electrode (RE), respectively. The distinctions between the system and commercial electrochemical workstation (CHI660E, Chenhua, China) were calculated in the groups that contained 3 different concentrations of redox couple (5 mM, 2.5 mM, and 1.25 mM) and 3 different scan rates (0.1 V/s, 0.05 V/s, and 0.01 V/s).

2.4. The method of rGO/APBA modification on screen printed electrodes

GO (~ 99% purity, 5 mg, XFNANO Materials Tech Co., Ltd. Nanjing, China) was made by Hummers method and dispersed in deionized water (5 mL) for the dispersion of GO nanosheets. The obtained solution was sonically oscillated in ice-water bath (0 °C) for 1 h and centrifuged for 15 min to obtain the dispersed GO supernatant (1 mg/mL). APBA (2 mg) could react with carboxyl groups on GO for functionalization. APBA was immobilized to GO via N-hydroxysulfosuccinimide (NHS, 5 mg) and 1-ethyl-3-(3-dimethylamino-propyl) carbodi-imide hydrochloride (EDC, 2 mg). These two solutions were added into the GO supernatant (5 mL) and oscillated 3 min. The obtained solution was sonically oscillated in ice-water bath (0 °C) for 1 h and then mixed with APBA (2 mL, 5 mM, in solvent absolute ethyl alcohol). The solution was oscillated for 1 min and then incubated at 0 °C for 4 h. Then the hybrid solution centrifuged at 12000 r.p.m. (4 °C) for 2 h to obtain the clear and well-precipitated GO/APBA sediment. After the supernatant was dislodged entirely, the 1 mg/mL GO/APBA sediment was prepared with absolute ethyl alcohol and stored under 4 °C for 4 h.

SPE was printed on 3 cm × 1 cm polyethylene glycol terephthalate (PET) substrate as WE (5 mm diameter) and CE, while RE was printed by silver. Before connected, the electrodes were respectively rinsed with ethanol and deionized water to remove the organic residues from the substrate. Then it was activated through sodium sulfate (100 μL,

0.5 M) and dried in nitrogen. After the preparation, the GO/APBA solution (50 μL) and sodium sulfate (50 μL, 0.1 M) were dropped onto the SPE. In order to immobilize and reduce the GO/APBA on the electrode through CV, the initial voltage (−1 V), the final voltage (1 V), the cycles (20), and the scan rate (0.05 V/s) were configured with the App of the smartphone. The modified electrode could be restored under indoor temperature (25 °C).

2.5. Smartphone-based CV system for glucose detection

In order to perform detection, the SPE could be linked with the sensor electrical sockets of the hand-held CV detector to execute electrochemical measure. The voltage range was set on the App from −0.8 to 0.8 V and the scan rate was 0.01 V/s. Glucose was diluted into five different concentrations with human blood serum. 50 μL glucose and 50 μL redox couple was added to the electrode, while the blood serum without glucose was used as the blank control. CV was recorded and calculated into normalized peak-to-peak current change (NPPCC), which was defined as followed equation:

$$\mathrm{NPPCC} = \frac{I_b - I_a}{I_b} \quad (1)$$

where I_a and I_b were the peak-to-peak current with and without glucose, respectively.

Uric acid (UA), ascorbic acid (AA), sodium chloride (NaCl), and bovine serum albumin (BSA) were used for selective tests. The latter three substances were prepared at 5 mM in deionized water and blood serum, while uric acid (5 mM) was diluted with sodium hydroxide (NaOH, 1 M). The detection of solutions was performed with the same steps as glucose detection. All the other chemical reagents were on the analytical grade and purchased from Sigma–Aldrich.

3. Results and discussions

3.1. The performance of the smartphone-based system

The system was composed of these main portions: the sensor, portable electrochemical detector, and the smartphone (Fig. 1a). The SPE were modified with rGO and sensitive substance by the system as the sensors for detection. A circuit was designed as the detector to build the important part of the system, which could generate stimulation of the triangular wave signal and measure the current on the sensors.

