Facile Synthesis of Pt-CuO Nanocomposite Films for Non-Enzymatic Glucose Sensor Application

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Nanocomposite films of Pt-CuO were synthesized via galvanostatic electrodeposition combined with galvanic replacement and post-synthesis thermal anneal. First, Cu-Cu2O composite was prepared by galvanostatic electrodeposition; heat-treatment of the as-prepared Cu-Cu2O composite at 375 °C for 10 h resulted in a CuO electrode showing response to glucose with long term stability. Further enhanced response to glucose was obtained with a Pt-CuO electrode, which was synthesized by galvanic replacement of Cu-Cu2O in 10 mM PtCl4 solution for 30 s followed by annealing at 375 °C for 10 h. The resulting Pt-CuO electrode showed excellent response to glucose in alkaline solution with an analytical sensitivity of 3812 μA·mmM−1·cm−2, a limit of detection (LOD) of 7.5 μM, and a linear response range to glucose up to 0.6 mM. These results may be extended to the fabrication of other noble metal-metal oxide nanocomposite electrodes for sensor applications.

In this report, we describe a facile method for the synthesis of CuO and Pt-CuO films on the ITO electrode by combining galvanostatic electrodeposition with galvanic replacement, followed by a heat-treatment. In companion studies, we presented the applicability of this hybrid approach to the preparation of Au-BiVO4 and Au-Bi2O3 nanocomposites for heterogeneous photocatalysis applications for environmental remediation. In contrast, galvanostatic deposition of Cu-Cu2O nanocomposite was used for the first time in this work to successively prepare Cu-CuO- and Pt-CuO-based non-enzymatic glucose sensors. These sensors exhibited high analytical sensitivity, low limit of detection (LOD), fast response, and long term stability for the amperometric determination of glucose in alkaline media.

Experimental

CuSO4, lactic acid, NaOH, PtCl4 and glucose were from Sigma-Aldrich, and used without further purification. Electrodeposition of Cu-Cu2O was performed in a conventional three-electrode electrochemical cell consisting of an ITO working electrode (geometric area, 0.2 cm2), an Ag/AgCl/3 M NaCl reference electrode, and a Pt-wire counter electrode. All potentials below are quoted with respect to the Ag/AgCl/3 M NaCl reference electrode. Before electrodeposition, ITO working electrode (sheet resistance: 10 ohms/square) was cleaned by sonication in a mixture of ethanol/H2O (1:3) and acetone/H2O (1:3) for 20 min. respectively and finally rinsed with distilled water.

All experiments were performed at room temperature except the thermal anneal step, which was carried out at 375 °C using an electric furnace (Electric Muffle Furnace Model J-FM2, Korea). X-ray diffraction (XRD) patterns were recorded on a Philips XPERT-MPD diffractometer with Cu Kα radiation source. Film morphology and composition were obtained on a field emission scanning electron microscope (JEOL Model 6700F) equipped with an energy-dispersive X-ray emission analysis (EDX) probe.

Results and Discussion

Since the initial reports by previous researchers, potential oscillations observed during the electrodeposition of Cu-Cu2O composite at a constant cathodic current have been extensively studied using voltammetry and electrochemical quartz crystal microgravimetry (EQCM).18–20 It is thus well known that Cu2O is electrodeposited during the positive-going spikes in potential, while Cu and CuO composites are electrodeposited during the negative-going excursions.18 Figure 1 shows potential oscillations during the deposition of Cu-Cu2O composites at a constant current density of 0.825 mA/cm2 in 3 M lactic acid containing 0.4 M CuSO4. The pH of the electrolyte was

Millions of people worldwide are affected with diabetes, a disease necessitating regular monitoring of blood glucose levels. Amperometric sensing2–13 is a particularly popular approach to glucose sensing but classical methodology is based on enzymatic monitoring using glucose oxidase which oxidizes the catalytic conversion of glucose to glucooctone. However, a perennial problem with the enzymatic approach is the lack of long term stability and robustness of the sensing device. In terms of selectivity and sensitivity, enzymatic sensors do generally exhibit better performance than non-enzymatic ones.2,4,5,6 However, as noted earlier, they suffer from several problems including poor stability, high cost, fragility of the enzyme component, and difficulty of active sensing component preparation.2,4,5–7

