



Glucose Oxidase and Horseradish Peroxidase Like Activities of Cuprous Oxide/Polypyrrole Composites



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ABSTRACT

Cu₂O/Ppy composites coated linen texture (LT) papers possess enzyme activities of glucose oxidase (GOx) and horseradish peroxidase (HRP) in alkaline solution (0.5 M NaOH). At the potential of 0 V vs. Ag/AgCl reference electrode, H₂O₂ was produced through oxidation of glucose on the functional LT paper electrode in the presence of O₂. The as-produced H₂O₂ was reduced on the electrode at the potential of −0.57 V vs. Ag/AgCl reference electrode. Cyclic voltammograms (CVs) reveal that Cu(I)/Cu(II), Cu(II)/Cu(I), and Cu(I)/Cu transitions occur at ca. 0, −0.57, and −0.85 V respectively. The electrode allows detections of glucose and H₂O₂ down to 0.16 and 0.41 mM, respectively. The high catalytic activity of the Cu₂O/Ppy composites is attributed to the stable coatings of Ppy and the high-index facets of Cu₂O octahedra and microflowers. Having advantages of a low onset potential (ca. −0.02 V), high sensitivity (28 μA mM^{−1} cm^{−2}), and selectivity, the stable and durable LT paper electrode has been validated for the quantitation of glucose in blood samples, showing its great potential for monitoring blood glucose levels.

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1. Introduction

According to world health organization (WHO), 422 millions of people in the world are affected by diabetes, which reflects the importance of low-cost and simple techniques for accurate monitoring of blood glucose levels [1,2]. The blood glucose concentrations in diabetic patients are in the range of 9–40 mM, which are higher than that (3–8 mM) of healthy people [3]. Various optical and electrochemical sensing systems have been used for the detection of glucose [4–10]. Electrochemical systems are more attractive, mainly because of their simplicity, cost effectiveness, sensitivity, and selectivity [1,7,11–13]. To provide selectivity toward glucose, most of the electrochemical systems require glucose oxidase (GOx) that catalyzes β-D-glucose to glucono-δ-lactone and H₂O₂ in the presence of O₂ [7,11,13,14]. The as-produced glucono-δ-lactone is subsequently converted to gluconic acid through hydrolysis. By monitoring the current generated from reduction of H₂O₂, the concentration of glucose can be determined [13]. Although these approaches are sensitive and selective, durability and short self-life of the electrodes are two other issues.

Several nanomaterials have been used as enzyme mimics for the electrochemical detection of glucose [15–24]. Although GOx is not required, catalysts like Fe₂O₃ [15], Ni [16,22], and Ag [17] provide poor selectivity and low catalytic activity. On the other hand, use of high-cost Co₃O₄ [18], Au [20], or Pt [23] nanomaterials is a concern. Less-expensive metallic copper (Cu) and its oxides (e.g. CuO and Cu₂O) have become popular for the detection of glucose [21,25]. When compared to spherical like Cu/CuO_x nanoparticles [26,27], hierarchical nano/microstructures such as nanowires [24] and nanorods [21] having greater reaction sites and higher surface energy are more electrochemically active toward glucose. It has also been shown that crystal facets of Cu₂O play an important role in the glucose oxidation [28].

Oxidation of glucose on a Cu electrode forms products such as gluconic acid (pKa 3.60) through four steps: (i) adsorption of glucose onto the surface of Cu(I) or Cu(II) hydroxides/oxides, (ii) formation of Cu(III) species, (iii) formation of glucose/copper complexes, and (iv) C–C bond cleavage [29]. Under alkaline conditions, several oxidized products, including gluconic acid, glucuronic acid, and formic acid have been detected, which suggests that different mechanisms likely occur in the glucose oxidation [30]. Because it is extremely difficult to isolate the products, simple and innovative strategies for the identification

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and quantification of each of the products are highly demanded for providing a detailed mechanism for glucose oxidation.