When running a CV measurement, a DAC on the circuit was used for producing a stimulation of the triangular wave signal (V_B) and a constant voltage (V_A) for the pin of potentiostat. Then, the low cost potentiostat module was designed based on transimpedance amplifier (Fig. 1b). It was applied to set the voltage on the WE and RE in the electrochemical testing and to measure the current, which was then measured with the transimpedance amplifier (Eq. S1, in the Supplement material). The schematic diagram of the smartphone-based CV system is shown in Fig. 1c. As the schematic diagram shown, the hand-held CV detector and sensors were applied to constitute detecting unit, while the smartphone was used to control, analyze and display the results.

As shown in the Fig. 1a, an App was designed as interactive interface between users and the system. There were two buttons on its welcome interface. The 'Enter' button was applied to enter the real-time supervision interface directly. The 'Exit' button was used to terminate the App. After entering, the users could employ smartphones to search and link the hand-held CV detector. Then, the users could set initial voltage, final voltage, scan rate, and cycles in the interface. In measurements, the cyclic voltammogram could be plotted in real time, the values of peak currents were shown under the graph. A demonstration of the designed APP was shown in the Video (in the supplement material).

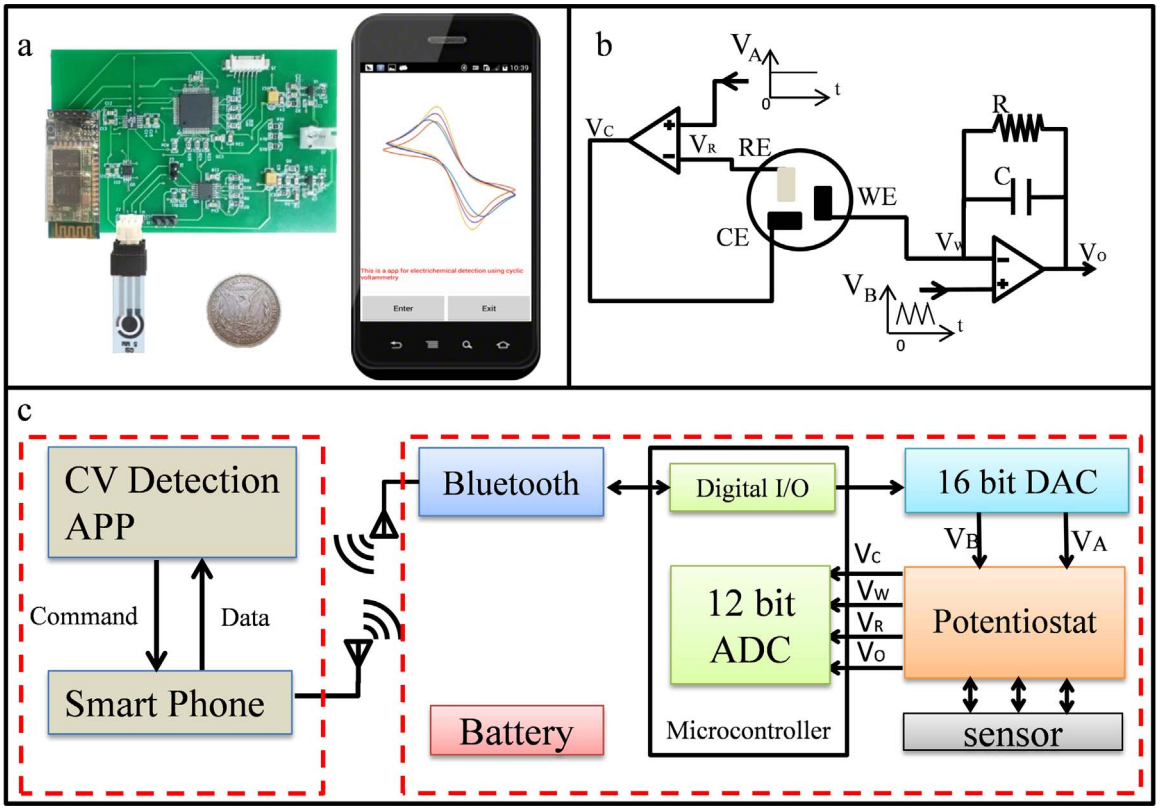

Fig. 1. The schematic and the design of the smartphone-based CV system. (a) The image of the hand-held detector connected with SPE and the welcome interface of the App on the smartphone. (b) The circuit design of the potentiostat based on a resistive feedback transimpedance amplifier. (c) A schematic diagram of the smartphone-based CV system.

