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# Fabrication of Carbon Paste Electrode Containing $[PFeW_{11}O_{39}]^{4-}$ Polyoxoanion Supported on Modified Amorphous Silica Gel and its Electrocatalytic Activity for $H_2O_2$ Reduction

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## Abstract

$[PFeW_{11}O_{39}]^{4-}$ ($PFeW_{11}$) supported on the surface of 3-aminopropyl(triethoxy)silane modified silica gel was synthesized and used as a bulk modifier to fabricate a renewable three-dimensional chemically modified electrode. The electrochemical behavior of the modified electrode was investigated. Cyclic voltammetry studies showed that the $PFeW_{11}$ on the electrode surface sustained the same electrochemical properties as that of the $PFeW_{11}$ in solution. The preparation of chemically modified electrode is simple and quiet reproducible using inexpensive material. The modified electrode had high electrocatalytic activity towards $H_2O_2$ reduction and it was successfully applied as an electrochemical detector to monitor $H_2O_2$ in flow injection analysis (FIA). The electrocatalytic peak current was found to be linear with the $H_2O_2$ concentration in the range 10 – 200 μmol $L^{-1}$ with a correlation coefficient of 0.998 and a detection limit (3σ) of 7.4 μmol $L^{-1}$ $H_2O_2$. The electrode has the remarkable advantage of surface renewal owing to bulk modification, as well as simple preparation, good mechanical and chemical stability and reproducibility.

**Keywords:** $PFeW_{11}O_{39}^{4-}$; Silica gel; Carbon paste electrode; Electrocatalysis, Hydrogen peroxide.

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## 1. Introduction

Polyoxometalates (POMs) have attracted increasing attention in recent years. This is because of their excellent properties such as the possibility of tuning POM size, shape, charge density, acidity, redox potential, stability, and solubility characteristics [1, 2]. These properties have led to many applications of these compounds in analytical science [3-9] catalysis [10 - 12] medicine [13], and material science [14, 15].

Transition metal-substituted POMs constitute the largest subclass of polyanions, which are of particular interest in catalysis and electrocatalysis. These compounds that contain one or more transition metal ions coordinated to a totally inorganic tungsten-oxo framework which are inert to typical ligand oxidation reactions, have attracted considerable attention due to the possibility of replacing porphyrins as catalysts in many reactions. Up to now, a series of transition-metal-substituted polyoxometalates have been studied extensively, especially with respect to their electrochemical and electrocatalytic properties [16 - 20].

Although, there is an increasing interest in the electrocatalytic properties of POMs, their application in the development of chemically modified electrodes (CMEs) is limited. The key reason is the high solubility of POMs in aqueous solutions. Practical applications of POMs for the preparation of CMEs depend on successful immobilization of these compounds. Immobilization of POMs onto electrodes simplifies their electrochemical studies and facilitates their applications in electroanalysis. There are several methods for the immobilization of POMs onto electrode surface including: electrochemical deposition [21 - 23], adsorption [5, 24, 25] use of carbon nano tubes [26], as dopant in a polymer matrix [6, 27, 28], layer by layer molecular self-assembly process based on electrostatic attraction as the driving force [29-33] and entrapment in sol-gel matrix [8, 9]. A serious drawback of the electrodes modified by these methods is their poor long-term stability. Moreover, the electrode surfaces can not be renewed in the event of leakage, contamination or passivation. In order to overcome this problem, it is desirable to develop a new simple and reliable procedure for the preparation of three-dimensional bulk POM modified electrodes. There are two main methods used to prepare three dimensional bulk modified electrodes: carbon ceramic electrodes (CCEs) and carbon paste electrodes (CPEs). Since the pioneering work of Lev's group [34] on





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ceramic graphite composite electrodes (CCEs), much effort has been devoted to the fabrication of POM-chemically modified CCEs [35 - 37]. This is due to a number of advantages, including low-temperature encapsulation of active species, tunability of physical characteristics, mechanical rigidity, and low chemical reactivity [37]. The main advantages of such electrodes are their long-term stability and especially reproducibility of surface renewal. But, the silica sol–gel matrixes also have some obvious shortcomings, such as fragility, hydrolysis at high acidity, and complicated procedures. The shortcomings limited their applications in chemically modified electrodes [17].

Carbon paste electrode (CPE) is one of the convenient conductive matrixes to prepare the chemically modified electrodes (CMEs) by simple mixing of graphite/binder paste and modifier [38]. These kinds of electrodes are inexpensive and possess many advantages such as low background current, wide range of used potential, easy fabrication, and rapid renewal. Generally, the modifiers used in direct mixing should be insoluble in the analytic solution, or at least should be strongly adsorbed to the paste components to avoid its leaching during the measurements. Owing to their solubility, the traditional POMs cannot be directly used as bulk modifiers in CPE. Recently, an interest has focused on the design and preparation of novel POM-based hybrid materials, as well as their application in the three-dimensional bulk-modified CPE by direct mixing. Carbon paste electrodes modified with phosphomolybdic anions encapsulated in modified mesoporous molecular sieve MCM-41 [39], $(H_{3/4}pbpy)_4[PMo_{12}O_{40}].1.25H_2O$ [40], $(Hbpy)_4[SiMo_{12}O_{40}]$ [41], $(C_{21}H_{38}N)_3PMo_{12}O_{40}.H2O$ [3], and $[Cu(phen)_2]_2PVW_{11}O_{40}$ [42], $H_2[Cd(phen)_3]_2\{[Cd(H_2O)(phen)_2](V_{16}O_{38}Cl)\}\cdot 2.5H_2O$ and $H_2[Cd(bipy)_3][Cd(H_2O)(bipy)_2]\{[Cd(H_2O)(bipy)_2](V_{16}O_{38}Cl)\}\cdot 1.5H_2O$ [43] have been prepared and their electrochemistry and electrocatalytic effects have been reported.

Iron-substituted POMs has attracted considerable attention [20, 44, 45]. This is because of its catalytic applications due to the easily accessible $Fe^{2+/3+}$ redox couple. Iron-substituted POMs are effective catalysts for the $H_2O_2$-based epoxidation of alkenes and electrocatalysts for the reduction of $H_2O_2$ and $O_2$ [20]. Although, the investigation of electrochemical behavior of iron-substituted POMs were the subject of some research articles, on the best of our knowledge, there is only one report on the application of iron-substituted POMs as mediator in preparation of modified electrodes [6]. In that work,

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Popescu et al. [6] immobilized $PFeW_{11}$ within two different polymeric films, including polypyrrole as an electroconductive polymer and polyvinyl alcohol as an inert polymer. The polyoxoanion, immobilized in both polymeric films exhibited clear electrochemical redox activity associated with the Fe(III) centers of the POM, qualitatively retained its electrochemical behavior exhibited in solution, but for both the immobilization matrices the electrocatalytic efficiency and the sensitivity toward $H_2O_2$ reduction were lower. Popescu et al. have given emphasis to the low stability of the modified electrodes and need to the development of softer immobilization techniques.

