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Easy preparation of a reticular nickel film deposited on a barrel-plating gold electrode with a high catalytic activity towards the oxidation of glucose

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A reticular and porous Ni film was deposited on a barrel-plating gold electrode by an easy approach and was demonstrated to significantly enhance the catalytic activity towards glucose oxidation.

Our group recently reported a technique for fabricating disposable amperometric glucose sensor strips by inserting a gold barrel plating electrode (AuBPE) into an injection moulding base.[1–3] The primary function of barrel plating is to provide an economical way to electroplate manufactured parts that meet specific finishing requirements.[4,5] The amperometric sensors fabricated by such a method offers a relatively straightforward means to produce sensor strips on a mass scale and represents a useful platform for the development of a highly precise glucose sensor. In this work, we report the application of an AuBPE as a substrate to electrochemically deposit reticular nickel film (Ni–AuBPE) and the highly porous electrode was demonstrated for high performance electrocatalyic oxidation of glucose. Direct electrooxidation of glucose on different substrates such as platinum, gold, alloys and copper as well as electrodes modified with copper, nickel, bismuth, silver and mercury has been explored.[6–16] However, most of these electrodes suffer from the drawbacks of low sensitivity and surface poisoning from the adsorbed intermediates and chloride. Lately CuO and ZnO nanowires and ultrathin Ni film coated nanoporous gold were reported with highly enhanced sensitivity.[17–19] The high surface area architecture obviously plays the major role in achieving such a high performance.

In this study, the Ni–AuBPE was prepared easily by electrodeposition of Ni on an AuBPE at a deposition potential of 1.09 V (*vs.* Ag/AgCl) in a modified Watts bath (pH 7.1) containing 0.13 M $NiSO_4·6H_2O$, 0.13 M CH_3COONa and 0.1 M Na_2SO_4 with the amount of deposition charge controlled to 0.05 C.[20,21] The deposited film then underwent thermal treatment at 300 °C for 1 h in air. This low temperature annealing treatment was found to increase the electrode stability as well as the catalytic ability, as will be discussed later. The morphology of Ni film on both Ni–AuBPE and annealed Ni–AuBPE was first characterized by SEM and energy dispersive spectroscopy (EDS). As shown in Fig. 1, compared to a smooth surface of AuBPE, a highly porous and reticular Ni film was successfully deposited on AuBPE. The annealing treatment was found to retain the quasi-dendritic structure of the Ni film according to the SEM images. In effect, during the annealing procedure, the appearance of Ni–AuBPE was observed to change from olive-green into deep yellow, as illustrated in the inserted pictures. This would indicate a variation of Ni film after the thermal treatment. It is most likely the formation of Ni oxide film, as confirmed by the decrease of Ni/O ratio from 2.40 to 1.28 in EDS analysis.

The variation in reticular morphology of the Ni films supported on AuBPE substrate before/after annealing treatment can be revealed by AFM studies. As shown in Fig. 2, a much denser ripple was observed at the annealed Ni–AuBPE with the microscopic surface area increased by ~1.5 times after the annealing process (Fig. 2(c)). In other words, a higher surface area of Ni was generated during the annealing process.

The voltammetric behavior of the annealed Ni–AuBPE was further compared with those of the nickel barrel plating electrode (NiBPE) and AuBPE. Similar to the electrochemical characteristics of the activated NiBPE,[22] an oxidation peak at +0.53 V and a reduction peak at +0.38 V were observed for the annealed Ni–AuBPE. This can be attributed to multilayer formation and reduction of Ni oxide at the annealed Ni–AuBPE. Meanwhile, the observation of a much smaller peak response at the AuBPE, as shown in the inset of Fig. 3(a), was inconsistent with the SEM observation as the reticular Ni possesses a very high electroactive surface area. Most importantly the highly porous and reticular Ni film was found to increase its stability after a low-temperature annealing process of 300 °C for 1 h, as verified through the stability test by continuous cyclic voltammetric experiments. As shown in Fig. 3(b), the redox peak at Ni–AuBPE was found to decrease with consecutive CV scans between −0.2–0.8 V in 0.1 M NaOH solution. The annealed Ni–AuBPE, on the other hand, was highly stable to retain virtually the same peak signals for over 50 scans (Fig. 3(c)).