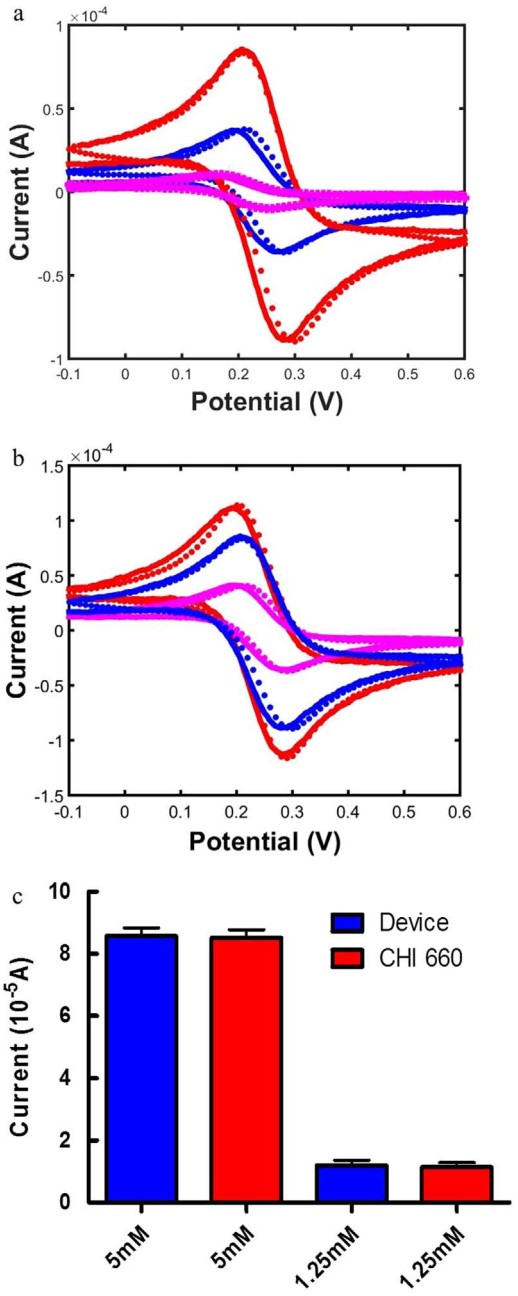

Fig. 2. CV testing of the smartphone based system. (a) Performance of the smartphone-based system (solid line) and the commercial electrochemical workstation (dotted line) under different scan rates (red line for 0.1 V/s, blue line for 0.05 V/s and violet line for 0.01 V/s) measurement. (b) Performance of the smartphone-based system (solid line) and the commercial electrochemical workstation (dotted line) in redox couple detection (red line for 5 mM, blue line for 2.5 mM and violet line for 1.25 mM) measurement. (c) Statistic for peak currents for different concentrations of redox couple solution by the smartphone-based system (blue) and the electrochemical workstation (red) (mean ± SD, n = 10). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.bios.2017.07.027.

Experiments of redox couple detection were conducted to test the performance of the system, whether it could detect the currents and potentials accurately. The results were compared with those of commercial electrochemical workstation. First, the system and workstation were used to test the redox couple (5 mM) at different scan rates (0. 1 V/s, 0.05 V/s and 0.01 V/s). Then, the system was used for different concentrations (5 mM, 2.5 mM and 1.25 mM) of redox couple at constant scan rate (0.01 V/s). As shown in Fig. 2a and b, the obtained curve by the system were very the same as that of electrochemical workstation, indicating that this CV system could accurately measure the currents and potentials of CV at different situation. Fig. 2c has shown the statistic for peak currents by the system and the electrochemical workstation in the different concentrations (5 mM and 1.25 mM) of redox couple to verify the stability. The peak current of the smartphone-based CV system matched well with those of the electrochemical workstation. The results proved that the system could stably perform CV measurement to obtain the accurate peak current.

