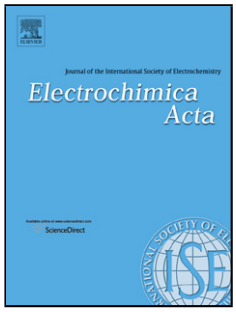

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Electrochemically roughened nanoporous platinum electrodes for non-enzymatic glucose sensors

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A sensitive and reliable non-enzymatic electrochemical blood-glucose sensor has been fabricated using a nanoporous platinum sensing interface prepared by successive electrochemical formation and reduction of thick hydrous platinum oxide layers. The fabricated nanoporous platinum electrode exhibits sensitive amperometric responses to glucose in phosphate buffered saline (PBS) as well as ascorbic acid and uric acid. At an applied electrode potential of + 0.4 V (vs Ag|AgCl|satd. KCl) the oxidation current is non-linear with glucose concentration following a Langmuir-like relation, with $r^2 = 0.994$. The sensitivity over a linear range of 1 – 10 mM is (5.67 ± 0.18) μA cm^{-2} mM^{-1} with a detection limit of 0.8 mM. The lower limit of quantitation, at which the relative standard uncertainty is 10 %, is 2.3 mM. The sensor measured glucose concentration in human blood samples, showing good agreement with a commercial sensor. The results obtained make the proposed sensor a promising device for practical glucose monitoring in human blood.

Keywords: glucose sensor; nanoporous platinum; electrocatalysis; calibration; Langmuir equation

1 Introduction

In recent years, glucose biosensing has drawn considerable attention not only by the well-known rising demands for advanced blood sugar measurement devices for clinical diabetic diagnostics but also for its application in wastewater treatment, the food industry and biotechnology [1-3]. Electrochemical biosensors based on immobilised glucose oxidase (GOx) are widely used for the measurement of glucose concentration due to their good selectivity and high sensitivity [4-6]. However, the lack of stability due to relatively complicated enzyme immobilisation, and enzyme activity sensitive to pH, temperature and humidity challenges the practical application of such sensors [7, 8]. To overcome these intrinsic problems of enzyme-based glucose sensors, there has been much effort to use inert metals as electrocatalysts for direct glucose oxidation without an enzyme catalyst. Platinum is the most frequently investigated material due to its high catalytic activity towards glucose oxidation. However, smooth platinum showed low sensitivity and poor selectivity for non-enzymatic glucose sensors [9, 10].

Recently, non-enzymatic glucose biosensors with nanoporous electrodes have demonstrated promising performance due to their high surface area and high electrocatalytic efficiency [11-14]. The kinetically-controlled electro-oxidation of glucose is sensitive to nanoscopic surface area rather than geometric area [13-16], as it would be if the reaction were diffusion controlled. Therefore, nanostructured platinum with large specific surface area favours kinetic control and a greater sensitivity can be obtained in the measurement of glucose. Furthermore, because the electro-oxidation of the interfering electroactive species ascorbic acid and uric acid are diffusion controlled and therefore depend on the geometric surface area [13], nanostructured electrode with a greater sensitivity for glucose can also obtain better selectivity.

Nanoporous platinum structures can be fabricated by several techniques including platinum particle assembly from aqueous solutions, the hydrothermal growth of platinum films, electrochemical deposition of platinum on a template and electrochemical dealloying [12, 13, 17, 18]. Ideally, an efficient approach to synthesise platinum nanostructures should be simple and free of surface contaminants. However, the synthesis of platinum nanostructures by the above-mentioned procedures involve complicated, multiple processes and are difficult to scale up [12, 19]. Accordingly, a simple and effective method to produce platinum nanostructure is desired to promote practical application.

Electrochemical roughening is a simple process to fabricate nanoporous platinum structures by successive formation and reduction of thick hydrous platinum oxide layers [20]. The porosity of the electrochemically roughened nanoporous platinum film can be controlled by varying the oxidation-reduction cycle duration, wave-frequency (or sweep rate) and the switching potential limits [20, 21]. This two-step electrochemical method of fabricating platinum nanostructures has attracted increasing attention for its simplicity, reproducibility and durability of the synthesised nanostructures. The method is relatively simple and fast compare to most methods where platinum nanostructures are commonly fabricated through reducing platinum precursor salts with the excessive use of organic reducing agents and surfactants at relatively high temperatures and usually involve multistep operation [11-14, 22]. Also, the nanostructures produced by this method adhere strongly to the electrode as they are formed from an existing surface; hence have greater integrity than the deposited platinum nanoparticles [23]. Although bulk platinum may be expensive, the nanostructures produced by this method can enhance the surface area several fold. This allows the amount of platinum to be reduced and still produce nanostructures with enhanced surface area for practical applications.

This electrochemical method of producing nanostructures has previously demonstrated the applications for neural stimulation and water oxidation [23, 24]. In this paper, we show that a nanoporous platinum structure prepared by electrochemical roughening has sufficient sensitivity and selectivity for non-

enzymatic measurement of blood glucose concentration. We also develop a non-linear calibration equation based on a model of oxidative adsorption of intermediate species.