Non-enzymatic approaches, therefore, have gained traction in recent years. Thus non-enzymatic amperometric sensors8–13 have been electrolysytically used using MnO2, CuO, or cobalt oxide/hydroxide as the active sensor materials. Several reviews are available in the area of non-enzymatic glucose sensors.8–13 Among the non-enzymatic glucose sensing components based on metals and metal oxides, CuO is one of the more promising materials due to its low cost, high stability and earth abundance.1,4,14 Copper(II) oxide (CuO) which is a semiconductor with a bandgap 1.2 eV has been widely used in many applications including catalyst, gas sensor, battery, and biosensor.2–5 This inorganic semiconductor has also shown good electrochemical activity and capability of promoting facile electron transfer rates at low overpotentials in alkaline electrolytes.15

Noble metals such as Pt, Au and Ag have been extensively used to improve sensing performance due to their excellent electrocatalytic activity and biocompatibility.2 Especially, Pt-based metal oxides have been proposed for improving the sensitivity and selectivity of non-enzymatic glucose sensors.2,4,13 Unlike CuO-based glucose sensors, however, there is more limited precedent research on Pt-CuO nanocomposite films for the electrochemical determination of glucose.1–3 We are only aware of three prior studies on this topic. Grace and co-workers reported a Pt-CuO sensor that exhibited high sensitivity and a linear detection range for glucose.2 In this work, the sensing element was prepared by immobilization of Pt-CuO hybrid nanostructures within a Nafion matrix on the electrode surface. The Pt-CuO nanocomposite was synthesized by a co-precipitation method.2 In another study, CuO/Pt/Si nanoarrays were prepared by ion etching combined with electrolysytically.3 Finally, Pt-CuO decorated reduced graphene oxide was prepared by precipitation followed by drop casting.3

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Figure 1. Potential oscillations obtained at a current density of 0.825 mA/cm² on the ITO electrode. The deposition solution was 3 M lactic acid containing 0.4 M CuSO₄ at a pH of 9.0. The pH of the solution was adjusted with 5 M NaOH solution.

adjusted to 9.0 using a 5 M NaOH solution. As shown in the figure, the potentials oscillate between ~−0.35 V and ~−0.55 V with a regular frequency. Oscillation potentials are not constant at the early stages of the deposition, but stabilized after ~10 min. The inset in Figure 1 shows a few cycles of potential oscillations observed from 620 s to 780 s.

The XRD results in Figure S2 clearly confirm that the as-deposited film contains both Cu and Cu₂O. The film was prepared by the same procedure as described in Figure 1. Except the peaks due to the substrate (ITO) at 21.0°, 30.0°, 35.0°, 37.0°, 44.0°, 50.5° and 60.0°, all other peaks can be assigned either to metallic Cu or to Cu₂O as indicated in the figure.21–23 The mixed phase films are designated in what follows as Cu-Cu₂O.

As a prelude to the ultimate synthesis of Pt-CuO, however, we investigated the electrochemical (amperometric) response of the as-deposited Cu-Cu₂O film surfaces to glucose in alkaline media. The cyclic voltammograms in Figures 2a and 2b were obtained from the 1st and the 5th runs respectively on a Cu-Cu₂O modified ITO electrode in 0.1 M NaOH solution containing 0.1 mM glucose. The anodic peak at ~0.45 V is due to glucose oxidation. Interestingly, the voltammogram in Figure 2b demonstrates that current response to 0.1 mM glucose decreased dramatically as the number of cycles increased, which implies the instability of as-deposited Cu-Cu₂O nanocomposite films. Further, the Cu-Cu₂O films could be mechanically peeled off after the voltammetric cycles, and changes in the surface morphology could be discerned even with the naked eye. Figure 2c demonstrates that (the underlying) bare ITO electrode surface shows no current response toward the oxidation of glucose.

To improve the stability of the electrode, the as-deposited Cu-Cu₂O electrode was annealed at 375°C for 10 h. This procedure resulted in a CuO electrode as displayed in the XRD patterns in Figure 3. The major peaks at 38.73° and 48.72° clearly confirm that CuO could be successfully synthesized from Cu-Cu₂O by heat-treatment.2,7,14 Importantly, the XRD patterns also show that the peaks due to metallic Cu have disappeared. Other peaks are due to the (underlying) ITO electrode support as in Figure S2. Taken as a whole, these results demonstrate the successful synthesis of CuO electrodes by galvanostatic electrodeposition followed by post-deposition heat-treatment.