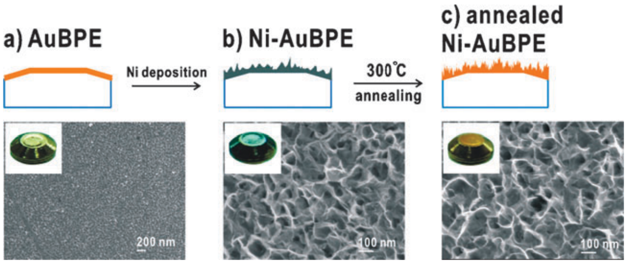

Fig. 1 Schematic of the fabrication process and the SEM images of (a) AuBPE, (b) Ni–AuBPE and (c) annealed Ni–AuBPE, respectively.

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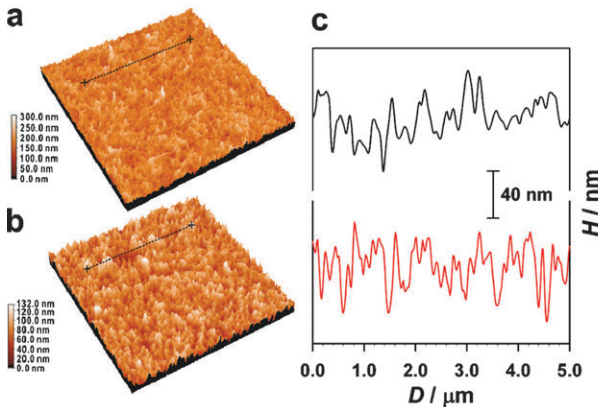

Fig. 2 AFM images of (a) Ni–AuBPE and (b) annealed Ni–AuBPE, respectively. (c) The surface outlines of Ni–AuBPE (black line) and annealed Ni–AuBPE (red line).

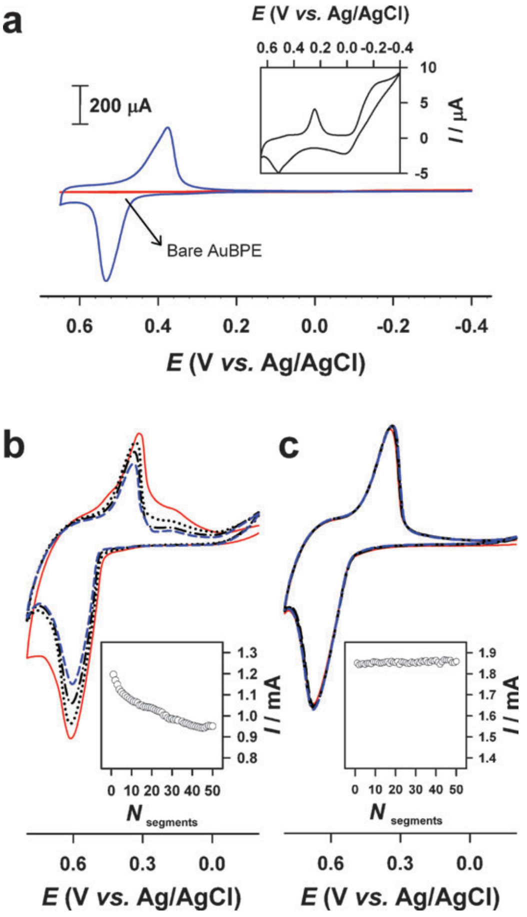

Fig. 3 (a) CVs recorded on an annealed Ni–AuBPE and a bare AuBPE, respectively, at a scan rate of 10 mV s^{-1} in 0.1 M NaOH solution. The inset in (a) is the enlarged CV at a bare AuBPE. Multiple-scan CVs of consecutive 50 cycles at (b) Ni–AuBPE and (c) annealed Ni–AuBPE; 1st cycle (solid line), 12th cycle (dotted line), 25th cycle (dash–dot line) and 50th cycle (short dash line) with inserted graphs showing the variation of Ni oxidation peak current during 1 to 50 cycles.

