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A novel ion-imprinted electrode prepared by in-situ polymerization

for detection of platinum

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Abstract

To develop a convenient method for sensitive and selective determination of platinum in complicated matrices, an ion-imprinted electrode was studied by *in-situ* polymerization of Pt(IV) ion-imprinted membranes (Pt(IV)-IIMs) on the surface of glassy carbon electrode (GCE). After the experimental parameters for the preparation of Pt(IV)-IIMs such as functional monomer, molar ratio of template, monomer and cross-linking agent together with extraction condition were optimized, the electrode with good regeneration, high stability and specific recognition to Pt(IV) was obtained by modifying GCE with Pt(IV)-IIMs prepared in acetonitrile using allyluread (NAU) as functional monomer, ethylene glycol dimethacrylate (EGDMA) as cross-linking agent, azobisisobutyronitrile (AIBN) as initiator under the molar ratio of template (H_2PtCl_6), NAU and EGDMA as 1:4:40. The resulting electrode named as Pt(IV)-IIMs/GCE exhibits high response sensitivity to Pt(IV) in phosphate buffer (pH 5.29). The calibration graph for the determination of Pt(IV) by Pt(IV)-IIMs/GCE is linear in the range of $2.0\times10^{-8}\sim2.5\times10^{-4}$ mol L^{-1} with the detection limit of 4.0×10^{-9} mol L^{-1}. There is no metal ions tested at the concentration 25 times higher than that of Pt(IV) interfered in the determination. The electrode was successfully applied to determine platinum in catalyst and plant samples with the relative standard deviation (RSD) of less than 3.0% (*n*=5) and recoveries in the range of 97.8~103.6%.

1 Introduction

Ion imprinting has been widely recognized as a powerful technique for construction of materials containing binding sites that can recognize metal ions as given target. The most attractive aspect of this technique is the use of metal ion or its complex formed with a suitable ligand as template to assemble functional monomers around them into complementary orientations [1, 2]. After ion imprinting polymerization, the template is removed from the polymeric matrix by leaching with mineral acid to leave cavities named as ''imprinted sites'' in the polymeric matrix that are complementary in shape and size of the template metal ion. As a result, the obtained ion-imprinted materials, including ion-imprinted polymers (IIPs) and ion-imprinted membranes (IIMs), possess high selective recognition to the template metal ions. The specific binding behaviors for the target ions together with its other advantages over the biological recognition element, liked stability, reusability, simplicity and low cost in preparation, make IIPs/IIMs become ideal candidates as recognition elements for electrodes [3-5], and several electrodes based on IIPs/IIMs were constructed for the determination of metal ions, including Zn(II) [6], Cd(II) [6-8], Cu(II) [8, 9], Pb(II) [10-12], Hg(II) [13, 14] and U(VI) [15]. To the best of our knowledge, there is a few studies have been published with respect to the preparation of Pt(IV) ion-imprinted polymers[16, 17], but no report related to the electrode modified by ion imprinted layer for Pt(IV).

Platinum is a valuable and scarce element that occurs naturally with other platinum metals only at about 0.001 μg mL^{-1} in the crust of the earth. It together with rhodium and palladium plays a decisive role in alloys and catalysts especially in the performance of exhaust systems to reduce the emission of gaseous pollutants by vehicles [18]. Although the benefits of car catalysts are indisputable, highly toxic elements including Pt, Rh and Pd are released into atmosphere, which is

found to increase the levels of contamination in environmental matrices, especially in soils, plants

and road sediments [19] as well as in airborne particles [20], and further imperil human health

together with increasing the environmental risk. The development of analytical methods for the

determination of trace amounts of platinum in environmental samples, biological matrices and

secondary resources is important not only for the pollution control of the environment but also as a

first step in the development of techniques for recovery of platinum from waste materials [21, 22].

So far, a series of methods have been developed for the determination of platinum, liked

spectrophotometric methods [23, 24], atomic absorption spectrometry (AAS) [16, 25], inductively

coupled plasma atomic emission spectrometry (ICP-AES) [26, 27], inductively coupled plasma

mass spectrometry (ICP-MS) [28, 22] and high performance liquid chromatography (HPLC) [29].

However, direct determination of platinum in complicated matrices especially at trace levels by

these methods is often restricted owing to interferences caused by matrix elements and in some

cases unsufficient sensitivity. Therefore, coupling of a separation/preconcentration procedure and

elimination of interfering species prior to detection are necessary [16, 22-29]. Electrochemical

methods are considered as the most favorable techniques for the determination of metal ions

because of their high sensitivity in addition to low costs, ease of operation and portability. And

several voltammetric methods have been reported for the determination of platinum [30-32]. But

such methods often use hanging mercury drop electrode as working electrode and demand a

stringent process of sample pretreatment because the technique is susceptible to interferences. I.

Švancara *et al* [33] developed a stripping voltammetric determination of platinum by a carbon

paste electrode modified with cationic surfactants. Also, the detection limit (LOD) of this method

is up to 7×10^{-7} mol L^{-1}.

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Considering that good selectivity and high sensitivity were obtained nearly in all of the studies with respect to the electrodes based on IIPs/IIMs [6-15], a Pt(IV) ion-imprinted electrode was investigated for simple, convenient, sensitive and selective determination of platinum by *in-situ* polymerization of Pt(IV) ion-imprinted membrane on a glassy carbon electrode (GCE). For this purpose, a new functional monomer named as allyluread (NAU), which can coordinate with Pt(IV) using two nitrogen atoms as donor atoms, was selected for the first time to prepare Pt(IV) ion-imprinted membrane according to the Lewis theory of acids and bases (HSAB theory), and the experimental parameters together with the analytical application and selectivity behavior of the electrode were investigated in detail.