In order to further reflect detecting stability and accuracy of the system, the distinction was used to precisely obtain the difference between the system and electrochemical workstation (Eq. (S2), in the Supplement material). All current values at different parameters were tabulated in Table 1. At scan rate of 0.01 V/s, the distinction was 2.16%, which was larger than that at other scan rates. In the different concentration tests, the distinction was often less than 3.77%. Compared with commercial electrochemical workstation, the smartphone-based CV system was proved its accuracy in current detection for different concentrations of redox couple and different scan rates. So the system could be used for electrochemical monitoring, such as electrode modification and detection.

CV is a broad-spectrum electrochemical method to analyze the electrochemical behaviors on the surface of electrodes, research redox reactions in electrolytic cell, modify and functionalize electrodes as well as perform quantitative determination (Mu et al., 2011; Chao et al., 2016). Taking advantages of CV, a portable smartphone-based CV system was constituted by the smartphone, the hand-held detector and the sensor in this study. At the same time, the scan rate could be also sited from 0.01 V/s to 0.1 V/s and voltage range could be sited from −1 to 1 V, respectively. Compared with the electrochemical workstation, the smartphone-based CV system was portable to perform CV detection. Compared with other smartphone-based CV detectors, the system could not only perform accurately CV detection, but also provide an effective and convenient method to modify the electrodes as well. With these advantages, the portable smartphone-based CV system could modify different sensitive substances by the excellent method of electrode modification for various detections.

3.2. The modification and characterization of screen printed electrodes

As shown in Fig. S2 (in the Supplement material), APBA could bind to the molecules with diol and be immobilized on the GO through the dehydration condensation reaction due to carboxyl groups (−COOH) (Wang et al., 2013; Zhang et al., 2015b; Harfouche et al., 2017). These

Table 1
Performance tests for the smartphone-based system under different scan rates with different concentrations of redox couple.

Peak current		Scan rate			Concentration of redox couple		
		0.1 V/s	0.05 V/s	0.01 V/s	1.25 mM	2.5 mM	5 mM
Electrochemical workstation (μA)	Current value	114.20	85.10	40.78	11.15	27.16	85.10
Smartphone-based system (μA)	Average value	113.35	83.93	41.66	10.50	28.18	83.93
	Standard deviation	1.54	1.42	0.96	0.27	0.45	1.42
	Distinction	0.75%	1.26%	2.16%	3.69%	3.77%	1.26%