2 Experimental

2.1 Materials

L-ascorbic acid and uric acid were obtained from Sigma Aldrich (Australia). All other chemicals: D-glucose, potassium phosphate dibasic, potassium phosphate monobasic, sodium chloride, potassium chloride and sulfuric acid were of analytical grade and were used as received from commercial sources. Solutions were prepared with Milli-Q water (18 MΩ cm^{-1}, Millipore, Sydney, Australia).

All electrochemical experiments were performed using a CHI 440C potentiostat (CH Instruments, USA). A conventional three-electrode system involving a 2 mm diameter platinum disk (purity ≥99.99%), platinum wire, and Ag|Ag_2SO_4|satd.K_2SO_4 or Ag|AgCl|satd. KCl were employed as the working, counter and reference electrodes respectively. The reference electrode for electrochemical roughening was constructed with Ag|Ag_2SO_4|satd.K_2SO_4, rather than Ag|AgCl|satd. KCl to avoid possible oxidation of leaked chloride, which adversely affects oxide formation. The Ag|Ag_2SO_4|satd. K_2SO_4 reference was calibrated against Ag|AgCl|satd. KCl, which gave a voltage of +0.25 V in 0.5 M H_2SO_4 solution. To facilitate comparison with other studies all potentials reported herein are referenced to Ag|AgCl|satd. KCl. The surface structure of electrochemically-roughened platinum electrodes was characterised with a scanning electron microscope (FEI Nova NanoSEM 230 FESEM).

2.2 Electrochemical roughening

Before use the platinum working electrode was mechanically polished with Carbimet paper (Buehler, USA) and alumina down to 0.05 μm to obtain a mirror finish. The electrode was further cleaned electrochemically in 0.5 M sulphuric acid solution by repeatedly cycling the electrode between –0.4 and 1.0 V at 0.5 V s^{-1} until there was no change in the cyclic voltammogram. The platinum surface was

electrochemically roughened using a repetitive square wave potential cycle [25]. A square wave of 1 kHz with lower and upper potentials of −0.4 V and +2.4 V vs $Ag|Ag_2SO_4|sat\ K_2SO_4$ was applied to the electrode in 0.5 M H_2SO_4 solution for 3 to 10 minutes. The electrode was then maintained at –0.4 V for at least 30 minutes for complete reduction of surface oxide. After roughening, the electrode was again cleaned electrochemically in a fresh 0.5 M H_2SO_4 solution until reproducible cyclic voltammograms of platinum were obtained. Surface roughness (f_R) was calculated as:

$$f_R = \frac{Q_H}{\sigma_{H,ideal} A_{geom}} \quad (1)$$

where Q_H is the measured charge of hydrogen adsorption on the surface, A_{geom} is the geometric area of the electrode, and $\sigma_{H,ideal}$ is the surface density of charge associated with monolayer adsorption of hydrogen, which has been reported as 210 μC cm^{-2} [26].

2.3 Measurement of glucose concentration

Amperometric measurements of glucose concentration were carried out in stirred, deaerated 0.1 M phosphate buffered saline (PBS) containing 0.15 M NaCl, at –0.2 V and +0.4 V. Steady-state currents at each glucose concentration were recorded. Current density was calculated by dividing the measured current by the geometric surface area. All solutions were deaerated with ultrapure argon (99.99%) before measurements, and argon was passed over the top of the solution during the experiments. All measurements were conducted at room temperature (25 ± 2 °C). The platinum electrode was electrochemically cleaned before each measurement.

2.4 Calibration equation

Steady state current/ glucose concentration data were fitted to the Langmuir-like equation (7) using the non-linear fitting routine Solver in Microsoft Excel (Office 2010), running on a Windows 10 computer. Standard errors and covariance matrix of the coefficients were obtained using ‘Solver Aid’ by De Levie

[27]. Results were checked by fitting with nlinfit (Matlab 2016a). The linear region between 1 – 10 mM was fitted in Excel with measurement uncertainty obtained using the method described in [28].

3 Results and discussion

3.1 Characterisation of electrochemically roughened platinum

The platinum surface was successfully roughened by repeated oxidation and reduction cycling at high frequency voltage pulses, which facilitated the exchange of surface oxygen with the bulk platinum atoms. This process exposes the inner layers of platinum to further oxidation, and complete reduction of the oxide results in an irregular arrangement of platinum atoms creating nanostructured surfaces [21]. Figure 1 shows representative SEM images of nanoscale surface morphology of the smooth and the electrochemically roughened platinum surfaces. As is evident from the images, (Figure 1b) the roughened surface has uniformly distributed pyramidal nanostructures with particle sizes in the range 40 to 50 nm.

Figure 1 about here.