In the present work, our preliminary study on the synthesis of POM supported on organofunctionalized silica gel and fabrication of three-dimensional POM-modified CPE [46] is extended to the synthesis of $PFeW_{11}$ supported on amorphous silica organofunctionalized with 3-aminopropyl(triethoxy)silane (APS) and its application in the preparation of $PFeW_{11}$ modified CPEs. The electrochemistry of the $PFeW_{11}$/ organofunctionalized amorphous silica (APS-$PFeW_{11}$) modified CPE was studied by cyclic voltammetry and it is found that $PFeW_{11}$ retains its electrochemical properties when it is supported on the surface of APS. The APS-$PFeW_{11}$ showed good electrocatalytic activity toward $H_2O_2$ reduction. Such a system can provide a novel electrochemical sensor for the reductive determination of $H_2O_2$. Since there is no leaching of the electrode material into the aqueous solution, because of the low solubility of $PFeW_{11}$ supported on APS, a single electrode surface can be used for multiple analytical determinations over several weeks. The chief advantage of the proposed modified-CPE is its renewability in a reproducible manner by squeezing a little carbon paste out the tube and providing a fresh surface whenever needed. The performance of the APS-$PFeW_{11}$ modified CPE was optimized for use as an analytical sensor for $H_2O_2$ detection. Being a preliminary attempt, the modified electrode was successfully utilized as an amperometric detector in flow injection analysis (FIA).

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## 2. Experimental

### 2.1. Apparatus

An Autolab electrochemical analyzer model PGSTAT30 (Eco Chemie, Utrecht, The Netherlands) controlled by a microcomputer with GPES 4.9 software was used for voltammetric measurements. A three electrode cell was used, including carbon paste electrode or carbon paste electrode modified with APS-$PFeW_{11}$ as working electrode, together with an Ag/AgCl (saturated KCl) and a platinum wire as reference and counter electrode, respectively.

Thermogravimetric analyses were carried out between 30 and 600 °C (under nitrogen at 5 °C/min) on a Mettler TA4000 thermobalance. Infrared absorption spectra were recorded on a FT-IR Bruker Vector 22 spectrometer, using KBr pellets.

A peristaltic pump model Minipuls3 (Gilson, France) with silicon tubing and a Rheodyne injection system model EV 700-100 with Teflon tubing (i.d.: 0.5 mm) were used for flow injection analysis. A home-made wall-jet cell was employed as the electrochemical detector with the potential monitored by a Metrohm 791 VA detector.

A Metrohm 713 pH meter was used for pH measurements.

### 2.2. Reagents and Solutions

All solutions were prepared with distilled water. All chemicals were of analytical grade from Merck and Fluka and used without further purification. Stock solution containing about 0.5 mole $L^{-1}$ hydrogen peroxide was prepared by dissolving 5 mL of 30% w/w hydrogen peroxide solution (d = 1.11 g $mL^{-1}$) in water and diluting to 100 mL. This solution was standardized against standard potassium permanganate solution. More dilute solutions were prepared by diluting this solution with water. Sulfuric acid solution was prepared by dissolving 2.7 mL of concentrated sulfuric acid (95 - 98% w/w) in water and diluting to 100 mL. Appropriate volumes of this solution were adjusted to the required pH with sodium hydroxide solution.

### 2.3. Preparation and Characterization of $PFeW_{11}$- Modified Silica Gel

The modified silica gel was prepared according to the methodology already described in the literature [47, 48]. This methodology contains two main steps. In the first step, silica

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gel derivatized by 3-aminopropyl(triethoxy)silane (APS) was prepared according to the following procedure: 100 g silica gel (K-60) was mixed with 300 mL 6 $molL^{-1}$ hydrochloric acid and the mixture was refluxed for 24 h. The resulting mixture was filtered, washed with large amounts of water and dried at 130$^{o}$C overnight to obtain activated silica gel. 10 g of the activated silica gel was added to absolute ethanol solution of APS (200 mL, 150 mmol $L^{-1}$) and stirred at room temperature for 24 h. The resulting material (Si-$RNH_2$) was washed by decantation with ethanol, and then dried at 95$^{o}$C overnight. For protonation of amino groups, 5 g of the resulting solid particles were mixed with 200 mL of 3 M $HClO_4$ for 24 h and then washed with large amount of water to eliminate protons adsorbed on the surface of silica. The product (Si-$RNH_3^+$) dried at 90$^{o}$C overnight.

In the second step of method, 100 mmole $Na_2WO_4.2H_2O$ was dissolved in 20 ml water. To this solution was added 9.1 mmole $Na_2HPO_4$ and 12 mmole $Fe(NO_3)_3$. The pH of suspension was adjusted to 4.5 with concentrated nitric acid under stirring condition, and then mixture was heated to 80-85°C. A white precipitate (APS-$PFeW_{11}$) was appeared in the hot reaction mixture by addition of 13.5 g APS. The resultant mixture was allowed to stir at room temperature for two days. Finally, the mixture was filtered and washed with 1M $HNO_3$ thoroughly to eliminate $PFeW_{11}$ residual molecules which might be adsorbed on silica gel matrix. The product then dried in air.

For comparison purpose, APS-$PW_{11}$ was prepared with similar method without addition of $Fe(NO_3)_3$ in second step of procedure.

Characterization of transition metal substituted 3-Aminopropyl-functionalized silica gel was accomplished by elemental analysis and infrared absorption spectroscopy. The elemental analysis data for APS (silica$(CH_2)_3NH_2$): C, 3.11%; H, 0.9%; N, 0.82%, and APS-$PW_{11}$Fe: C, 2.90%; H, 0.8%; N, 0.78%; W, 6.0%; Fe, 0.17% showed that about 8% (w/w) of polyoxometalate attached to the functionalized silica. From the analytical results (mole ratio of W/Fe = 10–11) it also can be suggested that no degradation of the Keggin type transition metal substituted polyoxometalate occurred

FT-IR spectra of APS-$PW_{11}$Fe showed the main strong bands for the silica framework and partially the characteristic bands of polyoxoanions corresponding to the

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stretching vibrations of P–O, W=O and W–O–W bonds in the 400–1100 $cm^{-1}$ infrared region.

Thermogravimetric analyses of APS-$PW_{11}Fe$ showed two step loos in weight: in first step, weight loss up to about 150 °C, assigned to the loss of hydration water, and in second step, beginning near 270 °C, assigned mainly to the decomposition of propylamine group.

