

AMPEROMETRIC DETERMINATION OF H₂O₂ BY CARBON PASTE ELECTRODE SURFACE MODIFIED WITH SELF-ASSEMBLED IRIDIUM COMPLEX PARTICLES



¹University of Novi Sad, Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection, Trg D. Obradovića 3, 21000 Novi Sad, Serbia ²Division of Physical Science and Center of Excellence for Innovation in Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkha, 90112, Thailand

INTRODUCTION

Hydrogen-peroxide (H_2O_2) has widespread use in many fields including chemical, pharmaceutical, textile and food industries, environmental protection, medicine, etc. On the other hand, it is also a by-product of classical biochemical reactions catalyzed by enzymes from the group of oxidases. Since H_2O_2 itself is an electro-active molecule, nowadays voltammetry and amperometry are among the most convenient methods for its determination because of their simple operation, low cost, high sensitivity, rapid response, wide detection range and suitability for real-time detection. One of the analyte that is often determined using carbon based electrodes is H_2O_2 and nowadays H₂O₂ detection is mainly focused on electrode modifications with the aim to decrease the overpotential and increase the electron transfer kinetics [1–3]. In present work, previously synthesized photoactive iridium(III) complex with 3-methyl-2-phenyl pyridine and 1,1-bis(diphenylphosphino)methane i.e. [lr(3m-ppy)₂(dppm)Cl] which showed potential anticancer activity [4], was investigated as surface modifier of carbon paste electrode (Ir/CPE) for novel H₂O₂ sensor design.

For the development of amperometric method for the determination of H_2O_2 as target analyte it was necessary to optimize some basic parameters including amount of Ir based modifier on the CPE surface, duration of activation step (Fig. 3) and selection of working potential (Fig. 4). Taking into account both the sensitivity and selectivity of the working electrode, 0.60 V was selected as suitable working potentials for the amperometric determination of H_2O_2 . The linearity of the calibration curve was acceptable from 1.75 to 17.28 μ g mL⁻¹ H₂O₂, with RSD lower than 3% and the evaluated LOQ as 0.245 µg mL⁻¹ (Fig. 5). Ir/CPE was successfully applied for determination of H₂O₂ content in commercially available color cream developers using optimized protocol and standard addition method (Fig. 6).

EXPERIMENTAL

All chemicals used were of analytical reagent grade and the solutions were prepared with doubly distilled water. Phosphate buffer solution (0.1 M, pH 7.50) was used as supporting electrolyte. Diluted H_2O_2 solutions were prepared daily as required from standardized 30% H₂O₂. Voltammetric and amperometric measurements were performed on PalmSens2 electrochemical analyzer operated via software PSTrace 4.2. The voltammetric cell included a three-electrode system with an unmodified CPE or an Ir/CPE as the working electrode, a saturated calomel electrode as reference and a platinum auxiliary electrode. The Ir/CPE was prepared in one step using optimized drop coating procedure which includes the dissolution of the appropriate mass of complex in methanol, and immobilization of such prepared solution on the pristine CPE surface.

RESULTS AND DISCUSSION

After the surface modification of CPE with Ir(III) complex, SEM measurements confirmed that, beside the expected basic carbonaceous matrix, randomly distributed bright spherical particles are present over the CPE surface. The local microanalysis showed that bright spherical particles are made of Ir(III) complex with Ir as central ion and P and CI detected from the organic ligand part of the complex (Fig. 1).





Fig. 3. Current intensities for 21.82 µg mL⁻¹ H₂O₂ presented in the form of histogram (A) obtained using CPE (set 1) and CPE modified with 3 µL (set 2) and 15 µL (set 3) of methanolic solution of Ir complex, without activation (a) and with activation at 1.20 V in different time intervals: 15 min (b), 30 min (c) and 45 min (d). Amperograms of H_2O_2 recorded with activated Ir/CPE (E_{act} =1.20 V) in different activation time intervals indicated on curves in H₂O₂ concentration range 21.82–168.69 µg *mL*⁻¹ (*B*). Working potential in all cases: 0.60 V.



Fig. 1. SEM of unmodified CPE (A) and Ir/CPE (B) surfaces and representative part of the Ir/CPE surface (C) with its appropriate EDS microanalysis spectra in the presence of the spherical particles (D).

The electrochemical characterization of the prepared electrodes was performed by cyclic voltammetric experiments. In the case of Ir/CPE, in the anodic branch of the CV one irreversible peak was observed with the maximum around 1.2 V which probably corresponds to oxidation of Ir(III) to higher oxidation state (Fig. 2A). CVs were also recorded with Ir/CPE in the absence of H_2O_2 and in the presence of three different concentrations of H_2O_2 as target analyte (Fig. 2B).

Fig. 4. Amperometric signals of H₂O₂ recorded with electrochemically activated Ir/CPE (E_{act}=1.20 V, t_{act}=60 min) in 0.1 M phosphate buffer pH 7.50 at different working potentials: from 0.30 to 0.60 V (A) and from 0.00 to -0.25 V (B). H₂O₂ concentration range: 17.47–136.00 µg mL⁻¹.

Fig. 5. Amperograms of H₂O₂ recorded with electrochemically activated Ir/CPE (E_{act}=1.20 V, t_{act}=60 min) at working potential 0.60 V (A) together with corresponding calibration curve (inset A). Repeatability of H₂O₂ signals at 0.60 V based on six repeated measurements with the same Ir/CPE surface (B). H_2O_2 concentration range: 1.75–17.28 µg mL⁻¹.

Fig. 2. CVs recorded in 0.1 M phosphate buffer pH 7.50 with CPE (curve 1) and Ir/CPE (first scan curve 2, second scan - curve 3, third scan - curve 4), scan rate: 25 mV s⁻¹ (A). CVs recorded with Ir/CPE after its electrochemical activation in the absence (curve 1, dashed line) and in the presence (full lines) of 285.6 (curve 2), 537.2 (curve 3) and 819.4 (curve 4) µg mL⁻¹ H₂O₂; scan rate: 50 mV s⁻¹ *(B)*.

Fig. 6. Schematic illustration of H₂O₂ determination in color cream developers.

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