

# Composite Palladium-Cobalt Oxide Films Modified N-silicon Electrode for Photo-electrochemical Detection of Hydrogen Peroxide

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**Abstract.** A novel nonenzymatic hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) sensor was fabricated, based on composite Pd-Co oxide films modified n-silicon electrode. The modified electrode was consisted of platinum coated n-silicon as substrate prepared by vacuum evaporating a platinum coating and composite Pd-Co oxide films deposited by electrochemical technique. The morphology of the modified electrode was characterized via scanning electron microscope (SEM). The analytical performances of the modified electrode for determination of H<sub>2</sub>O<sub>2</sub> were investigated by cyclic voltammetry (CV) and chronoamperometry. A new two electrodes photo-electrochemical cell has been used as sensor for H<sub>2</sub>O<sub>2</sub> determination by photocurrent measurements at zero voltage. The sensor showed good photocurrent responses by adding different concentrations of H<sub>2</sub>O<sub>2</sub> with a good stability. The linear ranges for the detection of H<sub>2</sub>O<sub>2</sub> are 2 to 48 μM with a detection limit of 0.57 μM in pH=7.0 phosphate buffer solution (PBS). In addition, the sensor also exhibited superior stability, anti-interference and portability. These features demonstrated that the new photo-electrochemical sensor was suitable for detection of H<sub>2</sub>O<sub>2</sub> on site outdoors..

## 1. Introduction

Photo-electrochemical (PEC) sensor has become a hot topic in analytical science and technology during recent years due to its remarkable sensitivity, inherent miniaturization, portability and easy integration, which has brought a wide and bright application prospect in the fields of biology, medicine, environment monitoring and etc [1]. PEC biosensor is a newly emerged analytical technique, which uses light to induce electron transfer between PEC-active species and electrode for generating the detectable photocurrent signal. Since the complete separation of excitation source(light) and detection signal (current), the undesired background signal is greatly reduced. Thus, photo-electrochemical technique possesses potentially higher sensitivity than the conventional electrochemical and optical methods [2]. Therefore, novel photoactive material should be developed and applied in PEC biosensors.

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The novel photoactive material should have appropriate energy bands to absorb almost the entire region of the visible spectrum while maintaining its structural and electronic integrity. Silicon material shows better photo-electrochemical performance owing to its excellent capability for photo-response, non-toxicity and ease of passivation and texturing [3]. In this study, we focus on Pd-Co composite oxide films, because they are easily synthesized by electrodeposition [4].

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is an essential mediator in food, pharmaceutical, clinical, industrial, and environmental analyses [5], so it is of great significance to determine the hydrogen peroxide rapidly, accurately, and conveniently. Various methods for  $\text{H}_2\text{O}_2$  determination have been developed, such as chemiluminescence [6], fluorescence-based imaging-fiber [7], high performance liquid chromatography [8], and electrochemistry [9]. However, it must be pointed out that these centralized and sophisticated analytical systems need complicated processes and expensive instruments. Therefore, many attentions have been paid to the development of high-performance hydrogen peroxide biosensors. In the present work, we report composite Pd-Co oxide films modified n-silicon electrode for photo-electrochemical detection of  $\text{H}_2\text{O}_2$  based on a two-electrode system at a zero voltage. The new sensor presents portability, high sensitivity, and long-term stability towards photocurrent determination of  $\text{H}_2\text{O}_2$ , which is potential for the development of bioelectronic devices and biosensors.

## 2. Experimental Method

**Materials, Chemicals and Main Apparatus.** A (111) oriented and phosphorus heavy doped silicon wafers (resistivity:  $0.003 \Omega \text{ cm}$ ) with 10-13  $\mu\text{m}$  epitaxial layer (resistivity: 3-5  $\Omega \text{ cm}$ ) were purchased from Semiconductor Materials Factory, Shanghai Nonferrous Metals Institute and referred to as n- $\text{n}^+\text{-Si}$ . High purity (>99.99%) platinum (Pt) wires (0.1mm) were purchased from Alfa Aesar Company. Palladium chloride ( $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ ) and cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) were purchased from Aladdin Chemistry Co. and Fuchen Chemical Reagent Factory (Tianjin, China), respectively. Analytical grade hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%) was obtained from the Shanghai Chemical Reagent Factory. In this work, 0.1 M pH 7.0 phosphate buffer solutions (PBS) were always employed as the supporting electrolyte after being deoxidized with high-purity nitrogen. Unless otherwise stated, reagents were of analytical grade and used as received. Aqueous solutions were prepared with doubly distilled water. Standard  $\text{H}_2\text{O}_2$  solutions were freshly prepared in a buffer solution before each experiment. A DM220 high vacuum system (Shanghai Optical Electron Company China) was used to evaporate Pt wires. Cyclic voltammetry (CV) and chronoamperometry experiments were performed using a LK 2005 electrochemical workstation (Lanlike Company, Tianjin, China).