### 2.4. Fabrication of the Carbon Paste Electrodes

The unmodified carbon paste electrode was prepared by mixing graphite powder with an appropriate amount of paraffin oil and thorough hand mixing in a mortar and pestle (75:25, w/w), and a portion of the mixture was packed into the end of an insulin syringe (i.d.: 2 mm). Electrical contact was made by forcing a copper pin down into the syringe and into the back of the composite. The modified electrode was prepared by mixing the unmodified mixture with APS-$PW_{11}Fe$ and then (for better homogeneity and reproducibility by polishing the electrode surface) diethylether was added to the resulted composite. The mixture was stirred by a magnetic stirrer till the solvent evaporated completely. The prepared modified composite was then air dried for 24 h and used in the same way as the case of the unmodified electrode. The surface of the electrode was smoothed on a piece of weighing paper. The new surface can be obtained by pushing some of paste out of the tube, removing the excess, and polishing again mechanically the electrode surface.

## 3. Result and Discussions

### 3.1 Cyclic Voltammetric Studies of APS-$PFeW_{11}$ modified electrode

The electrochemical studies of the APS-$PW_{11}$- and APS-$PFeW_{11}$-CPEs were carried out in acidic (pH 2) aqueous solution, because $PW_{11}$ and $PFeW_{11}$ are unstable in neutral and basic aqueous solutions. Figure 1a shows the cyclic voltammograms of the APS-$PW_{11}$-CPE in aqueous 0.5 M $H_2SO_4$ adjusted to pH 2 by concentrated sodium hydroxide solution. As can be seen, the voltammogram of APS-$PW_{11}$-CPE in the potential range 250 to -800 mV (vs. Ag/AgCl), exhibits two characteristic peaks of the polyoxoanion. The mean peak potentials, $E_{1/2} = (E_{pa}+E_{pc})/2$, were -0.493 V (I), and -0.690 V (II). In this

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Figure also shows voltammogram of the APS-$PFeW_{11}$-CPE in the same solution (curve b). The voltammogram of APS-$PFeW_{11}$-CPE shows three redox couples two of which are similar to the redox peaks of $PW_{11}$ [49]. Hence, the redox couple (III) with mean peak potential of 0.107 V corresponds to the Fe(III)/Fe(II) redox couple. The electrochemical behavior of APS-$PW_{11}$ and APS-$PFeW_{11}$ are similar respectively, to the behavior of $PW_{11}$ and $PFeW_{11}$ in solution [6]. This indicates that supporting of $PFeW_{11}$ and $PW_{11}$ retain their electrochemical properties when they are supported on the surface of 3-aminopropylated silica via electrostatic interaction.

In continuation, we focused our studies on the Fe(III)/Fe(II) redox couple. The electrochemical properties of the prepared modified electrode in the pH range 0.5 – 3.0 were investigated by recording the cyclic voltammograms. The results indicated that the mean peak potential of the iron redox couple did not change, but reversibility and peak currents changed with changing pH values. As shown in Fig. 2, peak currents are maximum and independent of pH in the rang 1.0 - 2.0. The decrease of peak current at pH range greater than 2.0 could be related to decrease in the mass transfer rate of $H^+$ to the electrode surface. The role of $H^+$ in this process is to maintain the electroneutrality within the APS-$PFeW_{11}$ modified CPE upon redox switching through the Fe(III/II) redox system. This observation is in good agreement with increasing the peak potential separation of the iron redox couple with increasing pH.

The effect of the carbon paste composition in the voltammetric response of the modified electrode was evaluated by cyclic voltammetry. As it was expected, the amount of APS-$PFeW_{11}$ in the carbon paste had a marked influence on the response of the electrode and the peak currents increased with increasing the modifier concentration in the CPE. However, at concentration higher than 10% of APS-$PFeW_{11}$ the paste is too rigid and its handling is very difficult. Hence, an electrode containing 10% APS-$PFeW_{11}$ was used for further studies.

The long term stability of the modified electrodes was very good. When the electrode was stored in the atmosphere, the current response remained almost unchanged even after 1 month (Fig. 3A). The working stability of the modified CPE was investigated by recording the repetitive cyclic voltammograms and monitoring the changes in peak current and peak potential of the electrode. The electrode retained 95% of its initial



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activity after 100 repetitive cycles in 0.5 M $H_2SO_4$ (adjusted to pH 2) in the potential range of -0.2 to 0.4 V (Fig. 3B). High stability of the APS-$PFeW_{11}$-modified CPE could be related to the strong electrostatic interaction between derivatized silica gel and $PFeW_{11}$ and insolubility of silica gel in water.

One of the main advantages of bulk modified electrodes over surface modified electrodes is that the electrode surface can be renewed easily. This is especially useful for electrocatalytic studies since the catalytic activity is known to decrease when the electrode is fouled. The reproducibility of the electrode surface was studied by renewing the modified electrode surface six times and performing cyclic voltammetry in 0.5 M $H_2SO_4$ (adjusted to pH 2) solution after each renewing step. The RSD of the measured cathodic peak currents was 4%.

### 3.2 The Electrocatalytic Reduction of Hydrogen Peroxide at APS-$PFeW_{11}$ Modified Carbon Paste Electrode

One of the objectives of current study was fabricating a modified electrode capable for the electrocatalytic reduction of hydrogen peroxide at reduced overpotential. Cyclic voltammetry was used to test the electrocatalytic activity of the APS-$PFeW_{11}$ modified CPE toward electroreduction of hydrogen peroxide. It is known the electroreduction of hydrogen peroxide requires a large overpotential, so no obvious response was observed in the range 0.35 to −0.15V on an unmodified CPE in 0.5 M $H_2SO_4$ solution (pH 2) containing 0.5 and 1 mM hydrogen peroxide, (Fig. 4A). The electrocatalytic reduction of $H_2O_2$ by APS-$PFeW_{11}$ modified carbon paste electrode can be clearly seen in Fig. 4B. From this Figure it can be seen that the reduction peak current increases with increasing hydrogen peroxide concentration, whereas the corresponding oxidation peak current decreases, suggesting that hydrogen peroxide is reduced by reduced species of polyoxometalate. The catalytic current increases with the concentration of hydrogen peroxide. Therefore, the electrochemical behavior of an APS-$PFeW_{11}$ modified CPE towards hydrogen peroxide could be regarded as an EC' catalytic mechanism.