The electrocatalytic behavior of CuO electrodes toward glucose oxidation in alkaline electrolyte was next investigated by cyclic voltammetry, see Figure 4. Unlike the Cu-Cu₂O electrode case described in Figure 2, electrode stability is now dramatically improved as apparent from comparison of the 1st run with the 50th run in 0.1 M NaOH solution containing 0.1 mM glucose; both voltammograms are almost superimposable on one another. These data show that a CuO electrode surface shows stable and reproducible current response to the oxidation of glucose in alkaline solutions. Notably, the electrode stability was tested after exposure to air for 4 months, and showed no substantial changes in current response from the as-prepared CuO electrode. This stability is due to the chemically stable CuO in alkaline media.6 Once again, the bare ITO surface shows no response toward glucose oxidation as evident from Figure 4c, which shows no substantial current in the potential range from 0.0 V to 0.8 V.

The amperometric response to glucose was obtained at a constant potential of +0.6 V. Upon successive addition of 0.1 mM aliquots of glucose to the 0.1 M NaOH solution, the oxidation current instantly increased and reached stable response in each case in less than 10 s. Figure 5b shows the calibration curve obtained from the

Figure 2. Cyclic voltammograms for Cu-Cu₂O electrodes in 0.1 M NaOH solution containing 0.1 mM glucose; (a) 1st run and (b) 5th run. (c) A corresponding trace for the ITO electrode in the 0.1 M NaOH solution containing 0.1 mM glucose is also shown for comparison. The Cu-Cu₂O nanocomposites were electrodeposited by the procedure described in Figure 1. Potential scan rate: 20 mV/s.

Figure 3. XRD pattern for a CuO film prepared by annealing a Cu-Cu₂O nanocomposite electrode at 375°C for 10 h. The Cu-Cu₂O composite electrode was previously electrodeposited by the procedure described in the text and in Figure 1.

Figure 4. (a) Amperometric response to glucose at CuO electrodes in 0.1 M NaOH solution containing 0.1 mM glucose; (b) Calibration curve for glucose obtained at a constant potential of +0.6 V. Upon successive addition of 0.1 mM aliquots of glucose to the 0.1 M NaOH solution, the oxidation current instantly increased and reached stable response in each case in less than 10 s. Figure 5b shows the calibration curve obtained from the
amperometric responses in Figure 5a. The analytical sensitivity was calculated from the slope of the calibration plot and was estimated to be 2859 $\mu$AmM$^{-1}$cm$^{-2}$ with a linear response range up to 0.6 mM. A LOD value (defined at a S/N ration of 3) of 7.7 $\mu$m was obtained. The CuO electrode described in this study shows better or at least comparable performance toward glucose oxidation in terms of both analytical sensitivity and LOD compared with other CuO-based non-enzymatic glucose sensors as summarized in Table I.

It is well known that noble metals can improve the electrocatalytic performance of amperometric sensors. For example, Pt or Au decorated CuO composite electrodes exhibited better performance toward glucose oxidation than the metal-free counterparts.1-4 Therefore, in this work, the hybrid electrodeposition/galvanic displacement approach, developed by us earlier,17,24,25 was used for decorating the CuO surface with Pt nanoclusters. Galvanic displacement (or replacement of one metal with another) is based on a spontaneous redox process driven by the difference in standard reduction potentials between the substrate and metal ions in solution. This reaction was used to prepare semiconductor nanocomposites such as CdSe-ZnSe, and more directly relevant to this work, Au-ZnO and Au-Bi$_2$O$_3$.17,24,25 To prepare Pt-CuO from Cu-Cu$_2$O, Cu-Cu$_2$O was first electrosynthesized at a constant current density on ITO support as described in Figure 1. The metallic Cu component in this film was then galvanically replaced with Pt by simply immersing the ITO-supported Cu-Cu$_2$O film in 10 mM PtCl$_4$ solution for 30 s at room temperature. Finally, further thermal treatment of Pt-Cu$_2$O at 375°C for 10 h produced Pt-CuO electrodes. The successful synthesis of Pt-CuO was confirmed by X-ray diffraction coupled with EDX analyses (see Supporting Information S1).

The Pt-CuO nanocomposite electrode was tested for its proclivity toward glucose oxidation, as displayed in Figure 6. Comparison of cyclic voltammograms obtained in 0.1 M NaOH solution containing 0.1 mM glucose revealed that Pt plays a key role in enhancing the amperometric response toward glucose. For example, compared with bare CuO electrode, the oxidation current at +0.6 V on Pt-CuO increased by 27.3% when 0.1 mM of glucose was added to the 0.1 M NaOH as shown in Figure 7a. Again, the amperometric response was instant and stable as in the bare CuO electrode case presented earlier (Figure 5). The improvement in analytical performance is evident from the slope of the calibration plot in Figure 7b. The analytical sensitivity was calculated to be 3812 $\mu$AmM$^{-1}$cm$^{-2}$ which is better than for bare CuO by $\sim$33%, while the linear range and LOD remained almost the same compared with the bare CuO electrode case.