**Electrode Fabrication.** Pd-Co composite oxide films were electrochemically deposited on a platinum film coated n- $\text{n}^+\text{-Si}$  (111) substrate. Before electrodeposition, silicon wafers were cleaned in HF solution, rinsed with water, and then dried with nitrogen gas. About 100 nm Pt film was coated on the front surface of n- $\text{n}^+\text{-Si}$  (111) wafers by vacuum evaporating to form Pt/n- $\text{n}^+\text{-Si}$  electrode. The back of the silicon wafer was coated with about 300 nm aluminum film in order to increase ohmic contact area. The coated wafers were annealed in vacuum at about 570 K for 25 min. The annealed Pt/n- $\text{n}^+\text{-Si}$  was placed onto a cell with an "O" shaped Teflon ring between the wafer and a hole with  $0.5 \text{ cm}^2$  of area on the wall of the cell, through which solution can reach the front surface of the electrode. The hole was covered with a freshly solution of electrodeposition solution containing 0.003 M  $\text{PdCl}_2$ , 0.0015 M  $\text{Co}(\text{NO}_3)_2$ , 0.1 M  $\text{H}_2\text{SO}_4$ . A three-electrode system was used for CV with Pt/n- $\text{n}^+\text{-Si}$ , a saturated calomel electrode (SCE) and a platinum plate as working electrode,

reference electrode and counter electrode, respectively, on the LK 2005 electrochemical workstation. An

illumination maintained from a 50 W bromine-tungsten lamp located 20 cm from the surface of the working electrode. The potential was then scanned from 0 to 0.70 V for thirty voltammetric cycles to electrochemically deposit the composite Pd-Co oxides on the electrode surface. The electrode was removed from solution and washed copiously to remove any residual species from the surface and referred to as Pd-CoO/Pt/n-n<sup>+</sup>-Si.

**SEM Analysis of the Modified Electrodes.** The morphology of the modified electrodes was observed with scanning electron microscope (SEM, Hitachi H-800).

**CV Measurement of H<sub>2</sub>O<sub>2</sub> on the Modified Electrode.** The photo-electrochemical behavior of the prepared Pd-CoO/Pt/n-n<sup>+</sup>-Si electrode in 0.1 M PBS (pH=7.0) was studied by CV measurements with successive addition of H<sub>2</sub>O<sub>2</sub> at a scan rate of 100 mV·s<sup>-1</sup> or in 0.5 mM H<sub>2</sub>O<sub>2</sub> concentration by different potential scan rate on the LK 2005 electrochemical workstation under illumination from a 50 W bromine-tungsten lamp. The Pd-CoO/Pt/n-n<sup>+</sup>-Si was used as working electrode. A SCE and a platinum plate were as reference electrode and counter electrode, respectively.

**H<sub>2</sub>O<sub>2</sub> Determination by Modified Electrode.** Chronoamperometry curves were obtained with two-electrode system consisting of the Pd-CoO/Pt/n-n<sup>+</sup>-Si electrode and a platinum plate counter electrode at zero applied voltage under illumination from a 50 W bromine-tungsten lamp located 20 cm from the surface of modified electrode. A 50 mL 0.1 M PBS (pH 7.0) was used as electrolyte and bubbled with high purity nitrogen for stirring.

### 3. Results and Discussion

**Electrodeposition of the Composite Pd-Co Oxide Films.** Fig. 1 shows the cyclic voltammograms in the electrodeposition process. Composite Pd-Co oxide films can be grown electrochemically on conductive substrates during a reduction process (CV) in a mixing solution containing Pd and Co salts [10]. Since in the oxidation and reduction process, dissolution and electrodeposition of films occurs alternately, so the deposited films are very compact and can adhere firmly to the electrode surface. With the increase of the scan number, the currents for both anodic and cathodic peaks increase steadily up to 30 runs, showing the increasing thickness of the films. Moreover, the films exhibit excellent conductivity and the outer deposited layers do not prevent the electrolyte ions diffusing to the vicinity of the already-deposited inner layers of the films [11].