The voltammetric results described above shows the feasibility of using the APS-$PFeW_{11}$-modified CPE for amperometric detection of hydrogen peroxide. Flow injection

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analysis was performed to verify whether the electrocatalytic reduction of hydrogen peroxide by the APS-$PFeW_{11}$-modified CPE can be conducted under flow conditions and to evaluate its potential as an electrochemical detector for determination of this compound. The carrier solution was 0.5 M sulfuric acid adjusted to pH 2 with sodium hydroxide solution. In order to obtain the best sensitivity and selectivity for the electrochemical detection for $H_2O_2$, the effect of various parameters including, applied potential, size of sample injection loop and carrier solution flow rate were studied. As it was expected, the applied potential had a remarkable effect on both catalytic and uncatalytic currents. The results of this study (not shown) indicated that the $H_2O_2$ reduction current on the modified CPE increased with changing the applied potentials in the range +200 - 0 mV while the observed current on the unmodified CPE was small and independent of the applied potential. At more cathodic potentials,the peak currents on both modified and unmodified CPEs increased by changing the applied potential. Therefore, a potential of 0 mV was selected as optimum analytical procedure. The effects of carrier flow rate and sample loop volume of FIA system were also studied. The best results were obtained at a flow rate of 0.6 mL $min^{-1}$ and an injection loop volume of 75μL.

Fig. 5A compares the amperometric response of the modified CPE to successive additions of hydrogen peroxide. As indicated from the resulting calibration plot (Fig. 5B), the response of the modified electrode is linear over 10–200 μM concentration range with a slope of 0.183 nA/μM and a correlation coefficient of 0.9985. The favorable signal to noise characteristics of these data indicate a detection limit of 7.4 μM (based on S/N = 3). These analytical parameters are comparable or better than results reported for analytical determination of hydrogen peroxide at the surface of different POM – modified electrodes (Table 1).

Fig. 6 displays the stability and reproducibility of the response for repetitive injections (ten times) of 100 μM $H_2O_2$ under the same experimental conditions every 40 s. The relative standard deviation of the peak current was found to be 4.6%.





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## 4. Conclusions

A modified carbon paste electrode containing $PFeW_{11}$ polyoxometalate supported on functionalized silica gel was fabricated. The cyclic voltammograms of the modified electrodes show a well-defined redox couple for the Fe(III)/Fe(II) system with surface confined characteristics. The Fe(III)/Fe(II) couple catalyzed the reduction of $H_2O_2$ and exhibited excellent sensitivity and stability for the determination of this compound, at the reduced overpotential. Table 1 shows a comparison of analytical parameters of different POM-modified electrodes for determination of hydrogen peroxide. The proposed electrode offers attractive properties compared to the pervious studies such as low detection limit (7.4 μM) and wide linear dynamic range (0.01 to 0.2 μM). Also the electrode offers attractive properties such as reproducibility, simplicity of electrode preparation, high stability and a distinct advantage of renewing and simple polishing in the event of surface fouling. Further, due to low solubility of APS-$PFeW_{11}$ in aqueous solution there is no leaching of the electrode material, hence a single electrode surface can be used for multiple analytical determinations. The main limitation of the proposed electrode which is common in most POM-modified electrodes is loss of stability and catalytic activity at biological pHs which make it impossible to measure hydrogen peroxide produced in enzyme reactions (c. f. Table 1). This drawback limits the utilization of POM-modified electrodes and directed our efforts toward the synthesis and applications of polyoxometalates with stability and catalytic activity at neutral pHs.

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Fig. 1. Cyclic voltammograms of 10% APS-$PW_{11}$ modified-CPE (a) and 10% APS-$PFeW_{11}$-CPE (b) in the 0.5 M $H_2SO_4$ with pH 2 solution. Scan rate: 50 $mVs^{-1}$.

Fig. 2. Variation of cathodic peak current of CPE modified with 10% of APS-$PFeW_{11}$ with pH of solution. Scan rate: 50$mVs^{-1}$.

Fig. 3. Cyclic voltammograms of the APS-$PFeW_{11}$ modified carbon paste electrode after 1 (dashed line) and 30 days (solid line) of preparation (A) and variation of cathodic peak current with number of repetitive cycles (B) in 0.5 M $H_2SO_4$ aqueous solution (pH 2). Scan rate: 50$mVs^{-1}$.

Fig. 4. Cyclic voltammograms of bare CPE (A) in 0, 0.5 and 1mM $H_2O_2$ (from inner to outer) and 10% APS-$PFeW_{11}$ modified-CPE (B) in solution of 0.5 $H_2SO_4$ with pH 2 containing $H_2O_2$ concentrations of 0.0, 0.5, 1, 5, 10, 30 and 40 mM $H_2O_2$ (from inner to outer). Scan rate: 50$mVs^{-1}$.

Fig. 5. FIA response of various concentrations of $H_2O_2$ at APS-$PFeW_{11}$-CPE. Carrier: solution of 0.5 M $H_2SO_4$ with pH 2.0. Applied potential: 0 mV (vs. Ag/AgCl). Volume of sample injection loop: 75μL and flow rate: 0.6mL $min^{-1}$.

Fig. 6. Repetitive flow injection measurements of 100 μM $H_2O_2$. Conditions as in Fig. 5.