The analytical performance of Pt-CuO is compared with other CuO-based non-enzymatic glucose sensors in Table I. The overall trend is in agreement with previous results that Pt acts as a co-catalyst to enhance electron transfer during the oxidation of glucose.5

Finally, the chronoamperometric response in the presence of interfering species was examined using ascorbic acid as a probe; this was done both for CuO and for Pt-CuO. As displayed in Figure 8, the addition of 0.1 mM ascorbic acid to 0.1 M NaOH in the presence of 1 mM glucose at an applied potential of +0.6 V, resulted in insignificant response to ascorbic acid for both electrodes. This observation

### Table I. Comparison of the analytical performance of various Cu based glucose sensors.

| Sensor | Sensitivity $\mu$AmM$^{-1}$cm$^{-2}$ | Detection limit $\mu$m | Ref. |
|--------|--------------------------------------|------------------------|-----|
| Cu-Cu$_2$O | 62.29 | 37 | 22 |
| CuO nanocube | 121.7 | 36 | 26 |
| CuO nanoleaves | 573.1 | 10 | 27 |
| Cu/MWCNTs | 1096 | 1.1 | 28 |
| CuO/Pr/Ti/Si | 2900 | 0.14 | 29 |
| Pt-CuO/Gr/O/SPE | 3577 | 0.01 | 1 |
| CuO | 2859 | 7.7 | This work |
| Pt-CuO | 3812 | 7.5 | This work |

Figure 4. Cyclic voltammograms for CuO electrodes in 0.1 M NaOH solution containing 0.1 mM glucose; (a) 1st run and (b) 50th run. (c) The same trace as in Figure 2c, for the ITO electrode in 0.1 M NaOH solution containing 0.1 mM glucose, is also shown. The CuO electrode was obtained by the same procedure as described in Figure 3. Other scan conditions as in Figure 2.

Figure 5. (a) Representative chronoamperometric responses of CuO electrodes to successive additions of 0.1 mM aliquots of glucose to the 0.1 M NaOH solution at an applied potential of 0.6 V. (b) Calibration curve of current vs. concentration of glucose obtained from the amperometric response in Figure 5a. Error bars in the calibration curve represent a standard deviation established from 5 replicate measurements.
Figure 6. Comparison of cyclic voltammograms in 0.1 M NaOH solution containing 0.1 mM glucose obtained from (a) Pt-CuO, (b) CuO, and (c) ITO. The traces in (b) and (c) are the same data as in Figures 4a and 2c respectively. To prepare Pt-CuO electrode, Cu-Cu2O was first converted to Pt-Cu2O by galvanic replacement from a 10 mM PtCl4 bath for 30 s, and finally converted in Pt-CuO by heat-treatment at 375°C for 10 h. Other scan conditions as in Figure 2.

Figure 7. (a) Representative chronoamperometric responses for Pt-CuO electrodes to successive additions of 0.1 mM glucose aliquots to 0.1 M NaOH solution at an applied potential of 0.6 V. (b) The calibration curve of current vs. concentration of glucose obtained from the amperometric response in Figure 7a.

Figure 8. Comparison of chronoamperometric responses of (a) CuO electrode and (b) Pt-CuO in 0.1 M NaOH with successive addition of 1 mM glucose and 0.1 mM ascorbic acid aliquots at an applied potential of 0.6 V. reaffirms that the amperometric sensors developed in this work, show high selectivity toward glucose oxidation in the presence of interfering species such as ascorbic acid.

Conclusions
A novel and facile method for the preparation of CuO and Pt-CuO has been described for non-enzymatic glucose sensor applications. Galvanostatically deposited Cu-Cu2O was thermally annealed to produce a CuO sensing surface showing better stability than the original Cu-Cu2O nanocomposite case. Further improvement in analytical performances was achieved by decorating CuO with Pt. To this end, the metallic Cu component (which is invariably present on electrodeposited CuO films) was utilized as a sacrificial reducing agent for galvanically depositing Pt on the Cu2O surface. As-prepared Pt-Cu2O was then converted to Pt-CuO by heat-treatment at 375°C for 10 h. The resultant Pt-CuO showed improved analytical sensitivity compared with CuO and other reported Cu-based glucose sensors reported in prior works. The approach described in this report can be generally used for decorating noble metals other than Pt with CuO as long as the relative reduction potential condition is met for driving galvanic exchange.

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