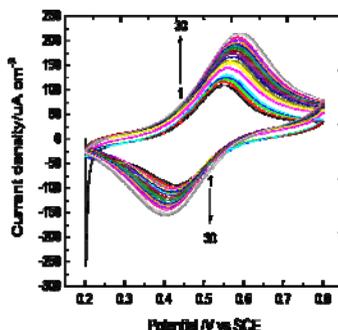


Fig. 1. Cyclic voltammograms in the electrodeposition process of composite Pd-Co oxide films from a solution mixture containing 3 μM PdCl<sub>2</sub>, 1.5 μM Co(NO<sub>3</sub>)<sub>2</sub>, 0.1 M H<sub>2</sub>SO<sub>4</sub> solution between 0 and +0.7 V at 50 mV·s<sup>-1</sup>. Cycles:30.

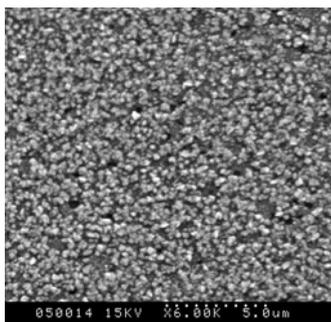


Fig. 2 SEM of composite Pd-Co oxide films (A) as-prepared by thirty voltammetric cycles from a solution mixture containing 3.0 m M PdCl<sub>2</sub>, 1.5 m M Co(NO<sub>3</sub>)<sub>2</sub>, 0.1 M H<sub>2</sub>SO<sub>4</sub> solution between 0 and +0.7 V at 50 mV·s<sup>-1</sup>.

Fig. 2 shows the SEM surface image of the Pd-CoO/Pt/n-n<sup>+</sup>-Si after using for 70 days of either aperiodic photocurrent measurements or storage in pure 0.1 M PBS (pH 7.0). We could see from the SEM images that the surface of silicon electrode covered with a composite membrane in compact and random accumulation. Even using as sensor for 70 days, the surface of modified electrode remained original nanocrystal structures and became slightly smooth. This indicates that the modified electrode is a considerable stable as a photo-electrode for more than once detections of H<sub>2</sub>O<sub>2</sub>.

**Photo-electrochemical Behaviors of H<sub>2</sub>O<sub>2</sub> on the Modified Electrode.**

Photo-electrochemical characterization of the Pd-CoO/Pt/n-n<sup>+</sup>-Si electrode was performed by CV under illumination. Fig. 3(A) shows CV scans of the modified electrode in 0.1 M PBS (pH=7.0) at a scan rate of 100 mV s<sup>-1</sup>. The concentration of H<sub>2</sub>O<sub>2</sub> from (a) to (f) is 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 mM, respectively. Oxidation current increased with H<sub>2</sub>O<sub>2</sub> concentration but the reduction current decreased with the H<sub>2</sub>O<sub>2</sub> concentration, which indicates obvious photo-electrocatalytic oxidation of H<sub>2</sub>O<sub>2</sub>. As shown in Fig. 3(B) a good linear relationship between the oxidation current at 0.46 V and H<sub>2</sub>O<sub>2</sub> concentration.

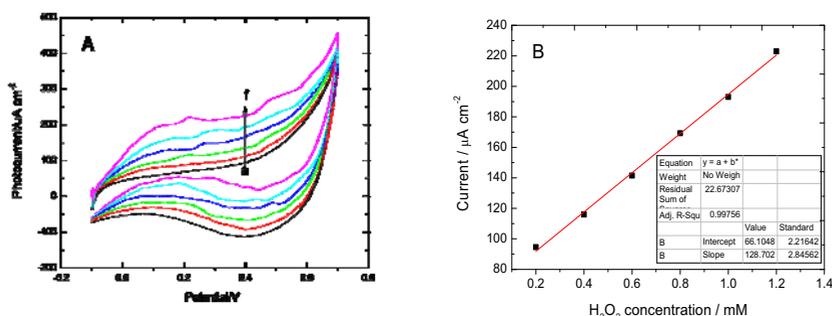


Fig. 3 (A) Cyclic voltammograms of the Pd-CoO/Pt/n-n<sup>+</sup>-Si electrode in 0.1 M PBS (pH=7.0) medium containing H<sub>2</sub>O<sub>2</sub> from (a) to (f) 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 mM, respectively, at a scan rate of 100 mV s<sup>-1</sup> (vs. SCE) under illumination. (B) the linear relationships of the oxidation current at 0.46 V.

