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A sensitive nonenzymatic hydrogen peroxide sensor using cadmium oxide nanoparticles/multiwall carbon nanotube modified glassy carbon electrode

Nutthaya Butwong^a, Lin Zhou^b, Wittaya Ng-eontae^a, Rodjana Burakham^a, Eric Moore^c, Supalax Srijaranai^a, John H.T. Luong^d, Jeremy D. Glennon^{b,*}

^a Materials Chemistry Research Unit, Department of Chemistry and Center for Innovation in Chemistry, Faculty of Science, KhonKaen University, KhonKaen 40002, Thailand

^b Innovative Chromatography Group, Irish Separation Science Cluster (ISSC), Department of Chemistry and Analytical, Biological Chemistry Research Facility (ABCRF), University College Cork, Cork, Ireland

^c Life Science Interface, Tyndall National Institute, Lee Maltings, University College Cork, Prospect Row, Ireland

^d National Research Council Canada, Montreal, Quebec H4P 2R2, Canada

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ABSTRACT

A simple sensing scheme for hydrogen peroxide has been described by electrochemical deposition of cadmium oxide (CdO) nanoparticles with ~50 nm in diameter on a glassy carbon (GC) electrode modified with multiwall carbon nanotubes (MWCNT). The CdO/MWCNT modified sensor, with a surface coverage of 1.13×10^{-8} mol/cm², displayed high synergistic electrocatalytic activity for H₂O₂. The sensor was capable of reducing H₂O₂ at -1.2 V vs. Ag/AgCl (H₂O₂ + 2H⁺ + 2e⁻ → 2H₂O) in a broad pH range. At the optimal pH 7, the sensor exhibited a detection limit of 0.1 μM, broad linearity from 0.5 to 200 μM, good reproducibility (RSD of 5.9%), and long-term stability. Uric acid, ascorbic acid and dopamine up to 100 μM provoked no signal response, attesting selectivity of the CdO/MWCNT modified electrode for hydrogen peroxide.

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1. Introduction

Hydrogen peroxide (H₂O₂) is a simple molecule but plays a critical role in diversified biological systems, clinical, food, and environmental chemistry [1]. It is also a by-product of enzymatic reactions using oxidases which are widely used in the construction of biosensors, enzyme assays and enzyme-linked immuno assays. To date, several schemes for sensitive and selective detection of H₂O₂ have been contemplated including chemiluminescence [2]. Electrochemical methods with different electrode materials including noble metals have also proved as an inexpensive and effective analytical procedure for H₂O₂ [3]. The main drawback of electrochemical detection is the requirement of overpotentials above +0.8 V for the oxidation of H₂O₂ (H₂O₂ → 2H⁺ + O₂ + 2e⁻). Several endogenous species in “real world” samples including uric acid, ascorbic acid, amino acids and neurotransmitters are also electroactive at such overpotentials, causing severe interferences. Electrode modification with mediators and enzymes provides an alternate to circumvent electroactive interferents [3–8]. Albeit this approach offers high detection sensitivity and selectivity, it often

suffers from poor reproducibility, repeatability, and storage as well as operational stability; inherent properties of the enzyme. Nano-scale metal oxides are a very promising class of electrocatalysts because they are active, inexpensive and thermodynamically stable [9]. To date, different metal oxide particles and nanoparticles such as copper oxide [10] zirconium oxide [11], ruthenium oxide [12], cobalt oxide [13,14], iron oxide [15,16] and nickel oxide [17–19], manganese oxide [20], titanium oxide [21] and zinc oxide [22] have been successfully used for sensing H₂O₂. Nanoscale CdO with different morphologies has been synthesized [23–25] and this oxide is known to possess high electrical conductivity, high carrier concentration and high transparency in the visible range of the electromagnetic spectrum [26]. Of particular interest is the formation of a thin CdO film by electrochemical deposition with specific composition, morphology and good adhesion between the deposited film and the substrate [26]. The CdO or oxyhydroxide layers on the glassy carbon (GC) surface with excellent electrocatalytic activity can be prepared by electrodeposition [27].