Different mechanisms have been suggested for glucose oxidation on various electrodes such as Cu_2O and metallic Cu electrodes [30,31]. On the surfaces of Cu/ Cu_2O , glucose as an enediol form is oxidized by various surface states of Cu through the transitions I–III [29,32]. The oxidation is mainly mediated by Cu(II)/Cu(III) transition to form gluconic or glucuronic acid and then to form formate and carbonate through C–C bond cleavage [27]. Surface properties of the electrode play a significant role in determining its electrochemical activity. For example, conducting polymers such as polyaniline and polypyrrole (Ppy) coated on the Cu/ Cu_2O surfaces can increase the conductivity and stability of the electrode and thus can reduce the overpotential for glucose oxidation [33–35]. Ppy is commonly used to control Cu_2O structures, mainly due to its greater electrochemical stability over a wide potential window [33]. Glucose oxidation on Cu_2O /Ppy electrodes in 0.1 M NaOH occurs in the potential range of 0 to 0.8 V [36]. Although the electrodes are useful for monitoring glucose levels in blood samples, mechanisms for glucose oxidation on the electrodes are still unclear.

In this study, we used Cu_2O /Ppy linen texture (LT) paper electrodes for the electrochemical oxidation of glucose in wide potential windows (–0.75 to 0.6 V and –1.2 to 0.6 V) under alkaline conditions (0.5 M NaOH). The Cu_2O /Ppy composites exhibited enzyme mimic activity of GOx to catalyze glucose in the presence of O_2 to form H_2O_2 at 0 V vs. Ag/AgCl reference electrode. The composites also showed enzyme mimic activity of horseradish peroxidase (HRP) to reduce as-produced H_2O_2 at –0.57 V vs. Ag/AgCl reference electrode. The functional LT paper electrode exhibited high selectivity toward glucose, with minimum interferences from various biological compounds. The high catalytic activity of the Cu_2O /Ppy LT paper electrode is attributed to the high-index facets of Cu_2O structures. We proposed a detailed mechanism for glucose oxidation on the paper electrode. Practicality of the functional LT paper electrodes was validated by the quantitation of glucose in human blood samples.

2. Experimental

2.1. Materials

Catechin hydrate (98%) was obtained from Sigma Aldrich (St. Louis, MO, USA). Copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 80%) was purchased from Showa (Tokyo, Japan). Pyrrole (99.5%) was obtained from Acros Organics (Geel, Belgium) and used without any further purification. Sodium hydroxide (pellet, 98.9%) was purchased from J.T. Baker (Phillipsburg, NJ, USA). Nafion 117 (5 wt%) was procured from Fluka (Buchs, Switzerland). Acetaminophen (≥ 99.8 wt%), L-ascorbic acid (≥ 99.8 wt%), Cu_2O particles ($< 5 \mu\text{m}$), cysteine (≥ 99.8 wt%), β -D-glucose (≥ 99.8 wt%), and uric acid (≥ 99.8 wt%) were purchased from Sigma (St. Louis, MO, USA). LT paper (A4 size, 6×2.5 cm with GSM of 247.5 g m^{-2}) was purchased from Sun Hong (Taipei, Taiwan). Terephthalic acid (TA) was purchased from Janssen Chimica (Beerse, Belgium). All aqueous solutions were prepared in ultrapure water ($18.2 \text{ M}\Omega \text{ cm}$) produced by a Milli-Q ultrapure system of Millipore (Billerica, MA, USA).