2 Experimental

2.1 Apparatus and Instrumentation

Cyclic voltammetric (CV) and amperometric measurements were carried out with a CHI 660D electrochemical workstation (Shanghai CH Instruments Co., China). A three electrode cell (10mL) with an ion-imprinted membrane modified glassy carbon electrode as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire electrode as counter electrode was used. All potentials were measured and reported versus SCE. Prior to modification, the glassy carbon electrode (GCE, 3 mm diameter) was firstly polished with 0.5 μm and 50 nm alumina slurry, successively rinsed thoroughly with absolute alcohol and water in ultrasonic bath, and then dried in air.

2.2 Reagents and chemicals

H_2PtCl_6, $PdCl_2$, Na_3RhCl_6 and Na_2IrCl_6 were obtained from Kunming Institute of Precious Metals (Yunnan, China). Allylurea (NAU), 2-acetamidoacrylic acid(AAA)，2-(allylthiol)nicotinic

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acid (ANA) and acrylamide (AM) were purchased from Sigma Aldrich (USA). Ethylene glycol dimethacrylate (EGDMA) was purchased from Suzhou Anli Chemical Factory (Jiangsu, China) and distilled under vacuum to remove the stabilizers prior to use. Azobisisobutyronitrile (AIBN) was purchased from Shanghai Reagent Factory (Shanghai, China) and purified by recrystallization from ethanol before used. The other reagents and solvents were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China).

The stock solution (1.0×10^{-2} mol L^{-1}) of Pt(IV), Pd(II), Rh(III) and Ir(IV) were prepared by dissolving appropriate amount of H_2PtCl_6, $PdCl_2$, Na_3RhCl_6 and Na_2IrCl_6 in 5.0 mL of 2.0 mol L^{-1} HCl and then diluted to 100 mL with de-ionized water, respectively. The stock solution (1.0×10^{-2} mol L^{-1}) of the other metal ions used in this work was prepared with their nitrate or chloride. The working standard solution was obtained by diluting the stock solution with de-ionized water. The supporting electrolyte was phosphate buffer solution (pH 5.29), which was prepared with $KH_2PO_4 \cdot 2H_2O$ and $Na_2HPO_4 \cdot 12H_2O$.

The reagents and solvents used without special illustration were of analytical reagent grade and used without further purification. De-ionized water was produced by a Millipore water system composed of Milli-RO 60 and Milli-Q SP.

2.3 Preparation of sample solution

Treatment of the leaves sample solutions: About 100 g of leaves were collected from the *cinnamomum pedunculatum* in 121 street of Kunming (Yunnan, China). The leaves were firstly washed with detergent, tap water and de-ionized water successively, and then dried at room temperature for 24 h followed by drying at 90 ^{o}C for 4 h. After that, 5.0000 g of the pulverized leaves was immersed with 10 mL of nitric acid for 12 h in a conical flask covered with a short

neck funnel, and then heated at 140 ^{o}C until the volume of solution was less than 1 mL. 5 mL of

aqua regia was added. The mixture was heated at 160 ^{o}C to near dryness and the residue was

dissolved with 5 mL of de-ionized water by boiling for 10 min. After cooling to room temperature,

the solution was filtered, and the filtrate was diluted to 25 mL with de-ionized water.

Preparation of the catalyst sample solutions: After the catalyst materials were ground to

pass through a 200 mesh size sieve to facilitate sample dissolution, 25.0 mg of samples was

weighed accurately into a Teflon high-pressure microwave acid digestion bomb and 5.0 mL of

concentrated nitric acid, 4.0 mL of hydrochloric acid and 10.0 mL of 30% hydrogen peroxide were

added. The bomb was sealed tightly and then positioned on the carousel of the microwave oven.

The system was operated at 600 W and 350 psi with a heating program as 120 ^{o}C (5 min, hold 2

min), 180 ^{o}C (6 min, hold 10 min). The digest was evaporated to near dryness. The residue was

dissolved with 2 mL of 2.0 mol L^{-1} HCl and then dilluted to 25 mL with de-ionized water.

2.4 Preparation of the imprinted and non-imprinted film modified electrodes

The Pt(IV) ion-imprinted and non-imprinted film modified electrodes were prepared by *in-situ*

polymerization technique. After 0.0125 mmol of H$_2$PtCl$_6$ and 0.05 mmol of NAU were added into

0.5 mL of acetonitrile and dissolved by ultrasonic at room temperature, 0.75 mmol of EGDMA

and 0.04 mmol of AIBN were added. The polymerization mixture was purged with N$_2$ gas for 10

min to remove molecular oxygen. Then, 4 μL of the above solution was dropped uniformly onto

the surface of glassy carbon electrode, followed by covering a piece of glass. The electrode was

heated by infrared lamp for 40 min, and a layer of transparent polymer membrane was formed on

the electrode surface. After that, the electrode was firstly suspended in de-ionized water until the

glass covered on the electrode dropped, and then immersed in 1:1(v/v) acetic acid/methanol for 3

h to remove Pt(IV) from the ion-imprinted membrane. A Pt(IV) ion-imprinted membrane modified

GCE (Pt(IV)-IIM/GCE) was obtained. Non-imprinted membrane modified GCE (NIM/GCE) was

prepared under the same conditions in the absence of H_2PtCl_6. All of the electrodes are stored in

water when not in use.