Multiwall carbon nanotubes (MWCNTs) with extraordinary mechanical strength, high surface to volume ratio, excellent electrical conductivity and high chemical stability have been advocated for a plethora of diversified applications [28,29] including the fabrication of electrochemical sensors and biosensors. CNTs can serve as promising catalyst supports [30] or together with

* Corresponding author. Tel.: +353 214902669.

E-mail address: j.glennon@ucc.ie (J.D. Glennon).

metal nanoparticles to form a composite with remarkable activity for small molecules [30–33].

This work focuses on the electrochemical deposition of CdO nanoparticles on the surface of a MWCNT modified GC electrode to form a composite layer with high activity for hydrogen peroxide. Electrochemical behavior of the CdO film was characterized by cyclic voltammetry and impedance spectroscopy. The analytical performance of the CdO/MWCNT modified electrode was then evaluated with respect to detection limit, linearity, stability and reproducibility. To our knowledge, it is the first demonstration for the combination of CdO nanoparticles and MWCNTs to achieve high detection sensitivity and selectivity for H_2O_2 .

2. Experimental

2.1. Chemicals

All chemical reagents were purchased from Sigma–Aldrich (Dublin, Ireland) and used as received. The phosphate buffer solution (PBS, pH 7) was prepared from NaH_2PO_4 and Na_2HPO_4 . The buffer solution pH was adjusted with HCl and NaOH solutions. CdCl_2 , H_2O_2 (30% w/w) and other reagents used were of analytical grade. Solutions were prepared from analytical or reagent grade chemicals using deionized water.

2.2. Apparatus

Electrochemical experiments were performed using a CHI electrochemical analyzer (CHI, Austin, TX, USA) equipped with a three electrode cell consisting of a reference electrode (Ag/AgCl), a Pt wire counter electrode and a glassy carbon disk (3 mm diameter) working electrode. Cyclic voltammetry on the CdO modified electrode was carried out in the cadmium ion free PBS buffer solution (pH 7). The surface morphology of the modified electrodes was examined by a JEOL 2100 High Resolution (Scanning) Transmission Electron Microscope (SEM, UK). Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR) spectroscopy were also used to evaluate the surface morphology, composition and structure of the electrodes prior and after modification. A Hitachi scanning electron microscope (SEM, S-2600N, Tokyo, Japan) was used for topographical analysis of the electrodes. The SEM was equipped with an Energy dispersive X-ray (EDX) spectrometer, LN2-free analytical silicon drift detector (INCA x-act, Oxford Instruments, UK). The SEM/EDX system was operated with a high vacuum mode at 10–20 kV, emission current of 60–80 μA , and a working distance of 3–20 mm with tilt angle of 30° for elemental analysis. EDX has software with a database of reference spectra for elemental analysis, compositional nano-analysis and mapping.

Electrochemical impedance spectra of the modified electrodes were recorded by the BAS-Zahner IM6 Impedance Analyzer (USA). The impedance data were analyzed using the ZSimpWin software (Princeton Applied Research). All experiments were carried out at ambient temperature.

2.3. Preparation of the CdO/MWCNT modified GC electrode

A GC electrode was polished with alumina (0.30 and 0.05 μm) on a polishing cloth followed by sonication in deionized water and then ethanol to remove adsorbed particles. MWCNTs were refluxed in a concentrated nitric acid and sulfuric acid solution (3:1) for 3 h. Resulting acid-treated MWCNTs (1 mg) were dispersed in 1.0 mL of dimethylformamide (DMF) with ultrasonication for 15 min to attain a dark black suspension. The GC surface was casted with 3 μL of the MWCNT–DMF suspension and dried under

ambient condition. Repetitive potential cycling (30 cycles at 100 mV s^{-1} from +0.8 to -1.3 V) in PBS, pH 7.0 containing 1 mM CdCl_2 was used for the electrodeposition of a cadmium oxyhydroxide thin film on the GC electrode surface [27]. The effective area of the modified electrode was determined from the cyclic voltammogram with 5 mM $\text{K}_3\text{Fe}(\text{CN})_6^{3-/4-}$ in 0.1 M KCl as a probe. The modified electrode was washed with deionized water and stored at ambient temperature.