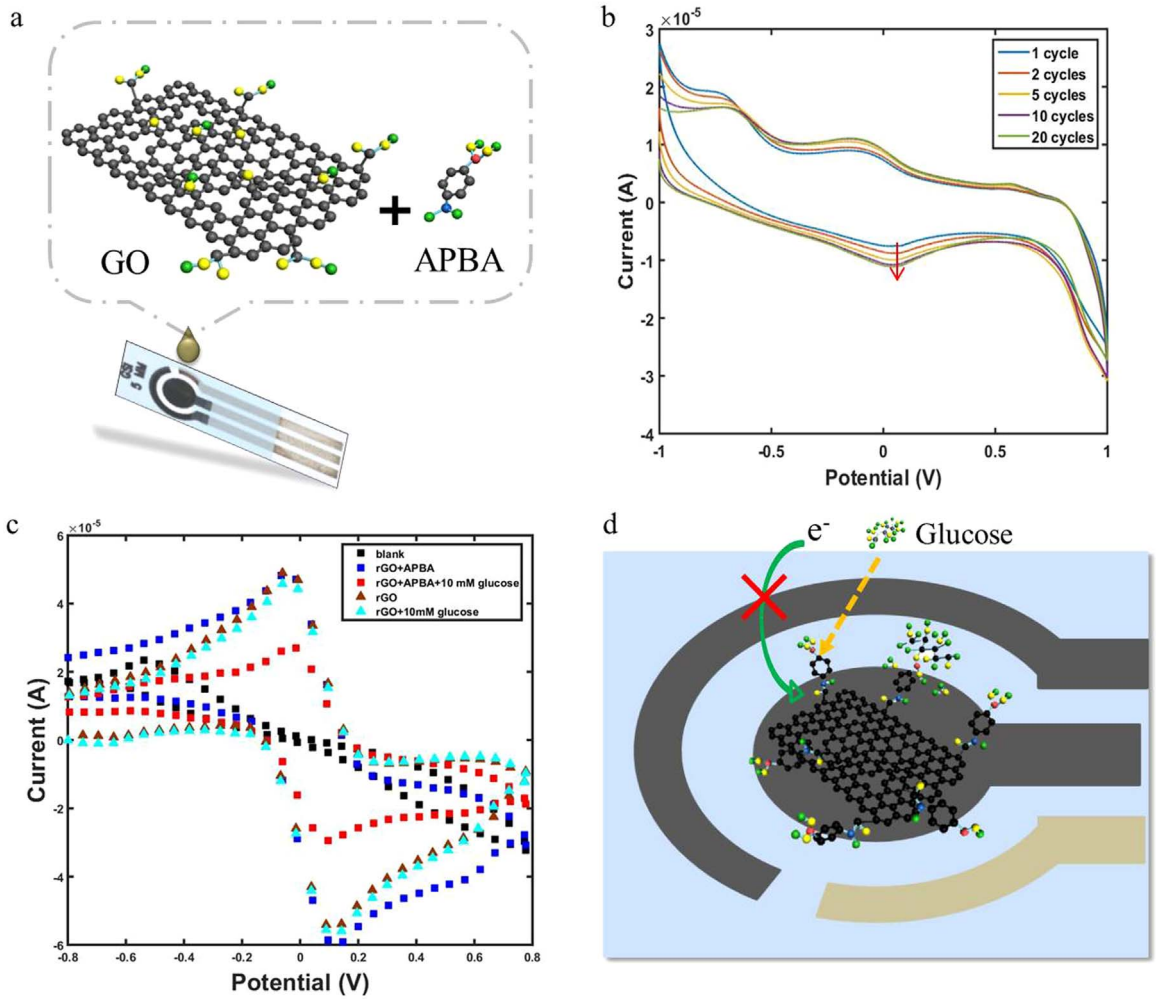

Fig. 3. The schematic diagram and the cyclic voltammogram of the modification of electrodes and detection of glucose (a) Procedure of modification and reduction. (b) The reduced process of GO/APBA by cyclic voltammogram. (c) The cyclic voltammogram of blank electrode (black), the rGO/APBA modified electrode (blue) and the detection of glucose with the modified electrode (red) using the system. The rGO modified electrode (brown) and the detection of 10 mM glucose with rGO modified electrode (cyan). (d) The schematic of glucose detection on the modified electrode. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

oxygen functional groups result in the hydrophily of GO and serve as sites for chemical modification. Thus, GO can be used as an ideal supporting material and a basic module for APBA and other small molecule. As shown in Fig. 3a, the GO/APBA nanocomposites solution and sodium sulfate were dropped on SPE and were used for fabrication rGO/APBA modified electrode by the smartphone-based CV system. After the GO was reduced to rGO, the electrochemical behavior of SPE was markedly changed. By utilizing the high conductivity of rGO, the electro-deposition could enhance the sensitivity of senor. The results of process to reduce GO/APBA nanocomposites were shown in Fig. 3b. It can be found that peak current increased in amplitude from 0.5 × 10^{-5} A to 1 × 10^{-5}A with the process of CV scanning. These results demonstrated that the GO/APBA nanocomposites were effectively reduced to rGO/APBA through redox reaction, and they were deposited on the surface of screen printed electrode by the smartphone-based CV system.

After the modification, the electrodes with and without rGO/APBA were detected with redox couple by the system for characterization. As shown in Fig. 3c, the peak current had a significant increase from 2.5 × 10^{-5} A to 5.2 × 10^{-5} A because of the generating of rGO. The conductivity of blank electrodes and modified electrodes were significantly changed at the same conditions. Moreover, changes of peak voltage position can also be observed in the Fig. 3c, which proved the electrodes had been modified by rGO/APBA. The CV curves of the rGO modified electrodes were similar to those of rGO/APBA modified electrodes in human serum without glucose. However, the responses of the rGO modified electrodes were merely changed in human serum with 10 mM glucose. As shown in Fig. 3d and Fig. S2 (in the Supplement material), since APBA combined with glucose molecules on the electrode and deterred electron transfer (Takahashi and Anzai, 2005; Egawa et al., 2011; Wang et al., 2013), it could be obviously observed that the modified electrode could provide a lot of current changes in presence of glucose, which allowed the further investigating to utilize the sensing capability of the electrodes for glucose detection.