Cyclic voltammograms of smooth and roughened platinum electrodes in 0.5 M H_2SO_4 are shown in Figure 2. The voltammogram of a roughened platinum electrode has nearly identical peak shapes and positions compared to a smooth electrode, an indication of a polycrystalline nanosurface. The current at a roughened electrode, however, is more than two orders of magnitude greater than at a smooth electrode. The roughness factor (f_R), as estimated from the ratio of the surface area determined from the H-adatom monolayer charge to the geometric surface area, for the 3 min-roughened platinum electrode (f_R = 330) is remarkably greater than that measured for a smooth platinum electrode (f_R = 1.8). The highly dispersed platinum nanostructures with enhanced surface area improve the sensitivity for glucose detection, as well as showing a better selectivity against interfering species.

Figure 2 about here

3.2 Electrocatalytic oxidation of glucose in phosphate buffered saline

Electrocatalytic activity of the electrochemically-roughened platinum electrode towards glucose oxidation in PBS was studied by cyclic voltammetry. The experiment was performed in PBS containing 0.15 M NaCl to provide equivalent conditions to physiological environments. It is noted that chloride concentration (0.1 M) has been reported to supresses glucose adsorption and decreases the oxidation rate on platinum [22].

Figure 3 presents voltammograms of smooth and roughened platinum electrodes in 0.1 M PBS (pH 7.4) in the presence and absence of 5 mM glucose. The roughened platinum in PBS showed two distinct Pt oxide reduction peaks (~ –0.15 and ~ +2.5 V) (Figure 3b) as compared to a single reduction peak (~ +0.05 V) on the smooth surface (Figure 3a). The reason for the splitting of Pt oxide reduction into two distinct peaks on highly roughened surface has been attributed to the reduction of $PtO_{ad}/Pt(OH)_{ad}$, which depletes H^+ of the solution near the electrode surface shifting the reduction potential towards more negative values [29, 30]. As shown in Figure 3a, the smooth platinum electrode showed negligible response to glucose. Figure 3b shows the CVs of roughened platinum electrode (f_R = 552) in the presence and absence of glucose. In the presence of glucose, the CV (red curve) shows intricate electrochemical behaviour. Oxidative adsorption of hydrogen molecules gives the anodic peak at ~ –0.58 V. The decrease in current of this hydrogen adsorption peak in glucose solutions is due to the competing chemisorption of glucose [31]. In addition in glucose solution, two oxidation peaks appear at ~ –0.3 V and ~ +0.22 V, which can be attributed to the adsorption and partial oxidation of glucose and then further oxidation of adsorbed intermediates [31, 32]. Chemisorption of glucose is known to be accompanied by dehydrogenation [31]. The electrocatalytic performance of the roughened platinum towards glucose oxidation can be attributed to the significantly increased electroactive surface area and catalytically-active sites of the nanostructured platinum surface.

Figure 3 about here

Figure 4 shows linear sweep voltammogram for glucose adsorption and oxidation on platinum electrodes with different f_R. Current density increased with increasing f_R, an indication that the electro-oxidation of glucose on platinum electrode is kinetically controlled. The platinum electrode with f_R = 971, having the greatest current for electro–oxidation of glucose, was used for subsequent analysis.

Figure 4 about here

3.3 Glucose oxidation current at the roughened platinum electrode

The linear sweep voltammogram for 5 mM glucose in PBS (Figure 4) shows two current peaks at ~ –0.2 V and ~ +0.4 V at a roughened platinum electrode (f_R = 971) which are associated with oxidative adsorption and oxidation of glucose respectively. Each peak is a candidate for calibration of a glucose sensor. Figure 5 compares the current at –0.2 V and +0.4 V with successive 1.0 mM additions of glucose to a stirred PBS solution. In both cases, currents increase rapidly after each addition of glucose to the stirred solution. However, at –0.2 V the steady state current plateaus after about 4 mM, whereas the current at +0.4 V increased with the incremental glucose concentration. At –0.2 V, the adsorbed glucose is not completely oxidised resulting in the formation of species on the electrode surface [33] which accumulate, blocking active sites and resulting in decreased current and the observed plateau [22, 34]. The increasing responses to higher glucose concentrations at electrode potential +0.4 V indicates glucose and its intermediates can be continuously oxidised on the roughened platinum surface. Therefore, an electrode potential of +0.4 V was selected for the amperometric measurement of glucose concentration.

Figure 5 about here

The performance of the electrochemically roughened platinum sensor to serial additions of glucose between 1 and 20 mM was investigated by measuring current at an applied potential of +0.4 V in stirred PBS. The calibration curve is shown in Figure 6. The current against concentration graph is clearly

curved, due to the two-step reaction with oxidative adsorption of intermediates from the electrocatalytic oxidation of glucose, followed by their oxidation [22, 34].