3. Results and discussion

3.1. Characterization of CdO nanoparticles

The pristine MWCNT modified GC surface showed the following elements in weight percent: C (95.94), O (3.74), and Fe (0.32). After treatment with acid, the acid treated MWCNT modified GC electrode showed an increase in oxygen (11.87) corresponding to a decrease in C (88.13) and the disappearance of Fe. The resulting CdO/MWCNT modified GC surface showed a further decrease in C (86.01) while the oxygen element increased to 13.13 together with the Cd element (0.86). Such results confirmed the formation of CdO nanoparticles on the MWCNT modified surface.

Repetitive cyclic voltammograms of the MWCNT modified GC electrode, subjected to 1 mM CdCl_2 in 0.1 M PBS (pH 7), exhibited an initial anodic peak at -1.05 V (Fig. 1, peak I). This anodic peak decreased with the increasing cycle number, indicating a slow and steady reduction of Cd (II) ion CdO ($\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}^0$) on the electrode surface. The other two anodic peaks (Fig. 1, peaks II and III) at -0.85 and -0.75 V, respectively were corresponding to the reduction of $\text{Cd}(\text{OH})_2$ to cadmium hydroxide or CdO (Fig. 1, peaks II and III). Two cathodic peaks (Fig. 1, peaks IV and V) could be assigned to the formation of $\text{Cd}(\text{OH})_2$ [26,27] and CdOOH , respectively on the reverse cycle [27]. A small cathodic peak at 0.10 V (Fig. 1, peak VI) might be related to the dissolution of the deposited cadmium layer [27]. Different segments of the electrode surface were observed by SEM to probe the formation and growth of CdO nanoparticles. After 30 cycles of cyclic voltammetry, a uniform film of CdO particles with an average size of ~ 50 nm was firmly deposited on the surface of the MWCNT modified GC electrode (Fig. 2).

3.2. Electrochemical characterization of the CdO/MWCNT–GC electrode

With $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ (5 mM each in 0.1 M KCl) as a probe, the bare GC displayed the quasi-reversible one-electron redox

Fig. 1. Cyclic voltammograms of MWCNT–GC electrode in 0.1 mM of cadmium solution in pH 7 buffer solution at scan rate of 100 mV s^{-1} with 30 cycles.

Fig. 2. SEM micrographs of the multiwall carbon nanotube modified glassy carbon electrode (A) and electrodeposited CdO on MWCNT-GC (B), scale bar 400 nm.

behavior ($I_{pa} \approx I_{pc}$) with ΔE_p (peak to peak separation potential) of 400 mV at 50 mV s^{-1} (Fig. 3A). The modification of the bare GC electrode with conductive MWCNTs resulted in higher I_p and smaller ΔE_p owing to an increase in the effective surface. The I_p of the CdO/MWCNT-GC modified electrode was even higher, illustrating high electrochemical activity of the CdO film layered on the MWCNT-GC surface. Fig. 3B presents a representative impedance spectrum of the bare GC (a), CdO/MWCNT-GC (b) and MWCNT-