The layered structure of GO was similar to graphite, but GO sheets was decorated by oxygen-containing groups (Zhu et al., 2010a; Yang et al., 2017). With oxygen-containing groups, GO can combine with sensitive substances, such as protein, peptide and antigen-antibody. However, the poor conductivity of GO can influence the electrochemical detection. As shown in Fig. S3 (in the Supplement material), the current of GO/APBA modified electrodes were smaller than that of blank electrodes, and also much smaller than that of rGO/APBA modified electrodes. When human serums contained 10 mM glucose, the decrease of current with GO/APBA modified screen printed electrodes was also smaller than the decrease of current with rGO/APBA modified SPE. Through CV procedure by the system, the GO was deposited on the surface of miniature sensors and reduced to rGO, which have the excellent conductivity and large surface area to enhance sensitivity of electrochemical detection. As shown in Fig. S4 (in the Supplement material), the surface of bare SPEs were rough, while the

surface of rGO/APBA modified SPEs showed typical graphene-like sheet form with folds and wrinkles. These results could prove the validation of the method. Compared with other method to obtain rGO with high temperatures, toxic reactant and long time, the system could reduce GO in 8 min. With this convenient modification method, this CV system could also be applied in water monitoring, food quality analysis and other detection fields.

The electrode modification and detection by the system had more remarkable robust detect abilities and could be less impressionable by environmental conditions such as temperature and humidity. Because all the modification and detection by the system were performed under indoor conditions in short period and the results were also favorable for further application. Besides, the low-cost, diminutive and convenient SPE were fabricated on the paper-thin flat surface. These advantages have made it as a good choice for smartphone-based CV system.

3.3. Glucose detection using the smartphone-based CV system

The smartphone-based CV system was performed to measure glucose through real-time CV monitoring with the rGO/APBA modified electrodes. In Fig. 4a the real-time cyclic voltammogram detection of glucose was displayed on the smartphone screen. The value of peak current and glucose concentration were printed under the plot. Fig. 4b displayed the CV curves with different concentrations of glucose reacting with the rGO/APBA modified SPE. All the values of peak current were normalized with the peak current of blood serum without glucose. After the blank detection, the glucose solution was added on the modified electrodes. The binding of glucose to APBA on the electrodes could cause the decrease of the peak current. To discover the correlativity between the concentration of glucose and the current response, NPPCC was used to calculate the value of obtained current difference and plot with the glucose concentrations. A dose-dependent curve of the smartphone-based CV system was adjusted with NPPCC from responses of glucose at different concentrations as followed equation:

$$\mathrm{NPPCC} = 0.1857\log C + 0.2911 \quad (2)$$

where C refers to the concentrations of glucose. As shown in the Fig. 4c, the curve showed a highly similar to the contrast curve from commercial electrochemical workstation in same conditions. The limit of detection (LoD) for glucose was about 0.026 mM with 3δ/slope calculation. Compared the LoD and linear range with other research teams, the system were suitable for practical application (Table S1, in the Supplement material). The prepared glucose solution at 4×10^{-3} M was measured for further testing the accuracy of the system. The NPPCC value of the prepared glucose solution was 0.40, which was plotted as blue cross in Fig. 4c. In accordance with the Eq. (2), the detected concentration was calculated into 3.874×10^{-3} M. The relative error of the detected concentration was shown about 3.15% with respect to veritable concentration.

For further testing, the real sample of blood glucose detection was used for evaluation the method. In order to obtain the actual blood glucose concentration, a commercial glucometer (ACCU-CHEK Performa, Roche) was used for control group of glucose detection. The blood was directly collected from the volunteer's finger. And then the blood glucose concentrations were measured by glucometer and smartphone-based CV system, respectively. The result showed in Fig. 4c (the green point). The concentration of blood glucose showed in the commercial glucometer was 5.3 mM. The NPPCC value of real sample was 0.42. In accordance with the Eq. (2), the detected concentration was calculated into 5.13 mM by the smartphone-based system. Compared with the commercial glucometer, the error was only 3.2%. Therefore, the smartphone-based CV system could be applied in real blood samples for glucose detection.