**Photocurrent Response Behaviors of the Modified Electrode toward H<sub>2</sub>O<sub>2</sub>** The composite Pd-Co oxide modified layer on the electrode surface acts as a catalyst for the oxidation of H<sub>2</sub>O<sub>2</sub> in PBS. The photocurrent response of H<sub>2</sub>O<sub>2</sub> on the Pd-CoO/Pt/n-n<sup>+</sup>-Si electrode coupled to a Pt counter electrode was measured at a zero voltage in 0.1 M PBS (pH=7.0) by successive addition of H<sub>2</sub>O<sub>2</sub>. Fig. 4 (A) shows the photocurrent response of increased step wise for successive additions of 2 μM, 2 μM, 4 μM, 8 μM, 8 μM, 8 μM and 16 μM H<sub>2</sub>O<sub>2</sub> into 0.1 M PBS. Fig. 4 (B) illustrates a good linear response range from 2 μM up to 48 μM. The linear relationship can be given as photocurrent (μA cm<sup>-2</sup>) = 0.1673x (μM) + 1.1071 (R<sup>2</sup> =0.9966, n=6). A detection limit of 0.57 μM was obtained with a signal-to-noise of 3.

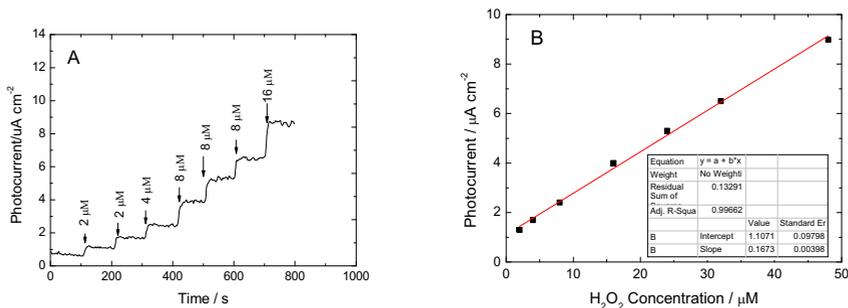


Fig. 4(A) Typical photocurrent signals of the Pd-CoO/Pt/n-n<sup>+</sup>-Si electrode during the successive addition of hydrogen peroxide 20 μM/time to PBS at zero voltage vs Pt counter electrode. (B): the relationship of photocurrent with concentration of H<sub>2</sub>O<sub>2</sub>.

**Selectivity and Stability of the Sensor for Detection H<sub>2</sub>O<sub>2</sub>** In order to verify the selectivity of the proposed modified electrode, ethanol, glucose, urea and L-cysteine were studied as interferential species for H<sub>2</sub>O<sub>2</sub> sensor. Experimental results showed that only small rise and fall of the photocurrent intensity of the modified electrode by injection of above mentioned interfering species. Therefore, the interference from the ethanol, glucose, urea and L-cysteine could be ignored compared with H<sub>2</sub>O<sub>2</sub> induced photocurrent. Stability tests for electrodeposited films were carried out under optimal conditions. Photocurrent response of the Pd-CoO/Pt/n-n<sup>+</sup>-Si electrode was over 80% of its original counterpart value after more than 70 days of intermittent usage and storage in 0.1 M PBS solution. This relative high stability could be attributed to the chemical composition of the composite Pd-Co oxide films and benign measurement conditions including no reference electrode and no applied voltage. This confirmed that the intermediate or product of the electro-oxidation reaction was not adsorbed at the composite Pd-Co oxide film surface and it represented an anti-fouling behavior towards the H<sub>2</sub>O<sub>2</sub> photoelectric oxidation or photoelectric reduction.

## 4. Conclusions

We fabricated a novel photo-electrochemical sensor for determination of hydrogen peroxide. The composite palladium-cobalt oxide films on silicon electrode were formed and characterized by electrochemical method and SEM. The modified silicon electrodes were used as sensors for a photocurrent detection of hydrogen peroxide. The new photo-electrochemical sensor presented a few of attractive features such as simplicity (two-electrode system), selectivity and good long-term stability, which were attributed to the absence of reference electrode and no applied voltage. So our sensor is more conducive to determining hydrogen peroxide on site outdoors.

## 5. Acknowledgement

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