GC (c) in 5.0 mM $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ containing 0.1 M KCl. In brief, the Nyquist plot shows a semicircle related to the redox probe $\text{Fe}(\text{CN})_6^{3-/4-}$ followed by a Warburg line in the low frequency region which corresponds to the diffusion step of the overall process. The collected impedance data were then analyzed using a modified Randles circuit (Fig. 3B, inset). The impedance of a faradaic reaction consists of an active charge transfer resistance R_{ct} and a specific electrochemical element of diffusion W , which is also called Warburg element $ZW = A_W/(j\omega)^{0.5}$, where A_W is the Warburg coefficient and ω is the angular frequency. The Warburg impedance (W), arising from diffusion of the redox couple to and from the electrode, is noticeable at low frequencies. The equivalent circuit was used mainly to determine C_{dl} and R_{ct} since R_s and W represent bulk properties of the electrolyte solution and diffusion of the applied redox probe, respectively, and are not sensitive to chemical transformation at the electrode interface [28]. Any change in C_{dl} should be negligible compared to the change in R_{ct} . A redox-active probe is useful in this case, resulting in a well-defined charge transfer resistance R_{ct} . The charge-transfer resistance R_{ct} of the MWCNT modified surface ($\sim 450 \Omega$) was significantly smaller than the bare GC electrode ($\sim 800 \Omega$), confirming the incorporation of conducting MWCNT on the electrode surface [34], in corroboration with the results described in Fig. 3A. With a thin CdO film layered on the electrode surface, the electron-transfer resistance R_{ct} was determined to be $\sim 1940 \Omega$ (curve b), implying the impediment of the electron transfer by the nano-CdO film.

3.3. Electrochemical properties of the CdO film deposited on MWCNT-GC electrode

From cyclic voltammograms (CVs) obtained for the modified electrode in $40 \mu\text{M H}_2\text{O}_2$, PBS pH 7, the anodic current plotted against the scan rate was linear (Fig. 4). The peak potential, however, was almost unaffected by the scan rate, illustrating a surface confined redox process without a kinetically controlled reaction or diffusion step. Such behavior could be attributed to the formation of the CdO film with high electroactivity for H_2O_2 . At lower sweep rates, the peak potentials were dependent on the scan rate due to the relative slow diffusion of hydroxide ions into the electrode surface [35]. With increasing scan rates, the peak potentials began to shift to negative reflecting the limitation arising from the catalyst properties of CdO. For an irreversible adsorption peak, the peak currents I_p can be related to the scan rate ν as follows [36]:

$$I_p = \frac{n^2 F^2 \nu A \Gamma_c}{4RT} = \frac{nFQ\nu}{4RT} \quad (1)$$

Fig. 3. Typical Nyquist diagrams of the impedance spectra of the bare GC electrode (a), The CdO/MWCNT-GC electrode (b) and the MWCNT-GC electrode (c) in 5 mM $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ in the ratio of 1:1 in 0.1 M KCl.

Fig. 4. Cyclic voltammetry response of CdO/MWCNT-GC electrode in 40 μM H_2O_2 (pH 7 buffer solution) at different scan rates; from inner to outer: 10, 20, 30, 40, 50, 70, 90, 110, 130, 150, 170, 190, 210, 230 and 250 mV s^{-1} . Insets, plot of peak currents (anodic peak) vs. scan rate.

where ν is the scan rate, I_p is the peak current (A), R is the gas constant, T is the temperature (Kelvin), Q (8.03×10^{-5} C) is the charge obtained by integrating the anodic peak at low scan rate (10 mV s^{-1}), A (0.0707 cm^2) is the working electrode area, n is the number of electron transfer, F is the Faraday's constant and Γ is the surface coverage (mol/cm^2). The estimated electron transfer number was ~ 1 , suggesting the oxidation reaction of H_2O_2 on the CdO/MWCNT-GC electrode is a one-electron transfer reaction, in agreement with the literature [26–27]. With a surface coverage (Γ) of $1.13 \times 10^{-8} \text{ mol/cm}^2$, the CdO/MWCNT-GC electrode possessed a high surface area for interaction with H_2O_2 . The sensor displayed excellent responses to H_2O_2 at pH 6 to pH 8 with the maximal current obtained at pH 7 (Fig. 5). The peak potential shifted to more positive when pH was decreased from 9 to 4. However, no peak current was observed at pH below 3 due to the disintegration of the CdO film in this acidic solution [37]. CVs obtained for five different electrodes in PBS pH 7 at 50 mV s^{-1} were almost identical (data not shown). The anodic peak current at -1.2 V obtained in the absence and presence of $20 \mu\text{M}$ H_2O_2 for the five electrodes was very comparable with RSD of 5.9%, confirming excellent reproducibility of the preparation of the CdO/MWCNT electrode.