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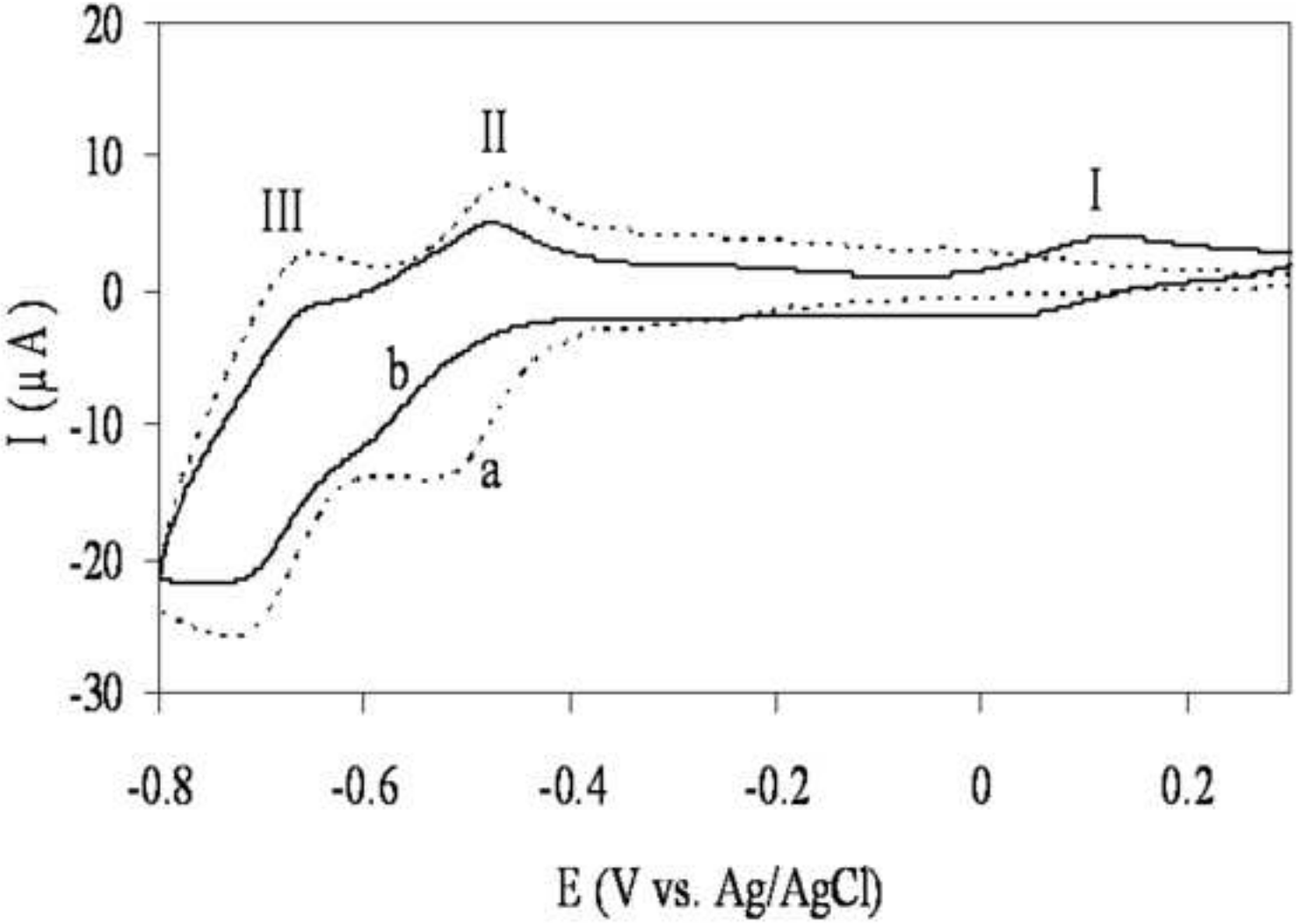