2.5 Electroanalytical measurements

The electrochemical characteristics of the modified electrode were characterized by cyclic

voltammetric and amperometric measurements. Cyclic voltammetric measurements were carried

out in 10 mL of 1/15 mol L^{-1} phosphate buffer solution (pH 5.29) at room temperature from -0.8 V

to +0.8 V with a scan rate of 100 mV s^{-1}. The amperometric detection was based on the change in

the current response (Δi) before and after different concentrations of Pt (IV) was added in

phosphate buffer solution and the potential for the determination of Pt (IV) was -0.6 V.

After each experimental run, the electrode was washed by immersing in 1:1 (v/v) acetic

acid/ methanol for 1 h to remove the impurities in the electrode surface. The electrode is reusable

after this cleaning procedure.

3 Results and discussion

3.1 Optimization of the conditions for preparation of Pt(IV)-IIM/GCE

Considering that the quantity of recognition sites in the imprinted materials is a direct function

of both the extent of the monomer-template interactions and the degree of cross-linking in the

polymerization [34], functional monomer together with the molar ratio of

template/monomer/crosslinking agent for the preparation of Pt(IV) ion-imprinted membrane were

optimized. For this purpose, a series of electrodes were constructed by *in-situ* polymerization of

Pt(IV) ion-imprinted membrane with different combinations on GCE, and the current response of

these electrodes were determined by amperometric measurements at the applied potential of -0.6

V in phosphate buffer (pH 5.29) containing 2.0×10^{-6} mol L^{-1} Pt(IV).

The results listed in Table 1 point out that the film does not form on the surface of GCE when

ANA is used as functional monomer, and the maximum response sensitivity is obtained with the

electrode prepared using NAU as functional monomer. Therefore, NAU was selected as functional

monomer for the preparation of Pt(IV)-IIM/GCE.

As expected, the amount of functional monomer (NAU) and crosslinking agent (EGDMA)

added in polymerization produced remarkably influence on the response sensitivity of the

resulting electrodes. Among all of the electrodes prepared using NAU as functional monomer, the

electrode (Pt(IV)-IIM/GCE4 in Table 1) obtained by modifying GCE with Pt(IV) ion-imprinted

membrane prepared with the molar ratio of Pt(IV), NAU and EGDMA as 1:4:40 shows the

maximum response sensitivity to Pt(IV), and the other electrodes prepared with more or less NAU

and EGDMA possess relatively weak current response. The molar ratio of Pt(IV), NAU and

EGDMA for the preparation of Pt(IV)-IIM/GCE was selected as 1:4:40.

It is very important for the sensitivity, selectivity and reproducibility of the imprinted electrode

to extract the template from the imprinted film completely, so the extraction solvent and extraction

time need to be optimized. 1.0 mol L^{-1} HCl, 1.0 mol L^{-1} HNO$_3$ and the mixture of acetic

acid/methanol with different volume ratio (1:3, 1:2, 1:1, 2:1, 3:1) were used as extraction solvent

to clear the template Pt(IV) from the imprinted film coated on GCE. The results indicate that the

stability and service life of the imprinted membrane is unsatisfactory by soaking in 1.0 mol L^{-1}

HCl, 1.0 mol L^{-1} HNO$_3$ and the mixture of acetic acid/methanol with the volume ratio of 2:1 and

3:1, and Pt(IV) is difficult to remove by using 1:3 and 1:2 (v/v) acetic acid/methanol as extraction

solvent. When the mixture of acetic acid/methanol with the volume ratio of 1:1 is selected as

extraction solvent, Pt(IV) can be removed from the imprinted membrane within 3 h (Fig. 1), and

the membrane can maintain integrity and stability under such conditions. Therefore, 1:1 (v/v)

acetic acid/methanol and 3 h were chosen as the optimum eluent and soaking time for template

removal, respectively.

3.2 Characterization of the imprinted film coated on GCE

The resulting Pt(IV) ion-imprinted film obtained by *in-situ* polymerization were

characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy

(SEM) and X-ray photoelectron spectroscopy (XPS). The FT-IR spectra of the non-imprinted film,

imprinted film before and after removal of Pt (IV) were recorded using KBr pellet method (Fig. 2).

By comparing the IR spectra of these resins, it is observed that there is almost no change in the

absorption peak of carbonyl group ($v_{C=O}$) located at about 1728 cm^{-1}, pointing out that the

carbonyl group in NAU does not participate in coordination with Pt(IV). After Pt(IV) was

removed from the ion-imprinted film, the absorption peaks of N-H (v_{N-H}) and C-N (v_{C-N}) shift

from 3525 cm^{-1} and 1449 cm^{-1} to 3542 cm^{-1} and 1458 cm^{-1}, respectively. These results confirm

that NAU can bind with Pt(IV) using two nitrogen atoms as donor atoms. Based on the Lewis

theory of acids and bases (HSAB theory), Pt(IV) is a soft acid. Compared to oxygen atom (hard

base), it is more easily combined with nitrogen atom (medial base). The IR spectra of imprinted

film after removal of Pt(IV) and the non-imprinted film are very similar, suggesting that the two

kinds of films possess a same chemical structure and the leaching process does not affect the

polymeric network.