Besides for the sensitivity, different kinds of chemicals in blood

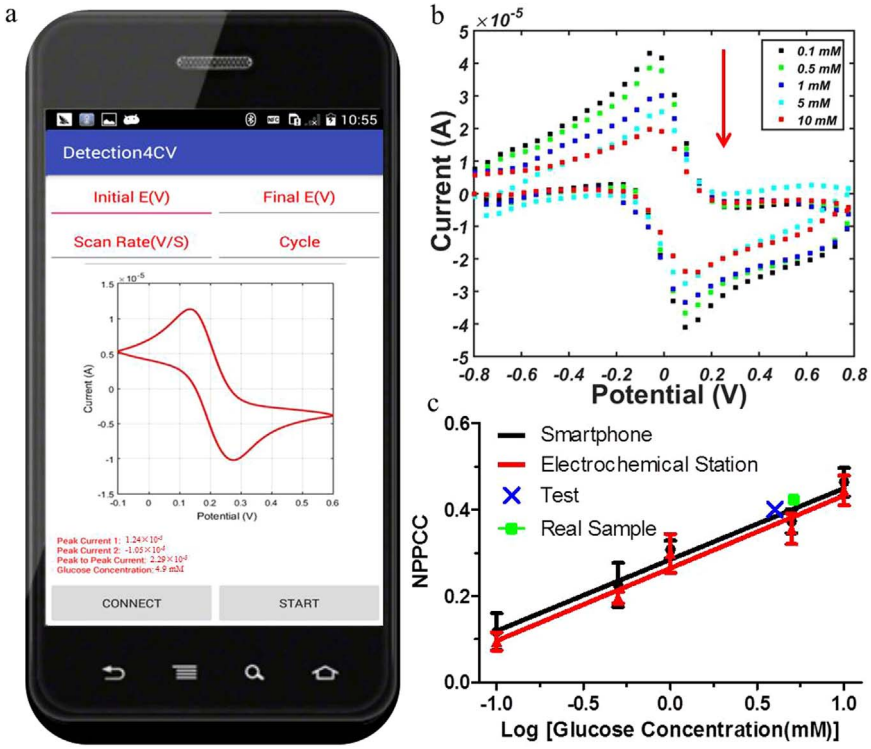

Fig. 4. Glucose detection using the smartphone-based CV system. (a) Real-time CV detection on the smartphone screen. The top half plots real-time CV curve, while the bottom half gives information about peak current, peak-to-peak currents and glucose concentrations. (b) The diagram of CV measurement using the system for glucose of different concentrations. (c) The dose-dependent curve of the system (black circular) and the commercial electrochemical workstation (red triangle). The NPPCC response to prepared glucose solution at 4×10^{-3} M was shown as blue cross. The real sample of blood glucose was shown as green square. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

