



Electrochemically roughened nanoporous platinum electrodes for non-enzymatic glucose sensors



Alexander Weremfo¹, Sui Tung Clara Fong, Asim Khan, David B. Hibbert*, Chuan Zhao*

School of Chemistry, UNSW Australia, Sydney, NSW, 2052, Australia

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ABSTRACT

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 $(5.67 \pm 0.18) \mu\text{A cm}^{-2} \text{mM}^{-1}$ 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.

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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 kinetically-controlled glucose oxidation and a greater sensitivity can be obtained in the measurement of glucose. Furthermore, because the electro-oxidation of interfering electroactive species such as ascorbic acid and uric acid are diffusion controlled and therefore depend on the geometric surface area [13], nanostructured electrodes 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, 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

* Corresponding authors.

E-mail addresses: b.hibbert@unsw.edu.au (D.B. Hibbert), chuan.zhao@unsw.edu.au (C. Zhao).

¹ Present address: Department of Biochemistry, University of Cape Coast, Cape Coast, Ghana.

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 compared to most methods where platinum nanostructures are fabricated through reducing platinum precursor salts with the excessive use of organic reducing agents and surfactants at relatively high temperatures and usually involve multistep operations [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 ($18\text{ M}\Omega\text{ cm}^{-1}$, 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 $\geq 99.99\%$), platinum wire, and Ag|Ag₂SO₄|satd.K₂SO₄ 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|Ag₂SO₄|satd.K₂SO₄, rather than Ag|AgCl|satd. KCl to avoid possible oxidation of leaked chloride, which adversely affects oxide formation. The Ag|Ag₂SO₄|satd. K₂SO₄ reference was calibrated against Ag|AgCl|satd. KCl, which gave a voltage of +0.25 V in 0.5 M H₂SO₄ 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 sulfuric 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 $+2.4\text{ V}$ vs Ag|Ag₂SO₄|sat K₂SO₄ was applied to the electrode in 0.5 M H₂SO₄ 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 H₂SO₄ solution until reproducible cyclic voltammograms of platinum were obtained. Surface roughness (f_R) was calculated as:

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

where Q_H is the measured charge of hydrogen adsorption on the surface, A_{geom} is the geometric area of the electrode, and $\sigma_{H,\text{ideal}}$ is the surface density of charge associated with monolayer adsorption of hydrogen, which has been reported as $210\ \mu\text{C cm}^{-2}$ [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 $+0.4\text{ V}$. 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 ($25 \pm 2\text{ }^\circ\text{C}$). 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]. Fig. 1 shows representative SEM images of nanoscale surface morphology of the smooth and the electrochemically roughened platinum surfaces. As is evident from the images, (Fig. 1 b) the roughened surface has uniformly distributed pyramidal nanostructures with particle sizes in the range 40 to 50 nm.

Cyclic voltammograms of smooth and roughened platinum electrodes in 0.5 M H₂SO₄ are shown in Fig. 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

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