The morphologies of non-imprinted film, imprinted film before and after removal of Pt (IV)

under SEM are showed in Fig. 3. It is clearly that there is great difference in the SEM images among the three kinds of film formed on the surface of GCE. Pt(IV) ion-imprinted membrane after removal of template Pt(IV) (b) is very rough, and Pt(IV) ion-imprinted membrane before removal of Pt(IV) (a) together with the non-imprinted membrane (c) both are smooth and homogeneous and no cracks can be observed. It is probably that the roughness of imprinted membrane after template removal is beneficial for improving the rebinding efficiency and enhancing the response sensitivity of the electrode. To verify this speculation, the elemental composition of imprinted film before and after removal of Pt(IV) as well as rebinding Pt(IV) were determined by XPS measurement. In XPS spectra (Figure 4), the Pt signals of Pt (4f) and Pt (4d) observed in the 0~400 binding energy in Figure 4a are not found anymore in Figure 4b, but emerge again in Figure 4c. Those results indicate that Pt(IV) were completely removed during the extraction process, and can rebind to the imprinted film in the process of electrochemical determination. To further confirm that the roughness of imprinted membrane is beneficial for improving the rebinding efficiency, the content of Pt in the imprinted and non-imprinted membrane after rebinding Pt(IV) was determined quantitatively by atomic emission spectrometry. The mass percentage content of Pt was found correspondingly as 0.76% and 0.11%, suggesting that the rebinding efficiency of imprinted membrane is better than that of non-imprinted membrane.

3.3 Electrochemical characterization of the imprinted film modified electrode

The electrochemical property of the resulting Pt(IV)-IIM/GCE was investigated by cyclic voltammetry in 10 mL of phosphate buffer solution (pH 5.29) containing 2.0×10^{-6} mol L^{-1} Pt(IV). It can be seen from the results shown in Fig. 5A that the peak current increases remarkably after GCE (curve b) is modified with Pt(IV) ion-imprinted film (curve a). These results demonstrate

that the specific recognition sites existed in the ion-imprinted film can enhance amperometric

response to Pt(IV). As comparison, the non-imprinted electrode (NIM/GCE) exhibits only a small

signal in the potential range from -0.8 to 0.8 V (curve c). This small response is presumably

attributed to the non-specific adsorption of Pt(IV) by the non-imprinted film. Fig.5B is the typical

cyclic voltammograms of Pt(IV)-IIM/GCE in phosphate buffer solution (pH 5.29) containing

2.0×10^{-6} mol L^{-1} Pt(IV) at the scan rate varied from 20 to 120 mV s^{-1}. It is clearly that the peak

currents are proportional to the square root of the scan rate, suggesting the electrode reaction is a

typical diffusion-controlled electrochemical behavior.

3.4 Optimization of the determination conditions

In order to improve the sensitivity of the ion-imprinted electrode, determination conditions

liked the composition and pH of electrolyte solution and applied potential were optimized.

The amperometric responses of the resulting Pt(IV)-IIM/GCE to 2.0×10^{-6} mol L^{-1} Pt(IV)

were examined in 0.1 mol L^{-1} citric acid buffer solution (pH 5.29), 0.2 mol L^{-1} acetic acid buffer

solution (pH 5.29) and 1/15 mol L^{-1} phosphate buffer solution (pH 5.29) to optimize the

composition of electrolyte solution. The results suggest that the Pt(IV)-IIM/GCE obtained its

maximum current response in phosphate buffer solution. Fig. 6 shows the effects of the pH value

of phosphate buffer on the current response of Pt(IV)-IIM/GCE to 2.0×10^{-6} mol L^{-1} Pt(IV). As can

be seen, the maximum current response of Pt(IV)-IIM/GCE is obtained in phosphate buffer with

pH of 5.29, and all of the other buffers with pH more or less than 5.29 produce a decrease in the

peak current. In strongly acidic media, the binding capacity of Pt(IV) is hindered because of the

protonation of the active sites in the imprinted film. Again, the decrease in binding capacity of pHs

greater than 5.29 is due to the competition between rebinding by formation of the complexes of

Pt(IV) with NAU anchored to the imprinted film with the formation of hydroxide of Pt(IV). Therefore, phosphate buffer with pH of 5.29 was used for the determination of Pt (IV) by Pt(IV)-IIM/GCE.

The effect of applied potential on the electrode response was studied in phosphate buffer (pH5.29) containing 2.0×10^{-6} mol L^{-1} Pt(IV). As can be seen from Figure 7, the response current of the electrode increases with decreasing the potential from 0.4 to -0.6 mV, and maintains its maximum value in the potential range of -0.6 to -0.8 mV. To avoid interference at high negative applied potential, a potential of -0.6V (vs. SCE) was selected as the applied potential for amperometric measurements.

3.5 Amperometric i–t curve and calibration curve for determination of Pt(IV)

The affinity of the resulting Pt(IV)-IIM/GCE, NIM/GCE and bare GCE to Pt(IV) in the concentration range over $2.0\times10^{-8}\sim2.5\times10^{-4}$ mol L^{-1} were investigated by amperometric i–t curve at the potential of -0.6V. As shown in Fig. 8, the amperometric currents of bare GCE is almost not varied with the concentration of Pt(IV), and the sensitivity of Pt(IV)-IIM/GCE is significantly higher than that of NIM/GCE. The mechanism of facilitated transport and lack of specific binding sites can be applied to explain the great difference between the amperometric current of Pt(IV)-IIM/GCE and NIM/GCE.

The current response of Pt(IV)-IIM/GCE increased with increasing of the concentration of Pt (IV), and the relationship between the response currents and concentrations of Pt (IV) shown as inset in Fig. 8. It can be seen that the calibration curve for the electrochemical determination of Pt(IV) is composed of two distinct straight lines, suggesting that there are two types of binding sites, which can be named as high affinity binding sites and low affinity binding sites, existed in

the Pt(IV)-imprinted membrane covered on GCE. This result is consistent with many studies of

imprinted polymers [35]. The linear regression equations in the Pt(IV) concentration range over

0.02~1.0 μmol L^{-1} and 1.0~250.0 μmol L^{-1} are obtained as Δi(μA)= 35.25+104.07c (μmol L^{-1})

(r=0.9958) and Δi(μA)=168.65+1.97c (μmol L^{-1}) (r=0.9965), respectively. The limit of detection

of the electrode, which is defined as the lowest concentration of Pt(IV) producing a peak current 3

times higher than the standard deviation of 9 blank measurements, is found to be 4.0×10^{-9} mol L^{-1}.