Figure 6 about here

Previous authors have constructed linear calibration relations at arbitrary high and low concentrations [22, 34-36] without regard to the likely form of the current concentration relationship. It is possible to fit the whole curve by a single, non-linear, equation that can be derived from a simple model of oxidative adsorption (corresponding to the reaction at about –0.2 V) followed by oxidation of the adsorbed species at +0.4 V.

$$C_6H_{12}O_6 + z_1/4\ H_2O \xrightarrow{Pt} [Ads] + z_1/4\ CO_2 + z_1\ e + z_1\ H^+ \quad (2)$$

$$[Ads] + z_2/4\ H_2O \rightarrow z_2/4\ CO_2 + z_2\ e + z_2\ H^+ \quad (3)$$

Assuming that ultimately glucose is completely oxidized to carbon dioxide then $z_1 + z_2 = 24$, and the overall oxidation is

$$C_6H_{12}O_6 + 6\ H_2O \rightarrow 6\ CO_2 + 24\ e + 24\ H^+ \quad (4)$$

The adsorbed intermediate [Ads] of unknown structure, is the result of partial oxidation of glucose and will occupy an unknown number of platinum sites. The assumption that reaction (2) is first order in glucose concentration [Glu] and first order in coverage of available platinum sites, leads to an analytical solution for the steady state current.

The rate of formation of the adsorbed species is

$$\frac{d\Gamma_{Ads}}{dt} = k_1[Glu]\Gamma_{Pt} - k_2\Gamma_{Ads} \quad (5)$$

where Γ_{Ads} is the surface concentration of the adsorbed species, Γ_{Pt} is the surface concentration of free platinum sites, [Glu] is the solution concentration of glucose and k_1 and k_2 are electrochemical rate constants, which are constant at constant potential and temperature. The total surface concentration of

platinum is constant, and if the oxidatively-adsorbed glucose intermediate occupies *n* sites, $\Gamma_{\text{Total}} = n\Gamma_{\text{Ads}} + \Gamma_{\text{Pt}}$, and at steady state $\mathrm{d}\Gamma_{\text{Ads}}/\mathrm{d}t = 0$.

The measured current is the sum of oxidation currents of the reactions in (2) and (3).

$$I = I_1 + I_2 = z_1 F k_1 [\text{Glu}]\Gamma_{\text{Pt}} + z_2 F k_2 \Gamma_{\text{Ads}} \tag{6}$$

where *F* is the Faraday constant. Algebra (See Supplementary Information) reduces the above equations to

$$I = \frac{aq[\text{Glu}]}{1 + q[\text{Glu}]} \tag{7}$$

where *a* and *q* are constants of unknown values, $a = (z_1 + z_2) F \Gamma_{\text{Total}} \frac{k_2}{n}$, $q = \frac{n k_1}{k_2}$.

Fitting the data of Figure 6, assuming constant measurement uncertainty across the concentration range, gives a = (154 ± 19) μA cm^{-2}, q = (0.057 ± 0.012) mM^{-1} and r^2 = 0.994. Note that it is not possible to obtain independent values of any of the electrochemical parameters. The inverse calibration relation is therefore

$$[\text{Glu}] = \frac{I}{q(a - I)} \tag{8}$$

Eqn. 8 may be used for calibration over the full range of concentrations of glucose, estimating uncertainty, including correlations between *a* and *q*, according to the Guide to the Expression of Uncertainty in Measurement (GUM) [37]. However for analysis of glucose in the concentration range of human blood, Eqn. 7 is linear for q[Glu] << 1, and a reasonably linear relationship between *I* and [Glu] can be established between 1 and 10 mM (Fig 6): I = (3.51 ± 1.04) + (5.67 ± 0.18) [Glu] μA/cm^2 with standard error of the regression 1.5 μA. The limit of detection (LOD) was estimated to be 0.8 mM (= $3s_{y/x}/b$, where $s_{y/x}$ is the root mean square error of the regression and *b* is the slope of the linear relation) and the lower limit of quantitation (LLOQ) is 2.3 mM when the relative standard uncertainty is 10 %. The excellent electrocatalytic activity of the electrochemically roughened platinum electrode can

be attributed to the highly ordered platinum nanostructures which increase the specific surface area and thus provide more active sites for glucose oxidation.

3.4 Effects of interferences on the measurement of glucose

One of the challenges in non-enzymatic glucose detection is interfering currents caused by oxidation of endogenous substances such as uric acid and ascorbic acid. Although the normal physiological level of glucose (3 – 8 mM) is much greater than those of the interfering species of ascorbic acid (typically ~ 0.1 mM) and uric acid (typically ~ 0.02 mM) [13, 15, 38], the faster electron transfer rates of these interfering species can generate oxidation currents of comparable magnitude to that of glucose [14, 39]. To evaluate the effect of the interfering species towards the measurement of glucose concentration at the operating potential of + 0.4 V, chronoamperometric currents of an electrochemically roughened platinum (f_R = 971) electrode in 0.1M PBS with successive addition of 1 mM glucose, 0.02 mM uric acid and 0.1 mM ascorbic acid is presented in Figure 7. The concentrations of uric acid and ascorbic acid used in this study are based on typical physiological levels. It is seen that additions of uric acid and ascorbic acid have negligible effect on the glucose oxidation current. This result demonstrates that the roughened platinum electrode with large effective surface area selectively favours the kinetically-controlled electro-oxidation of glucose over the oxidation of the interfering species. Thus roughened platinum can be used for specific detection of glucose in the blood.