Fig. 5. Cyclic voltammograms of the CdO/MWCNT-GC electrode in different pH solutions, from left to right, 9 to 3, scan rate 50 mV s^{-1} . Insets, the difference of the cathodic current in the presence and absence of $40 \mu\text{M}$ H_2O_2 in the same pH from 4 to 9, scan rate 50 mV s^{-1} .

3.4. Electrocatalytic oxidation of H_2O_2 on the CdO nanoparticles GC electrode

Fig. 6 shows CVs of the (c to f) and unmodified electrodes (a and b) in the absence and presence of $40 \mu\text{M}$ H_2O_2 . For the bare GC electrode, no redox response of H_2O_2 was observed in the potential range from -0.4 to -1.5 V . The MWCNT modified GC electrode (c and d) shows some oxidation current due to the electroactivity of MWCNTs [34] compared with a pronounced peak of the CdO/MWCNT-GC electrode (e and f). The anodic peak current was proportional to increasing H_2O_2 concentration $I (\mu\text{A}) = -0.242 C (\mu\text{M}) - 1.70$, $R^2 = 0.9977$ in the range of 1.5 – $300 \mu\text{M}$ with a detection limit of $0.5 \mu\text{M}$ ($S/N = 3$). In contrast, the cathodic peak diminished and then appeared with an increase in the H_2O_2 concentration (Fig. 7). According to the shoulder at $\sim -0.7 \text{ V}$, the CdO was a catalyst for the decomposition of H_2O_2 to water and oxygen, as described in Eqs. (2) and (3) [38].

From the synergetic excellent electrocatalytic property of MWCNT and catalytic property of CdO nanoparticle on the GC surface, a detection limit of the proposed electrode could be reach sub-micromolar level of H_2O_2 .

3.5. Amperometric detection of H_2O_2 at the modified CdO/MWCNT-GC electrode

As expected, no response current was observed for the bare GC electrode (Fig. 8a) whereas the MWCNT modified electrode only exhibited a very small signal for H_2O_2 (Fig. 8b) compared to the CdO/MWCNT-GC electrode. The CdO/MWCNT-GC electrode was insensitive to $100 \mu\text{M}$ dopamine, $100 \mu\text{M}$ uric acid and $100 \mu\text{M}$ ascorbic acid (Fig. 8c). Fig. 9 displays the typical response current with successive injection of $0.5 \mu\text{M}$ H_2O_2 at an applied potential -1.2 V vs. Ag/AgCl compared with PBS solution. From the response signal of H_2O_2 determination during 320 s of the experiment (Fig. 9b) remained stable, indicating no inhibitory effect of H_2O_2 and its oxidation products at the modified electrode surface. The response current was proportional to the H_2O_2 concentration from 0.5 to $200 \mu\text{M}$ with a limit of detection limit ($S/N = 3$) of $0.1 \mu\text{M}$. Thus, the electrode exhibited a better detection limit compared

Fig. 6. CVs of the modified and unmodified electrodes in the absence and presence of $40 \mu\text{M}$ H_2O_2 in buffer solution pH 7.0 at scan rate 50 mV s^{-1} .

Fig. 7. Cyclic voltammograms of CdO/MWCNT-GC electrode at different concentrations of H_2O_2 , scan rate 50 mV s^{-1} . Insets, the calibration curve of H_2O_2 at different concentrations.

Fig. 8. Chronoamperometric currents of the GC electrode (a), the MWCNT-GC electrode (b) and interfering effect of dopamine (DA), uric acid (UA) and ascorbic acid (AA) on the CdO/MWCNT-GC electrode (c) poised at -1.2 V in buffer solution (pH 7.0) for the addition of H_2O_2 (10 mM).

to several modified electrodes reported in the literature (Table 1). In brief, the methylene blue modified MWCNT and ruthenium oxide hexacyanoferrate electrode has a detection limit of $20 \mu\text{M}$ [39] and $2 \mu\text{M}$ [40], respectively. In this work, CdO shows better sensitivity than other metal oxide (Table 1). The linear range of the CdO-MWCNT modified electrode is also comparable with electrodes modified with metal or metal oxide nanoparticles [10–22].