3.6 Selectivity, repeatability and stability of Pt(IV)-IIM/GCE

The selectivity of Pt(IV)-IIM/GCE to Pt(IV) was evaluated by testing its current responses to

2.0×10^{-6} mol L^{-1} Pt(IV) in the presence of 5.0×10^{-5} mol L^{-1} of Zn^{2+}, Co^{2+}, Mg^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+},

Fe^{3+}, Cd^{2+}, Cr^{3+}, Pb^{2+}, Pd^{2+}, Rh^{3+} and Ir^{4+}, respectively. And the ratio of the response current (i_m/i_{Pt})

of the electrode to 2.0×10^{-6} mol L^{-1} Pt(IV) in the present (i_m) and absence (i_{Pt}) of interfering ions

was calculated. The results shown in Fig 9 indicate that the i_m/i_{Pt} in all of the case is in the range

of 0.97~1.05, suggesting that at least 25-fold excess of the metal ions tested in this paper have no

effect on the determination of Pt(IV).

To investigate the reproducibility of the electrochemical method, three Pt(IV)-IIM/GCE were

prepared under the identical experimental conditions and used for the determination of 2.0×10^{-6}

mol L^{-1} Pt (IV). The calculated RSD of the peak currents obtained with different electrodes is

2.4%. The repeatability and stability of the electrode were also investigated for 2.0×10^{-6} mol L^{-1} Pt

(IV). The electrode can retain more than 90% of its original response after used at least 100 times

or stored in water at room temperature for 80 day. The RSD of the peak currents of the same

electrode after continuous using for 5 times is 2.1%. These results suggest that the electrode can

be regenerated and possesses excellent storage stability.

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3.7 Sample analysis

Two real samples, including an automotive catalyst material and a plant sample, were analyzed by the resulting Pt(IV)-IIM/GCE to evaluate the precision and accuracy of the proposed electrochemical method. The results presented in Table 2 suggest that the recoveries of Pt(IV), which was obtained *via* the standard addition method, are in the range of 97.8~103.6%, and the reproducibility of the procedure, expressed as RSD, is less than 3.0%. To further verify the accuracy of the quantitative results obtained by Pt(IV)-IIM/GCE, the concentrations of platinum in sample solutions were also quantified by AAS method. Platinum does not be determined in plant sample solution by AAS and the concentration of platinum in catalyst sample solution is 6.50×10^{-6} mol L^{-1}. It can be seen that the quantitative results of platinum obtained by Pt(IV)-IIM/GCE are in agreement with that obtained by AAS, suggesting that the resulting Pt(IV)-IIM/GCE may be a feasible tool for the determination of Pt (IV) in the complicated samples.

4 Conclusion

In this work, a new electrode for the determination of Pt(IV) at trace levels was constructed based on the application of ion-imprinted membrane as a novel material for modifying glass carbon electrode. The ion-imprinted membrane coated on the surface of glass carbon electrode can not only act as the selective inducing agent but also play the role of a pre-concentrator. As a result, the developed electrode exhibits good selectivity and high sensitivity. The detection limit of this electrode is lower than most of the methods reported for the determination of Pt(IV) [23, 24, 26-30, 33]. The electrochemical method proposed based on the resulting Pt(IV)-IIM/GCE can be used for the direct determination of platinum at trace levels in complicated matrices.

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Figure captions

Fig.1 Effect of soaking time on the current response of Pt(IV)-IIM/GCE to 2.0×10^{-6} mol L^{-1} Pt (IV)

in phosphate buffer (pH 5.29) at the applied potential of -0.6 V.

Fig.2 FT-IR spectra of non-imprinted film (a), the imprinted film (b) after and (c) before removal

of Pt(IV) by KBr pellet method.

Fig.3 Scanning electron micrograph of the imprinted film (a) before and (b) after removal of

Pt(IV), and (c) non-imprinted film.

Fig.4 XPS analysis of Pt(IV) ion-imprinted film (a) before and (b) after removal of Pt(IV) and (c)

after rebinding Pt(IV).

Fig.5 (A) Cyclic voltammograms of Pt(IV)-IIM/GCE (a), bare GCE (b) and NIM/GCE (c) in the

presence of 2.0×10^{-6} mol L^{-1} Pt(IV) in phosphate buffer (pH 5.29); And (B) cyclic

voltammograms of Pt(IV)-IIM/GCE in the presence of 2.0×10^{-6} mol L^{-1} Pt(IV) in

phosphate buffer (pH 5.29) at various scan rates (from inner to outer curves: 20, 40, 60, 80,

100,120 mVs^{-1}). Inset: plots of peak current vs. $v^{1/2}$.

Fig.6 Effect of the pH value of phosphate buffer on the current response of Pt(IV)-IIM/GCE to

2.0×10^{-6} mol L^{-1} Pt (IV) at the applied potential of -0.6 V.

Fig.7 Effect of the applied potential on the current response of Pt(IV)-IIM/GCE to 2.0×10^{-6} mol

L^{-1} Pt (IV) in phosphate buffer (pH 5.29).