Fig. 1

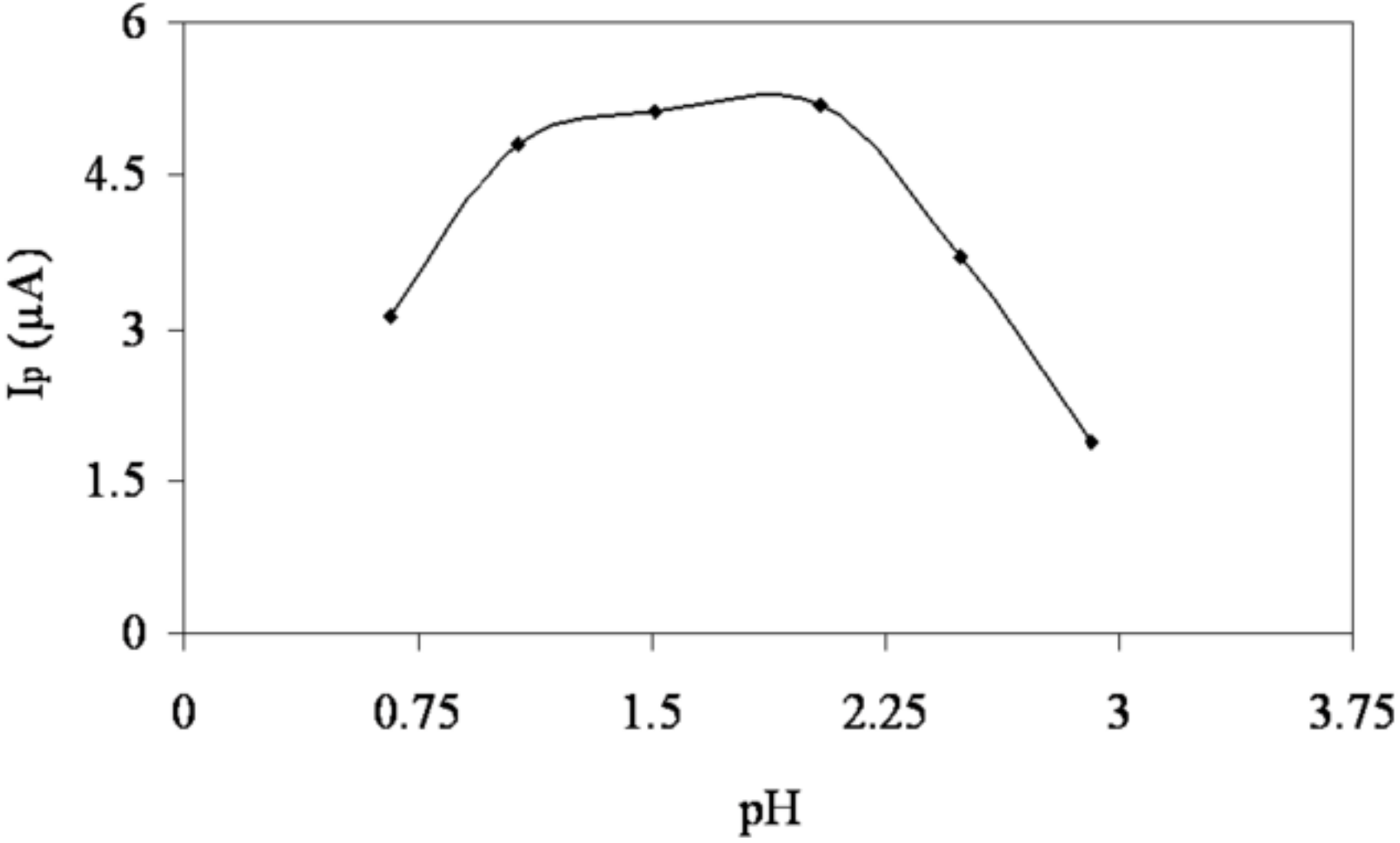
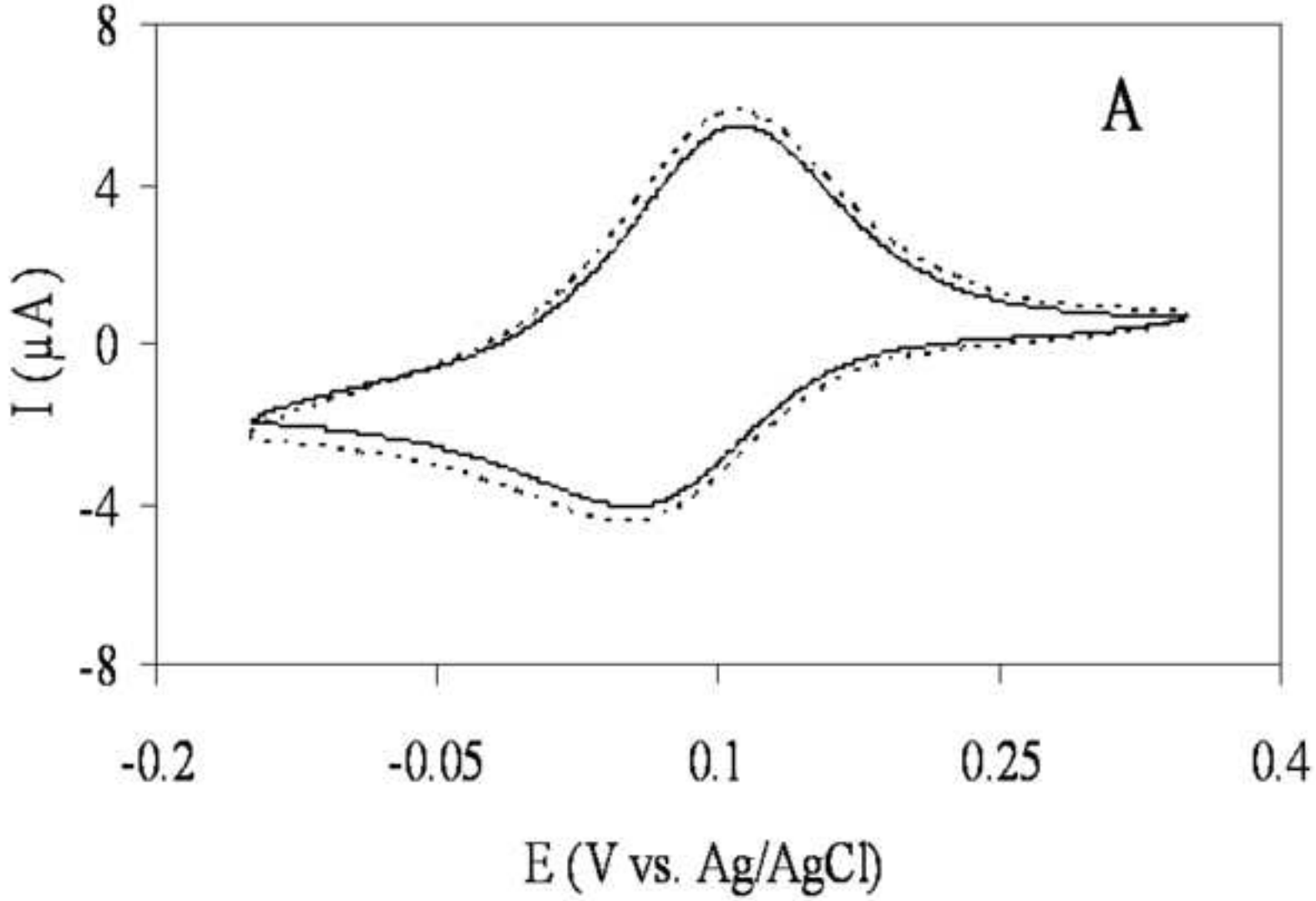