Figure 7 about here

3.5 Analysis of real samples

The practicability of the electrochemically-roughened platinum based non-enzymatic glucose (ERP-NEG) sensor was demonstrated by measuring glucose concentration in human blood samples. Currents were measured at + 0.4 V with the addition of 0.2 ml human blood in 8 ml of PBS solution (pH 7.4). For comparison, the glucose level in the blood samples was also obtained using a commercial enzymatic

glucose (CEG) sensor (WaveSense Presto Blood Glucose Meter). Results from measurements on four real samples using the proposed ERP-NEG sensor are in agreement with those obtained using the commercial CEG sensor (see Table 1). Each measurement was made in triplicate. The mean repeatability standard deviation of the commercial instrument was 0.03 mM, and of the ERP-NEG 0.15 mM. Although not a complete validation, these results demonstrate that the fabricated non-enzymatic glucose sensor could be used for practical determination of glucose in real samples with sufficient accuracy and precision.

Table 1 about here

4 Conclusions

We have demonstrated an amperometric non-enzyme glucose sensor using an electrochemical-roughened nanoporous platinum electrode. The nanoporous platinum electrode, prepared by facile electrochemical roughening, exhibits sensitive and selective glucose oxidation currents in PBS and interfering species uric acid and ascorbic acid. The proposed sensor provided accurate glucose measurement in real human blood samples. High electrocatalytic surface area and unique platinum nanostructures are considered to be key factors attributed to the performance of the sensor. The ease of fabrication, fast response and high sensitivity and selectivity make the proposed sensor a promising device for practical glucose monitoring. Non-linear calibration to a realistic model of oxidative adsorption allows estimation of coverage of adsorbed species and relative rates of oxidation of glucose and adsorbed intermediate.

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Figure captions

Figure 1 SEM images of (a) smooth (f_R = 1.8) and (b) electrochemically roughened (f_R = 330) platinum electrodes.

Figure 2 Cyclic voltammograms of smooth (black curve) and 3 min-roughened (blue curve) porous platinum electrodes in 0.5 M H_2SO_4 solution. Scan rate: 100 mV s^{-1}

Figure 3 Cyclic voltammograms of (a) smooth and (b) roughened (f_R = 552) platinum electrodes in 0.1 M PBS (pH 7.4) in the presence (red curve) and absence (black curve) of 5 mM glucose at a potential scan rate of 100 mV s^{-1}.

Figure 4 Linear-sweep voltammograms (sweep rate 10 mV s^{-1}) of electrochemically roughened platinum electrodes with different f_R measured in 0.1 M PBS (pH 7.4) containing 10 mM glucose.

Figure 5 Current at an electrochemically-roughened platinum electrode (f_R = 971) in 0.1 M PBS (pH 7.4) with successive additions of 1 mM glucose. Black line: E = –0.2 V, red line E = +0.4 V.

Figure 6 Current density at an electrochemically-roughened platinum electrode (f_R = 971) as a function of glucose concentration. Filled circles are measured data. Solid line is fit to equation (7) and dashed line is fit to linearised form of equation (7) for [Glu] = 1 – 10 mM . Open squares (right hand axis) show the fractional coverage of oxidatively-adsorbed glucose.

Figure 7 Current at a roughened platinum (f_R = 971) electrode in 0.1 M PBS with successive additions of 1 mM glucose (Glu), 0.02 mM uric acid (UA) and 0.1 mM ascorbic acid (AA), at an applied potential of +0.4 V.