Fig.8 Typical current response *i-t* curve of Pt(IV)-IIM/GCE, bare GCE and NIM/GCE with

increasing addition of Pt (IV) in phosphate buffer (pH 5.29) at the applied potential of -0.6

V. Concentration (mol L^{-1}) of Pt (IV): a: 0, b: 2.0×10^{-8}, c: 8.0×10^{-8}, d: 2.0×10^{-7}, e: 6.0×10^{-7},

f: 1.0×10^{-6}, g: 8.0×10^{-6}, h: 2.0×10^{-5}, i: 4.0×10^{-5}, j: 6.0×10^{-5}, k: 8.0×10^{-5}, l: 1.0×10^{-4}, m:

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1.2×10^{-4}, n: 1.6×10^{-4}, o: 2.0×10^{-4}, p: 2.5×10^{-4}. Inset figure is the calibration curve.

Fig.9 Current ratio (i_m/i_{Pt}) of Pt(IV)-IIM/GCE to 2.0×10^{-6} mol L^{-1} Pt(IV) (a) and 2.0×10^{-6} mol L^{-1}

Pt(IV) in the presence of 5.0×10^{-5} mol L^{-1} Zn^{2+} (b), Co^{2+} (c), Mg^{2+} (d), Ni^{2+} (e), Cu^{2+} (f),

Mn^{2+} (g), Fe^{3+} (h), Cd^{2+} (i), Cr^{3+} (j), Pb^{2+} (k), Pd^{2+} (l), Rh^{3+} (m) and Ir^{4+} (n), respectively.

i_m and i_{Pt} are the current of Pt(IV)-IIM/GCE to Pt(IV) in the presence and absence of

interfering ions, respectively.

Table 1

The current response of the sensors prepared by modifying GCE with Pt(IV) ion-imprinted membrane with different polymerization conditions.

Sensors	Polymerization conditions[a]			Current response[b] (μA)
	Functional monomers	Monomer added (mmol)	EGDMA added (mmol)	
Pt(IV)-IIM/GCE1	ANA	0.05	0.5	c
Pt(IV)-IIM/GCE2	AAA	0.05	0.5	12
Pt(IV)-IIM/GCE3	AM	0.05	0.5	16
Pt(IV)-IIM/GCE4	NAU	0.05	0.5	178
Pt(IV)-IIM/GCE5	NAU	0.05	0.25	10
Pt(IV)-IIM/GCE6	NAU	0.05	0.75	82
Pt(IV)-IIM/GCE7	NAU	0.05	1.00	44
Pt(IV)-IIM/GCE8	NAU	0.025	0.5	80
Pt(IV)-IIM/GCE9	NAU	0.075	0.5	42
Pt(IV)-IIM/GCE10	NAU	0.10	0.5	10

[a]All of the Pt(IV)-IIM/GCE sensors were prepared with H_2PtCl_6 (0.0125 mmol) as template, acetonitrile (0.5 mL) as porogen and AIBN (0.04 mmol) as initiator. [b]The current response were obtained by amperometric measurements at applied potential of -0.6 V in phosphate buffer solution (pH 5.29) containing 2.0×10^{-6} mol L^{-1} Pt(IV). [c]The film can not form on GCE when ANA as functional monomer.

Table 2 Determination of Pt(IV) in sample solutions by Pt(IV)-IIM/GCE (*n*=5).

Samples	Added / μmol L^{-1}	Found / μmol L^{-1}	RSD / %	Recovery / %
	0.00	6.35	3.0	-
	2.80	9.25	2.2	103.6
Automotive catalyst	8.00	14.40	1.8	100.6
	12.00	18.26	2.1	99.3
	0.00	N.D.[a]	-	-
	2.80	2.78	1.8	99.3
Plants	4.00	3.91	2.7	97.8
	8.00	8.03	2.4	100.4