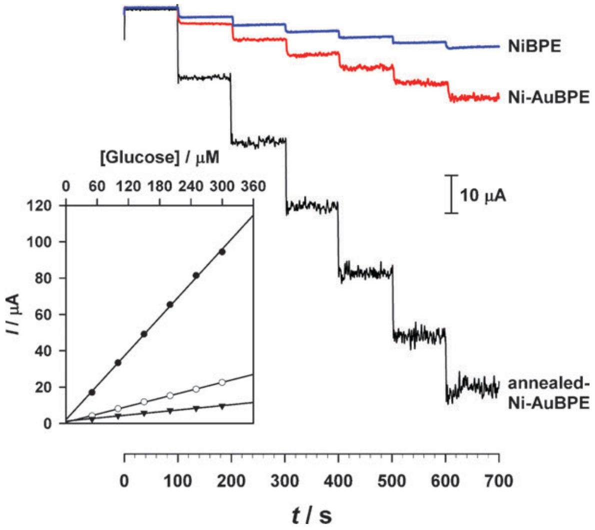

Fig. 4 The chronoamperometric experiments of the stepwise addition of 50 µM glucose at NiBPE, Ni–AuBPE and annealed Ni–AuBPE in 0.1 M NaOH. The inset shows linear calibration plots obtained at NiBPE (▼), Ni–AuBPE (○) and annealed Ni–AuBPE (●), respectively.

To further elucidate the catalytic activity of the annealed Ni–AuBPE, glucose was selected as a model analyte in this study. Note that the electrocatalytic oxidation of glucose by Ni electrode is well recognized.[9,22–24] Previously our group also reported amperometric determination of micromolar concentration sugars using a disposable NiBPE.[22] For comparison, the annealed Ni–AuBPE was evaluated by hydrodynamic chronoamperometric experiments for the determination of glucose. As can be seen in Fig. 4, a superior catalytic ability for the oxidizing of glucose was observed at the annealed Ni–AuBPE at a detection potential at +0.55 V *vs.* Ag/AgCl. The sensitivity was found to increase from 0.028 to 0.073 to 0.312 µA μM^{-1} for NiBPE, Ni–AuBPE and annealed Ni–AuBPE, respectively. Compared to the performance at NiBPE, the Ni–AuBPE with a three-dimensional structure enhanced the analytical response by ~2.6 times. The increase is even noticeable for the annealed Ni–AuBPE with an increase of ~11 times to that of NiBPE. Of course, this is related to the increase in surface area from the dendrite $Ni(OH)_2$/NiO(OH) architecture, as confirmed in AFM studies.

Our previous study also demonstrated the NiBPE to be useful for sugar detection by HPLC equipped with a specifically designed flow-through wall-jet cell with good reproducibility.[22] Since the Ni–AuBPE possesses exactly the same electrode structure as the NiBPE, it can allow us to detect glucose by flow-injection analysis (FIA).[25,26] The feature of FIA is advantageous for electroanalysis, as it allows reproducible detection at low analyte concentrations.[27] Furthermore, the performance characteristics for employing it as a glucose sensor were supplementary investigated in a FIA system. Flow-through electrodes are known to provide the most reproducible and stable hydrodynamics, which are necessary to investigate sensor response in a wide concentration range. FIA can also provide the advantages of high speed and simple technology for the purpose of routine sensing and can also be linked easily in HPLC system to extend its practicability. Under FIA conditions of detection potential = 0.55 V and flow rate = 500 µl min^{-1}, a linear range of up to 2 mM glucose (r^2 = 0.9998) was obtained. The detection limit (S/N = 3) was calculated as 31 nM in terms of seven determinations of 0.1 μM glucose. Note that this detection limit is much lower than those of 5 μM, 7 μM and 10 μM reported recently by the electrochemical systems of neodymium hexacyanoferrate nanoparticles glucose oxidase/chitosan modified glass carbon electrode,[28] self-assembling glucose oxidase on carbon nanotubes[29] and an osmium polymer-mediated carbon nanotube paste electrode, respectively.[30] Furthermore, our previous studies have successfully used the NiBPE to detect sugars, trivalent chromium (Cr^{III}) and tranexamic acid in cosmetic products.[22,31,32] The improved sensitivity observed here can also be expected to extend successfully for electroanalysis of these analytes and others.

In conclusion, the Ni films with a reticular morphology supported on a conducting AuBPE substrate have been prepared by a simple electrodeposition technique. The dendrite texture $Ni(OH)_2/NiO(OH)$ film was stabilized after a low temperature annealing treatment. This easy approach makes possible in manufacture on a mass scale and represents a useful platform for electroanalysis applications. The annealed Ni–AuBPE was demonstrated for the FIA of glucose at an applied potential of +0.55 V *vs.* Ag/AgCl with excellent sensitivity. Meanwhile, such a high surface area annealed Ni–AuBPE can be used as an anode in a sugar–air battery with higher energy densities.[33–35] The development of portable recycling nickel–metal hydride batteries[36–38] is growing at a record pace due to consumer demand. The research is currently under investigation in this laboratory.

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