Figures

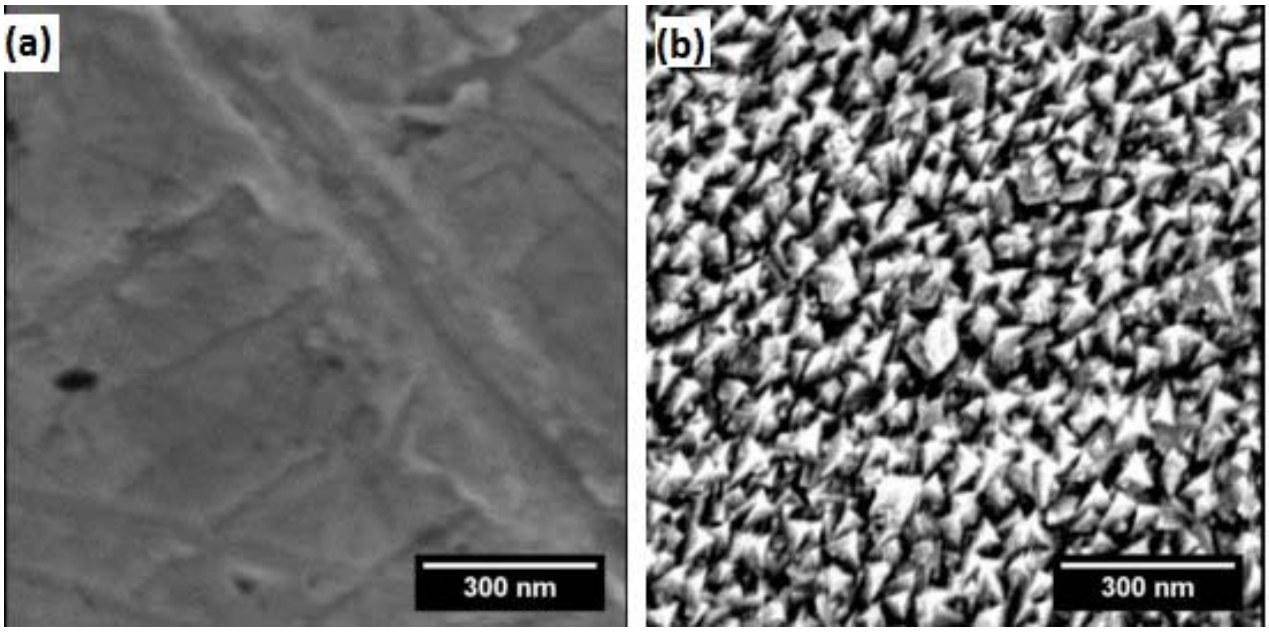

Fig. 1

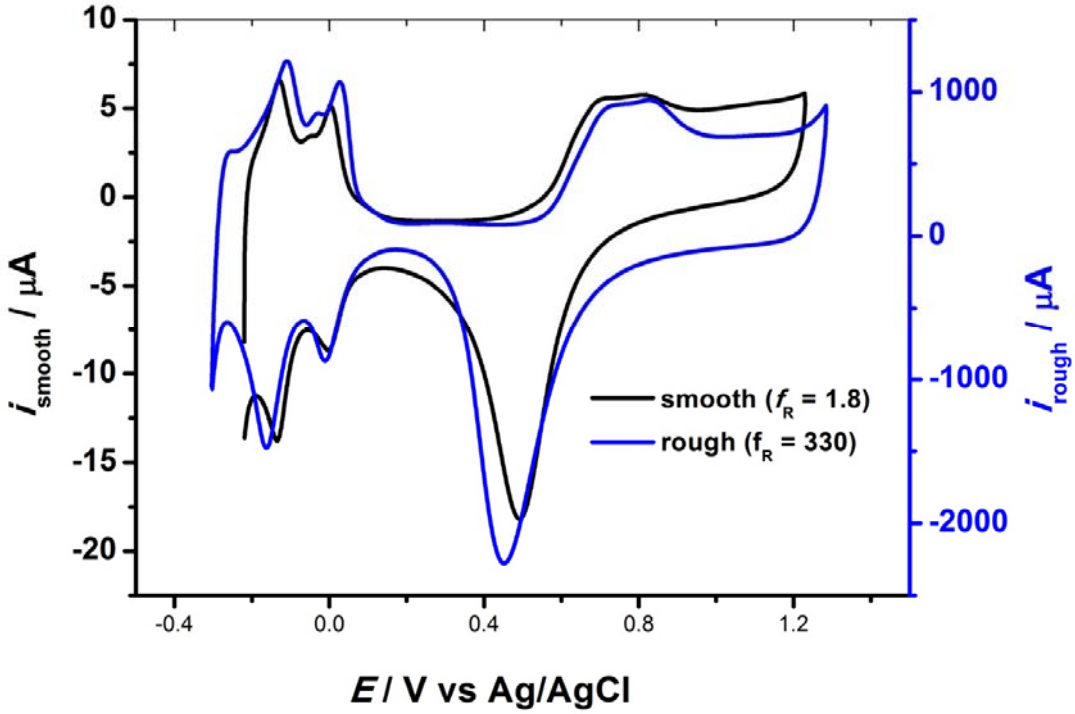

Fig 2

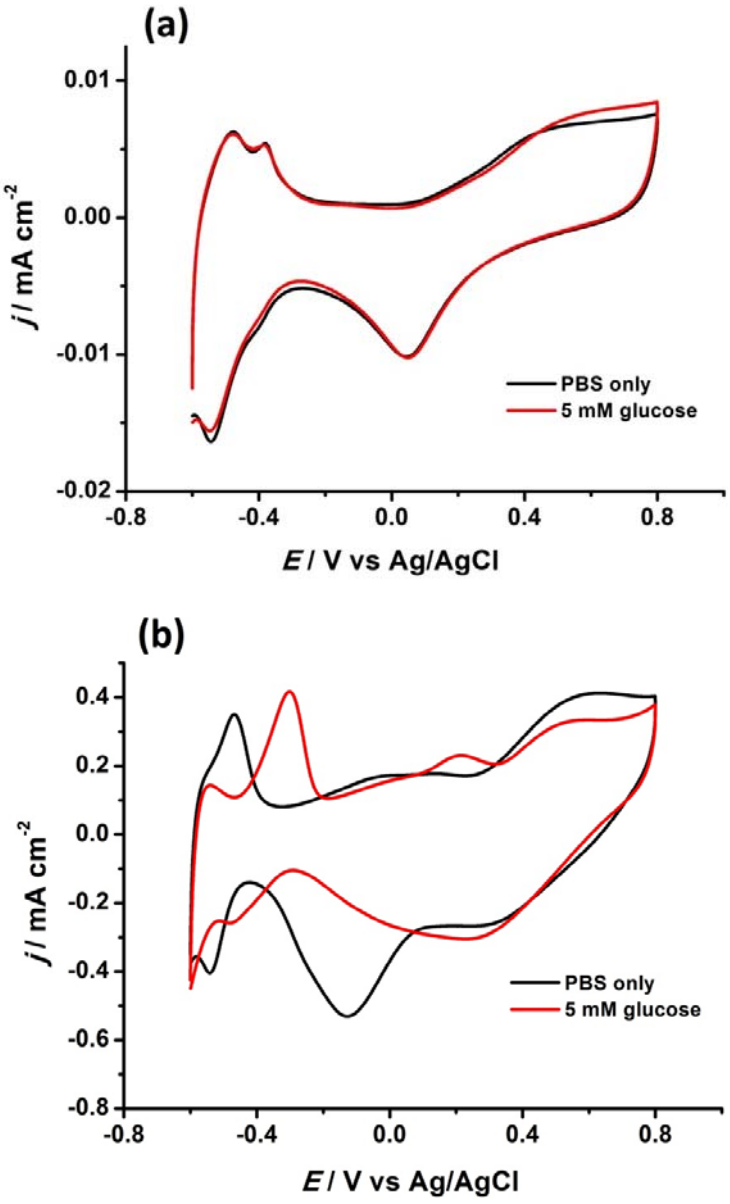

Fig. 3

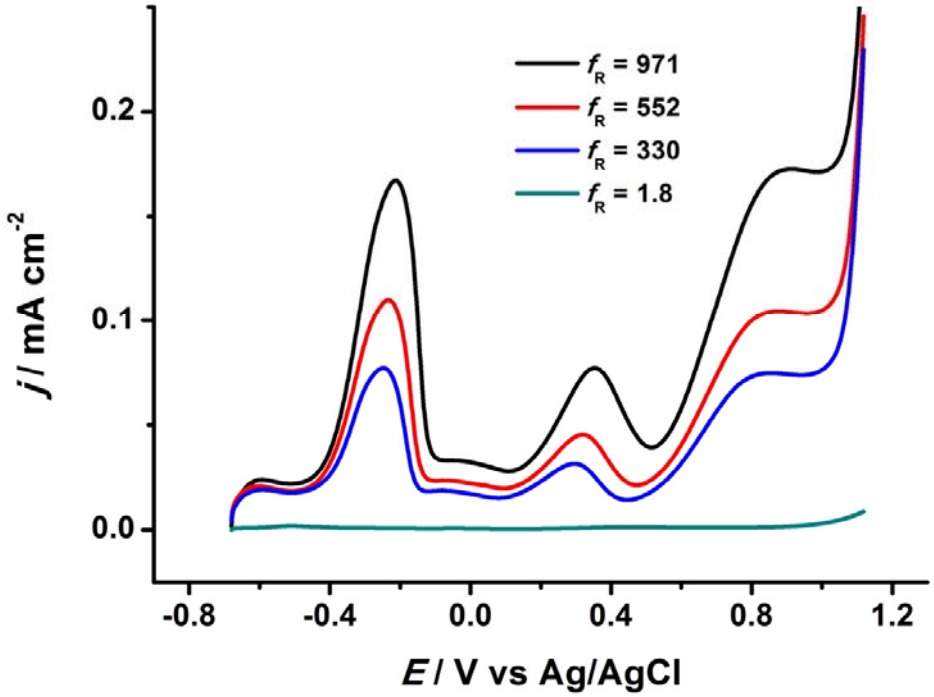

Fig. 4