3.6. Application for real samples

Hydrogen peroxide has been used as a tooth bleaching reagent in mouthwash. The maximum value is considered not over 3% (v/v) H_2O_2 in mouthwash. The determination of H_2O_2 in mouthwash samples were performed on the sensor utilizing standard addition method. After the current response was determined in 5.0 mL of 0.1 mol L^{-1} PBS buffer solution (pH 7) containing sample of 0.4 g (sample Nos. 1 and 2) and 2.5 mL (sample No. 3), H_2O_2 solutions was successively added to the system for standard addition determination. The accuracy of method (recovery) was also studied by spiking of an appropriate amount of H_2O_2 standard solution

Fig. 9. Chronoamperometric currents of the CdO/MWCNT-GC electrode in buffer solution pH 7. (a) for $0.5 \mu\text{M}$ H_2O_2 during a long period time (b) and for addition of H_2O_2 from 2.5 to $17.5 \mu\text{M}$. Insets, plot of peak currents (anodic peak) vs. H_2O_2 concentration.

Table 1
Comparison of nonenzymatic H_2O_2 sensors.

Sensor	Applied potential (V)	Linear range	Detection limit (μM)	Reference
Ag/MWCNTs	-0.2	$50 \mu\text{M}$ – 17 mM	0.5	[31]
PMB/MWCNTs	0.0	$100 \mu\text{M}$ – 3 mM	20	[39]
RuOHCF/MWCNTs	0.0	$100 \mu\text{M}$ – 10 mM	2.1	[40]
PB/MWCNTs	–	$80 \mu\text{M}$ – 1.0 mM	40	[41]
Pd/MCNs	-0.3	$7.5 \mu\text{M}$ – 10 mM	1.0	[42]
GSnano/CS	0.68	$5.22 \mu\text{M}$ – 10.43 mM	2.6	[43]
CdO/MWCNTs	-1.2	$0.5 \mu\text{M}$ – 0.2 mM	0.1	This work

PB = Prussian blue, RuOHCF = ruthenium oxide hexacyanoferrate, Pd = palladium, Ag = silver, MCN = mesoporous carbon nanosphere, GS nano = Silica nanoparticles on graphene oxide, CS = chitosan.

Table 2
Application of the proposed method for detection of hydrogen peroxide in mouthwash samples.

Sample	Add ($\mu\text{mol L}^{-1}$)	Found ($\mu\text{mol L}^{-1}$)	Recovery ($n = 3$)	H_2O_2 concentration found in sample
Sample 1	200	173	$86 (\pm 4.4)$	0.1288 g kg^{-1}
Sample 2	200	160	$80 (\pm 1.9)$	0.2390 g kg^{-1}
Sample 3	200	123	$61 (\pm 3.6)$	$401 \mu\text{mol L}^{-1}$

into samples. The recoveries and H_2O_2 concentration found in samples are shown in Table 2. The low recovery in sample 3 (61%) were noticed for samples spiked with $200 \mu\text{mol L}^{-1}$ H_2O_2 . The low recovery could be attributed to the presence of active ingredients in liquid mouthwash such as chloride fluoride and bromide ions, which would affect the ion exchange equilibrium on the CdO surface.

4. Conclusion

Potential cycling was used for the electrodeposition of CdO nanoparticles on MWCNT-GC electrode. The modified electrode showed well defined and stable voltammetric responses without interference from dopamine acid, uric acid and ascorbic acid.

Remarkable electrocatalytic activity, detection limit, greater analytical selectivity response of this modified electrode (prepared without using any specific reagent) are compared favorably to all other metal oxide modified electrodes employed as H₂O₂ sensors. Furthermore, the modification procedure is simple and more convenient than those used for other peroxide sensors. The analytical performance of the modified electrode indicates that it can be used as sensitive and selective amperometric detector for sub-micromolar concentration detection of H₂O₂.

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