[a]N.D.: not detected

Fig.1
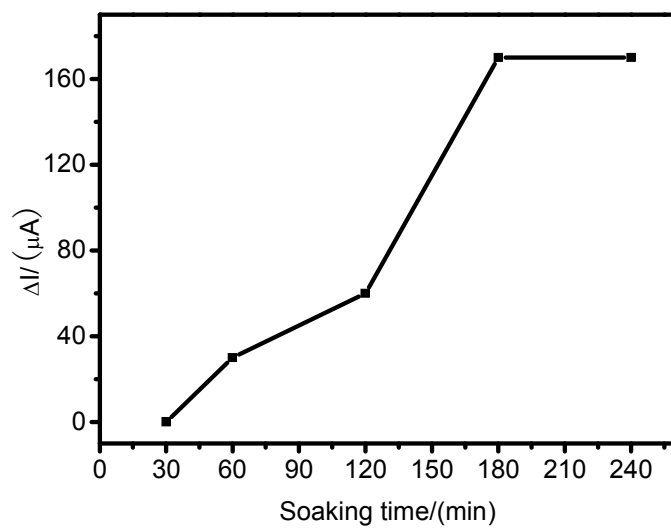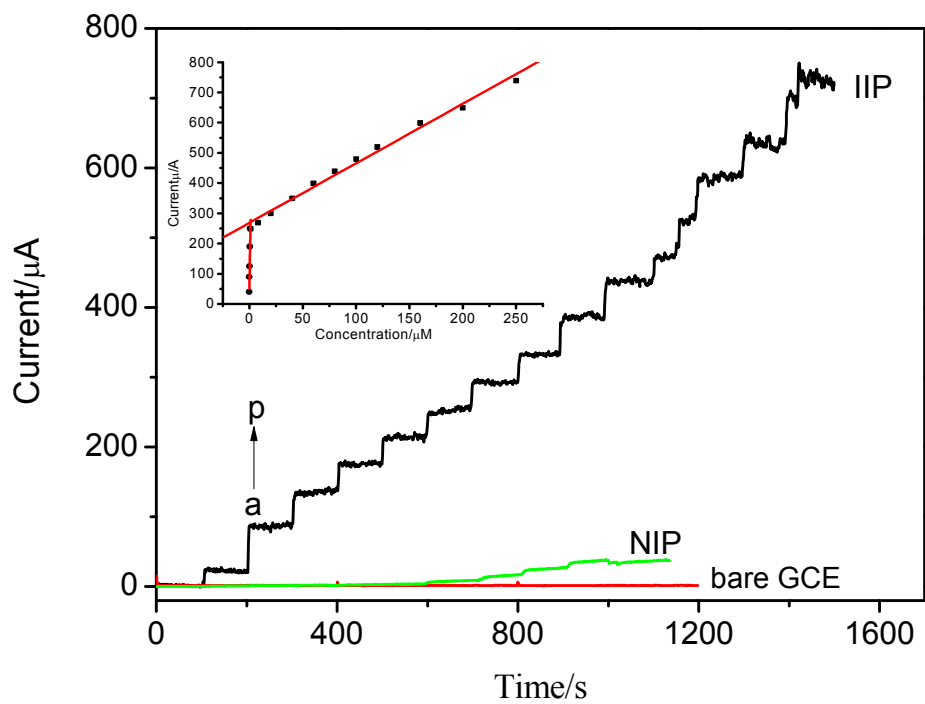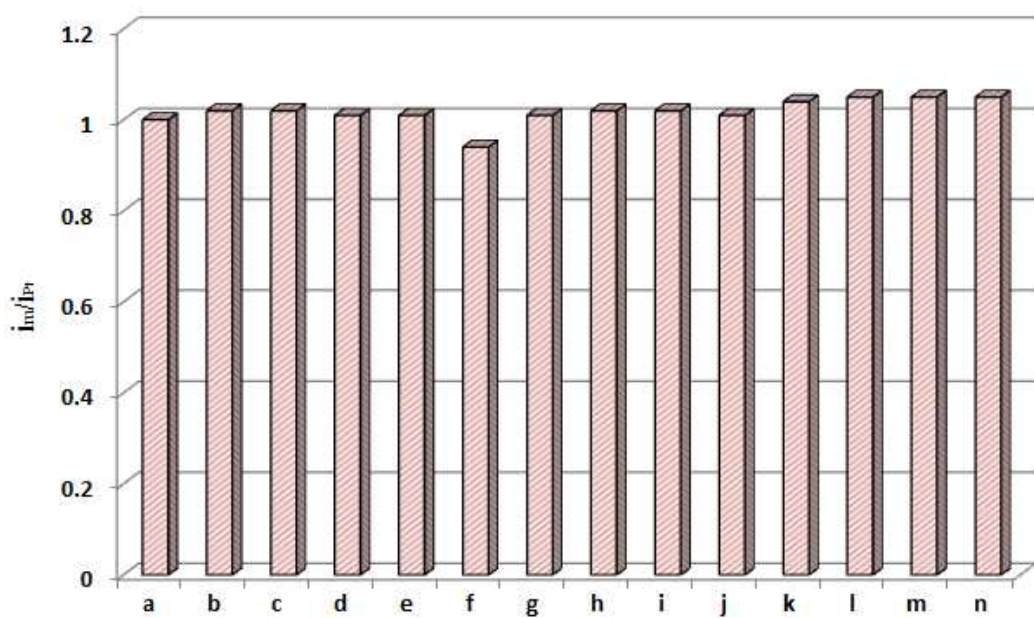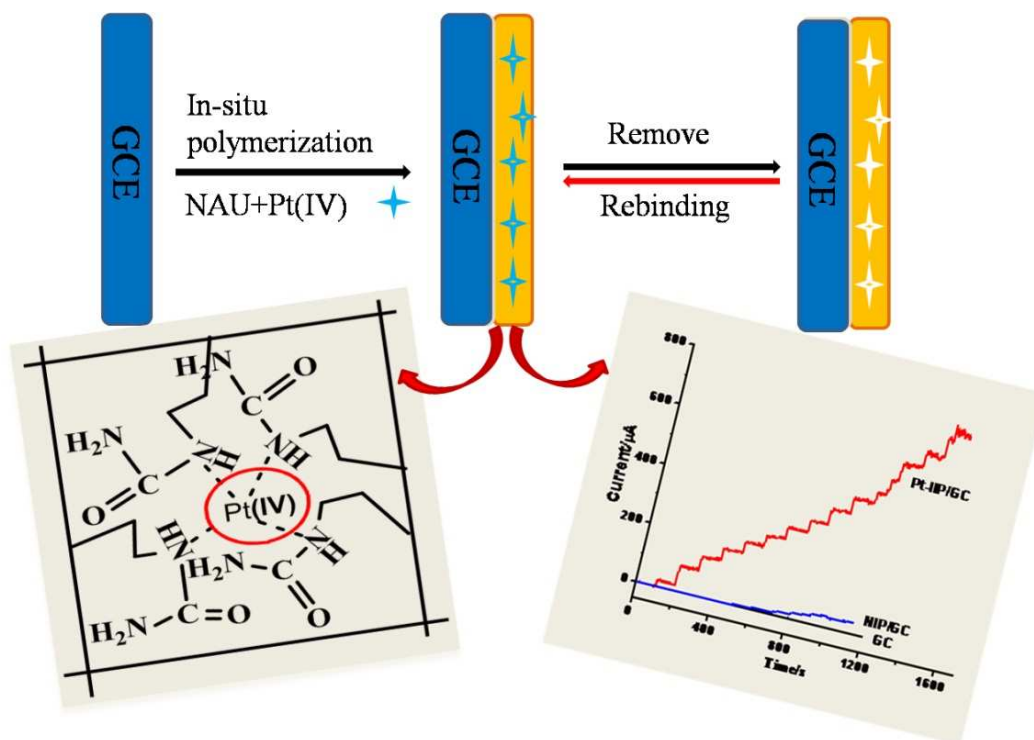
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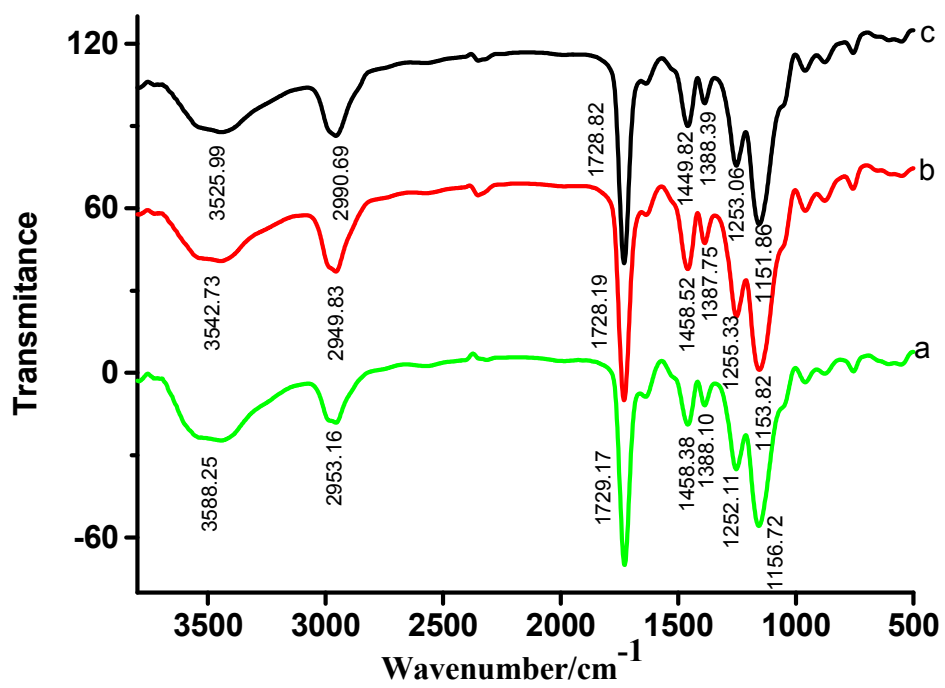