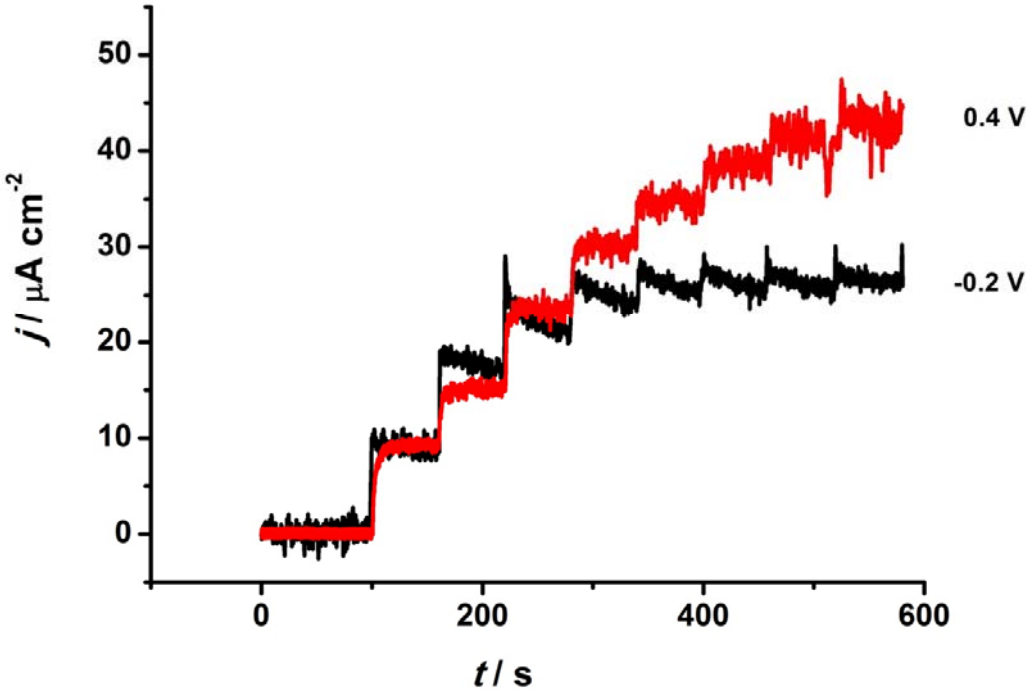

Fig. 5

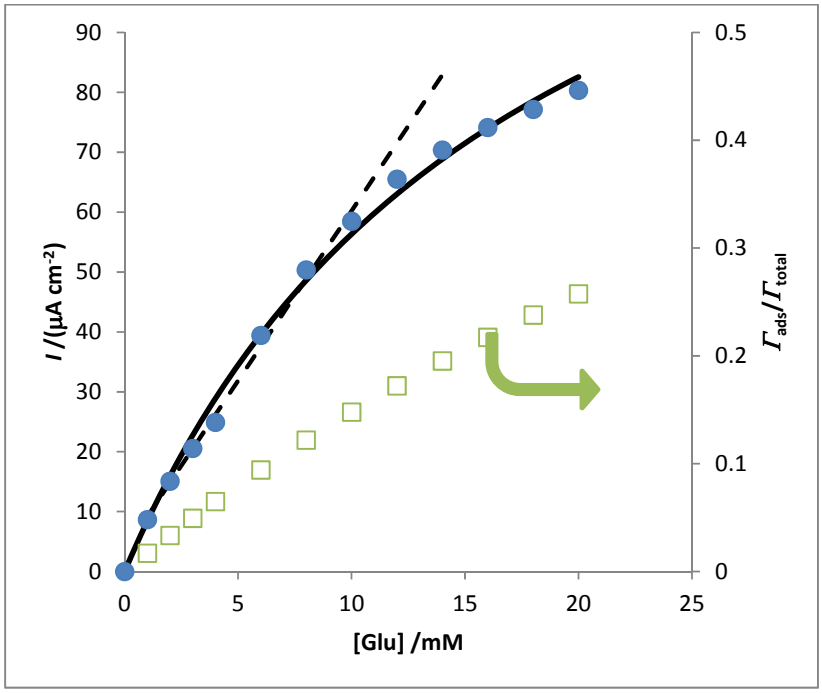

Fig. 6

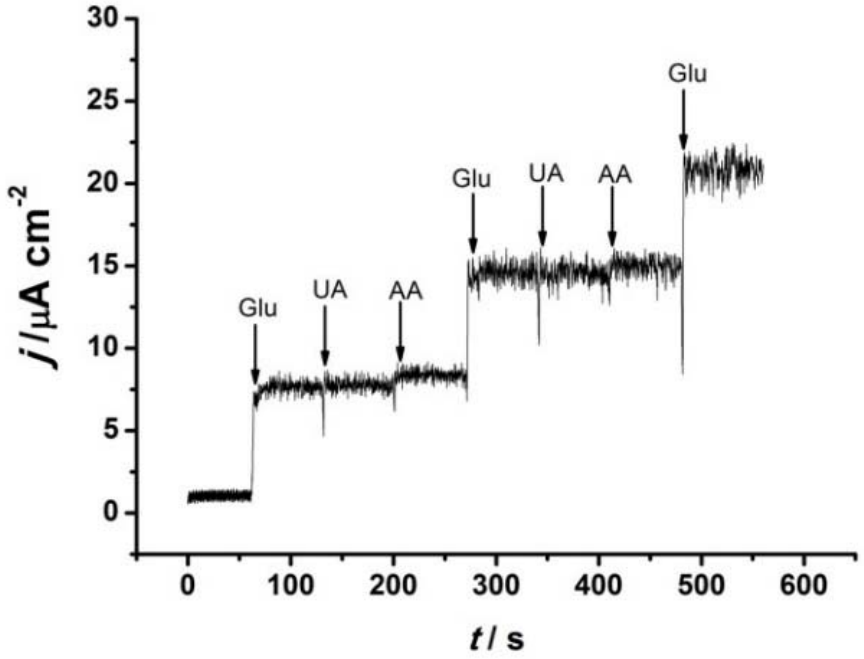

Fig. 7

Table 1 Determination of glucose in human blood samples. CEG (commercial) sensor: reference result, ERP-NEG sensor: test result.

Sample	CEG sensor /mM	ERP-NEG sensor ± 95 % probability interval /mM
1	5.4	5.6 ± 0.6
2	6.3	6.5 ± 0.5
3	6.1	6.4 ± 0.5
4	6.4	6.2 ± 0.5