2.2. Characterization

A JSM-1200EX II transmission electron microscope from JEOL (Tokyo, Japan) and a Hitachi S-2400 scanning electron microscope from Hitachi High-Technologies (Tokyo, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS) were employed to investigate the morphology and composition of Cu_2O /Ppy

composites. A Philips Tecnai F20 G2 FEI-TEM (Roanoke, VA, USA) was used to record high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images. STEM measurements were taken using formvar/carbon film Cu grids (200 meshes; Agar Scientific) coated with aliquots ($2 \mu\text{L}$) of Cu_2O /Ppy composites which were separated from the LT paper by soaking in aqueous solution and sonicating for 10 min. Prior to scanning electron microscopy (SEM) measurements, a Cu_2O /Ppy LT paper ($1 \times 1 \text{ cm}^2$) was dried overnight at ambient conditions (27°C). X-ray diffraction (XRD) pattern of Cu_2O /Ppy composites was obtained using a PANalytical X'Pert PRO diffractometer from PANalytical B.V. (EA Almelo, Netherlands) and Cu-K α radiation ($\lambda = 0.15418 \text{ nm}$). Prior to XRD analysis, the samples were prepared on Si substrates and dried overnight. The hydroxyl (OH^\bullet) radical formed during the electrochemical oxidation of glucose was determined by fluorescence. Aliquots ($300 \mu\text{L}$) of the liquid products were taken from the electrochemical cell and then mixed with aqueous solution of TA (3 mM, $100 \mu\text{L}$). The fluorescence of the product, 2-hydroxyterephthalic acid (TAOH), was recorded using a Cary Eclipse fluorescence spectrophotometer from Varian (Palo Alto, CA, USA). After electrolysis of glucose (5 mM) in 0.5 M NaOH solution on the Cu_2O /Ppy electrode for 43200 s, aliquots ($10 \mu\text{L}$) of the product solution were taken from the electrochemical cell and mixed with HgTe nanostructures ($10 \mu\text{L}$) for SALDI-MS measurements [37]. About $2 \mu\text{L}$ of this mixture was pipetted onto a stainless-steel 96-well MALDI target (Bruker Daltonics) and dried at ambient conditions. As controls, aliquots ($10 \mu\text{L}$) of glucose and gluconic acid solutions were used instead of the electrolyzed solution. SALDI-MS spectra of the sample were recorded using a reflectron-type time of flight (TOF) mass spectrometer purchased from Biflex III, Bruker (Bremen, Germany) equipped with a 1.25-m flight tube. SALDI-MS spectra of glucose and gluconic acid (controls) were recorded in positive and negative-ion modes, respectively. All the samples were irradiated by a nitrogen laser (emission at 337 nm) with a frequency of 10 Hz and pulse duration of 4 ns. The ions generated during laser desorption were stabilized within a delayed extraction period of 200 ns and accelerated through a linear TOF reflection before reaching the mass analyzer. An accelerating voltage of 20 kV was used. Each mass spectrum was obtained after 300 laser pulses.

2.3. Fabrication of Cu_2O /Ppy LT paper electrodes

The Cu_2O /Ppy composites coated on LT papers were prepared according to the literature [38]. Briefly, the pyrrole coated LT paper (0.011 g cm^{-2} , $6 \times 2.5 \text{ cm}$) was reacted with a mixture of $\text{Cu}(\text{NO}_3)_2$ (3 mL, 0.1 M) and NaOH (30 mL, 7.5 M) for 30 min to form the Cu^{2+} /pyrrole complexes. Then, catechin (60 mg) was added into this solution, which was heated at 80°C for 1 h to complete oxidative polymerization of pyrrole and reduction of Cu^{2+} ions to form PPy and Cu_2O particles, respectively [38,39]. The as-prepared Cu_2O /Ppy LT paper was soaked in 100 mL of ultrapure water for 10 min to remove excess NaOH and dried overnight prior to electrochemical experiments.

2.4. Electrochemical oxidation of glucose

A 50-ml three-necked glass cell was used in each electrochemical experiment. The Cu_2O /Ppy (mass loading: 0.2 mg cm^{-2}) LT paper fixed with a Cu tape (0.5 cm) on one end was used as a working electrode. The area of the working electrode in contact with the solution was about 5 cm^2 , which was considered as the final working area. All potentials were measured against an Ag/AgCl electrode. A Pt wire with 0.5 mm diameter was used as a counter electrode. Prior to each electrochemical measurement, O_2 gas was purged into the electrolyte solution for 30 min. During the

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