Fig. 2

**Figure(s)**



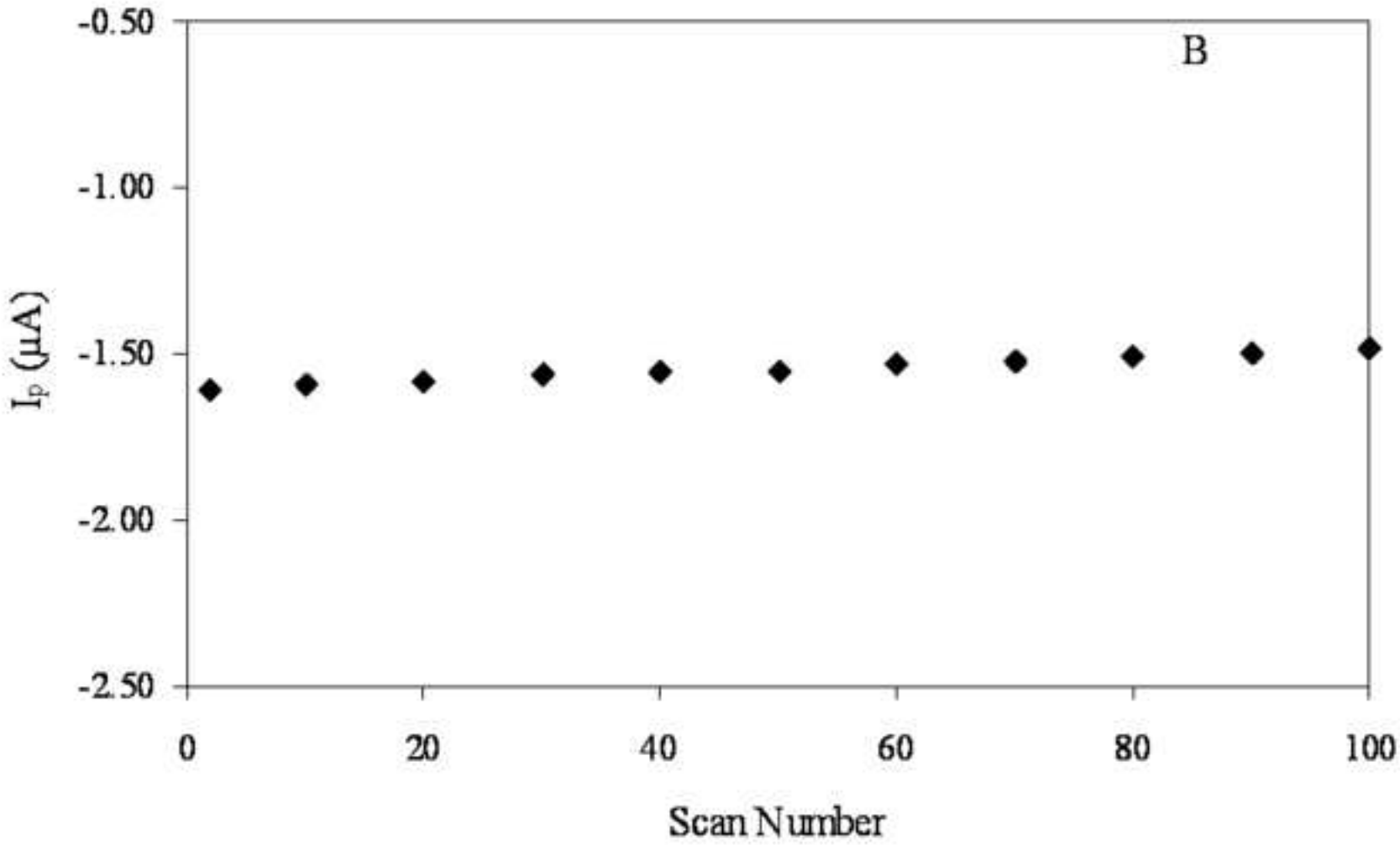



Fig. 3

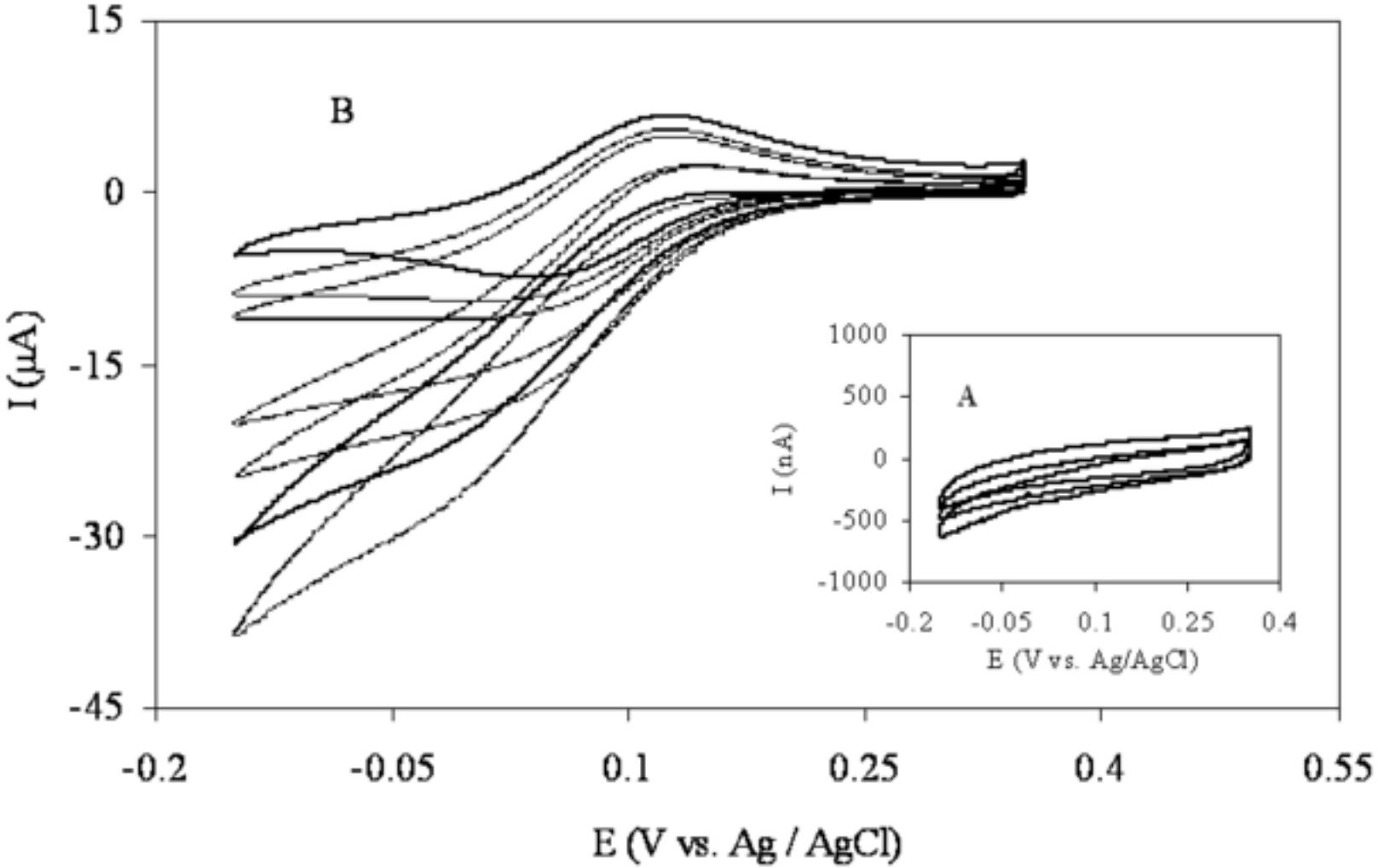

15
0
-15
-30
-45
I (μA)
B
-0.2
-0.05
0.1
0.25
0.4
0.55
E (V vs. Ag / AgCl)
1000
500
0
-500
-1000
I (nA)
A
-0.2
-0.05
0.1
0.25
0.4
E (V vs. Ag/AgCl)