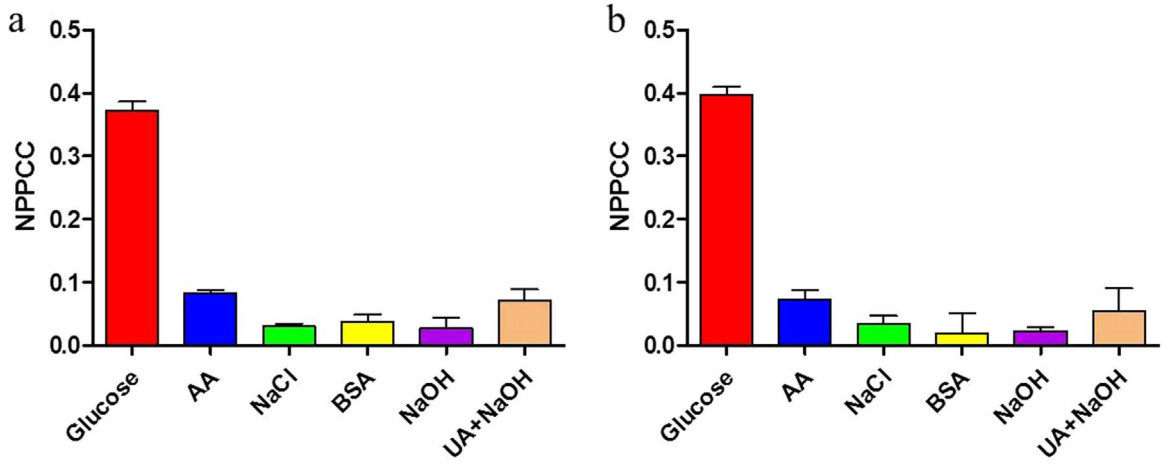

Fig. 5. Statistic for selective testing for glucose (a) NPPCC responses of different chemicals were detected by the smartphone-based system. The concentration of UA, AA, NaCl, NaOH and BSA were all fixed on 5 mM (mean ± SD, n = 5). (b) NPPCC responses to different chemicals in human serum with a dose of 5 mM.

were used to verify the selectivity of the system for glucose detection. These chemicals include some substance of blood, such as UA, AA, protein and the common electrolyte, which usually exists in blood. As the representative of protein, BSA was used to simulate the influence of bio-macromolecule to the glucose detection. NaCl and NaOH were detected to simulate the influence of inorganic salt to the detection. UA and AA were main substances of metabolite to affect the glucose detection. The NPPCC responses of these chemicals were acquired with the same method as the way of glucose detection. Fig. 5a showed the NPPCC responses of these chemicals with a concentration of 5×10^{-3} M. It was clearly exhibited that the NPPCC by glucose was conspicuously larger than that by electrolyte, protein, and metabolite. The largest influence was from AA, but the NPPCC of AA was only quarter of glucose's. These results indicated that the sensitivity and selectivity of the electrodes came from the reaction of rGO/APBA and glucose. To simulate the real samples, these chemicals were dissolved into human serum. Fig. 5b showed the NPPCC responses of these chemicals in human serum. All the same, the largest response was also from AA, but the NPPCC of AA was much small than the NPPCC of glucose. For further testing, all the interferent was equally mixed in human serum. As shown in Fig. S5 (in the Supplement material), the effect of interferent was small. These results demonstrated that the electrodes could specifically recognize glucose in human serum. The results could be also used to demonstrate the validation of the method. Hence, with the NPPCC the smartphone-based CV system could be performed for glucose detection in human serum.

In the past few years, lots of portable devices have been developed for different applications such as explosive analysis, water monitoring and biosensor (Nemiroski et al., 2014; Zhang et al., 2015a; Wang et al., 2015, 2017; Quesada-González and Merkoçi, 2017). Smartphone-based devices have such advantages as its low price, miniaturization, easy operation as well as obtaining the accurate and real-time data. CV not only can be used for detection and characterization, but also can be applied to modify the portable sensors. Therefore, CV as a widely used electrochemical technique can be performed for the miniaturized detection devices. The characterization, modification and detection were completely performed by the smartphone-based system. The system could be used to modify the electrodes near the place when the detection was needed, so that the sensors can remain active for portable detection. It obviously proved that the system was equipped with strong functions for detection.

Moreover, smartphone-based devices that have been configured with miniaturized sensors and circuits of devices were being developed into integration, which makes more requirements for mobility storage, data process and display devices. Smartphone, with the powerful function and most widely used equipment all over the world, was an excellent selection to control measurements, analyze and process data, display the results and plot graphs (Nemiroski et al., 2014; Sun et al., 2014; Zhang and Liu, 2016). By connecting to the Internet, the results of detection could be transferred and stored to the cloud server by 3G/4G. The continuous results were the significant basis for future analysis.

4. Conclusion

In summary, a portable CV system based on smartphone was developed and a convenient method was used for electrodes modification and detection. By combining SPE, hand-held CV detector, and smartphone together, the portable system could realize CV detection, electrodes modification and characterization. Taking glucose detection as a practical application, the system showed linear and specific responses to glucose with an rGO/APBA modified SPE as the sensor. As a result, the smartphone-based CV system was successfully constructed and performed for portable detection with a simple method of electrode modification. All of these suggest that the system can offer a detection platform for point of care testing.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (Grant No. 31671007) and the Collaborative Innovation Center of Traditional Chinese Medicine Health Management of Fujian province of China.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.bios.2017.07.027.

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