Fig. 4

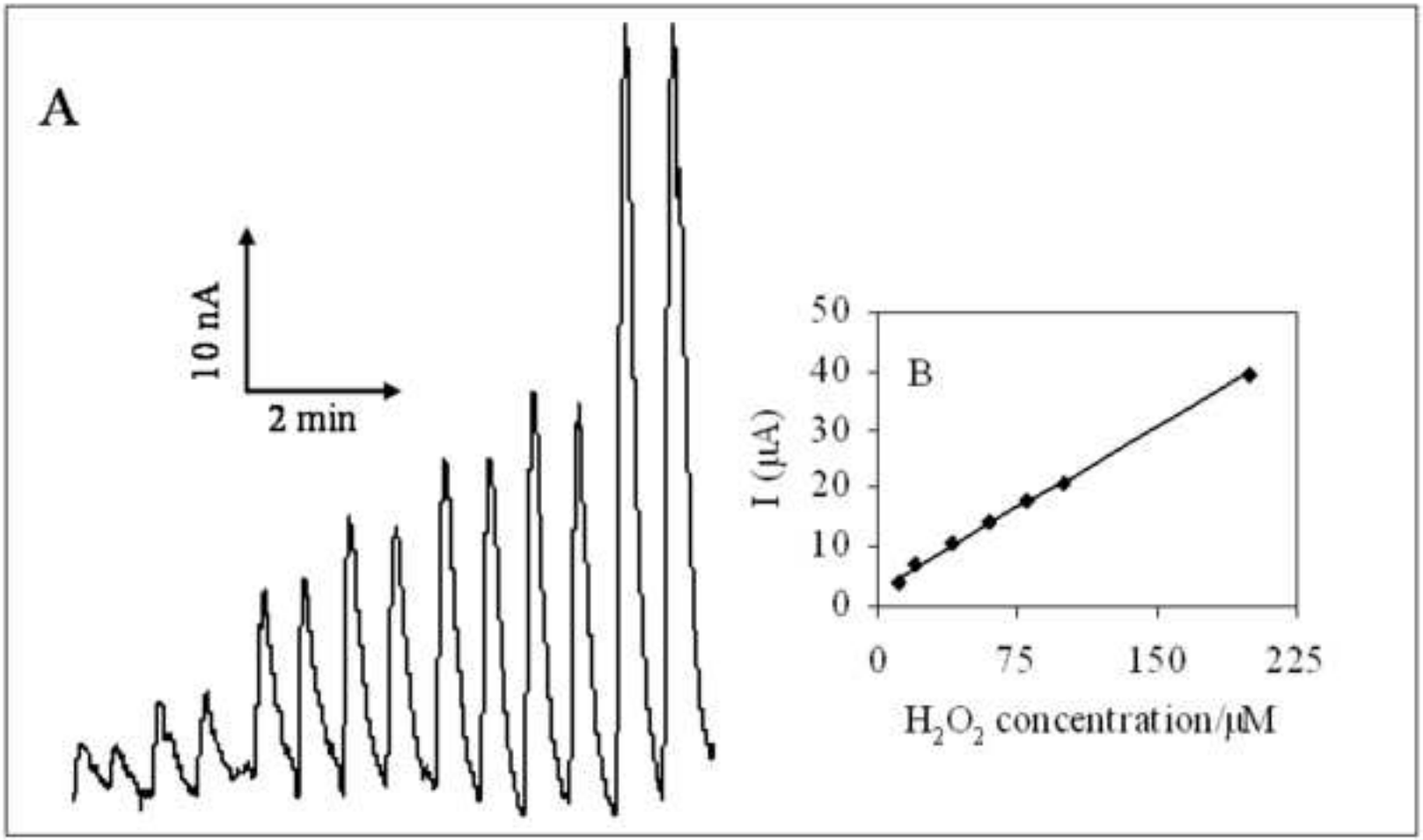

A
10 nA
2 min
B
I (μA)
50
40
30
20
10
0
0
75
150
225
$H_2O_2$ concentration/μM

Fig. 5

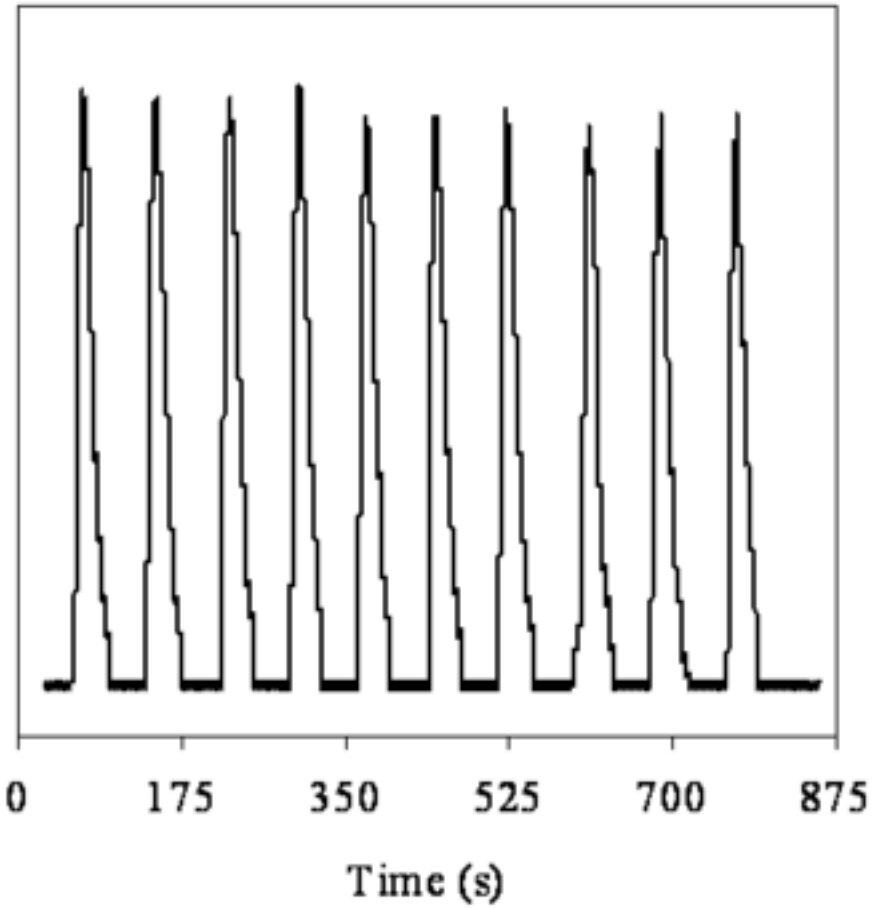



Fig. 6

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Table 1: Analytical parameters for several POM modified electrodes for hydrogen peroxide determination

| Electrode | POM | Modification method | Potential (mV) | Acid concentration or pH of electrolyte | LDR (mM) | LOD (μM) | Ref. |
|---|---|---|---|---|---|---|---|
| CPE | $PMo_{12}$ | Bulk | NR | 1 M $H_2SO_4$ | NR | NR | 3 |
| Graphite | $PFeW_{11}$ | Surface/doped in polymer | -40 | pH 2 | Up to 9 | NR | 6 |
| Pt | $PMo_{12}$ | Surface/ sol gel | 0 | 0.5 M $H_2SO_4$ | 0.02-30 | 7 | 9 |
| GC | $CoW_{11}Co$ | Surface | -400 | pH 1 | NR | NR | 17 |
| GC | $P_2Mo_{18}$ | Surface/adsorption | 350 | 0.5 M $H_2SO_4$ | down to 10 | NR | 25 |
| GC | $P_2W_{18}$ | Surface/LBL | -100 and -400 | pH 7.3 | NR | NR | 29 |
| GC | $P_2W_{18}$ | Surface/LBL | -400 | 0.5 M $NaHSO_4$ | Up to 0.4 | NR | 31 |
| ITO | $SiMo_9W_2$ | Surface/LBL | -400 | pH 3.84 | Up to 32 | NR | 32 |
| CCE | $P_2W_{17}V$ | Bulk | 435 | 0.5 M $H_2SO_4$ | 0.1-20 | 40 | 37 |
| CPE | $PMo_{12}$ | Bulk | -100 and +150 | 0.5 M $H_2SO_4$ | NR | NR | 40 |
| CPE | $SiMo_{12}$ | Bulk | 0 | 1 M $H_2SO_4$ | NR | NR | 41 |
| CPE | $PVW_{11}$ | Bulk | -500 | 3.85 | Up to 26.4 | NR | 42 |
| GC | $P_2Mo_{18}$ | Surface | NR | 1 M $H_2SO_4$ | 0.16-44 | 534 | 50 |
| GC | $PMo_{12}$ | Surface | 50 | 0.5 M $H_2SO_4$ | 2-15 | NR | 51 |
| CPE | $PFeW_{11}$ | Bulk | 0 | pH 2 | 0.01 – 0.2 | 7.4 | Present work |

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