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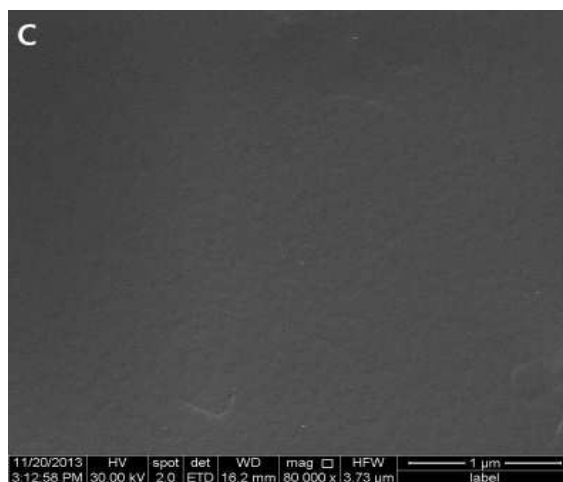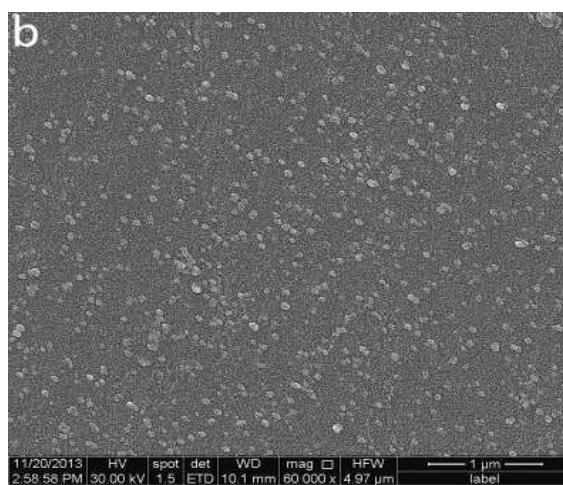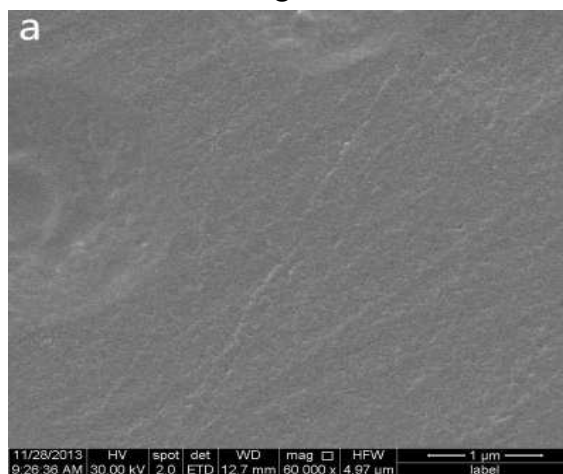
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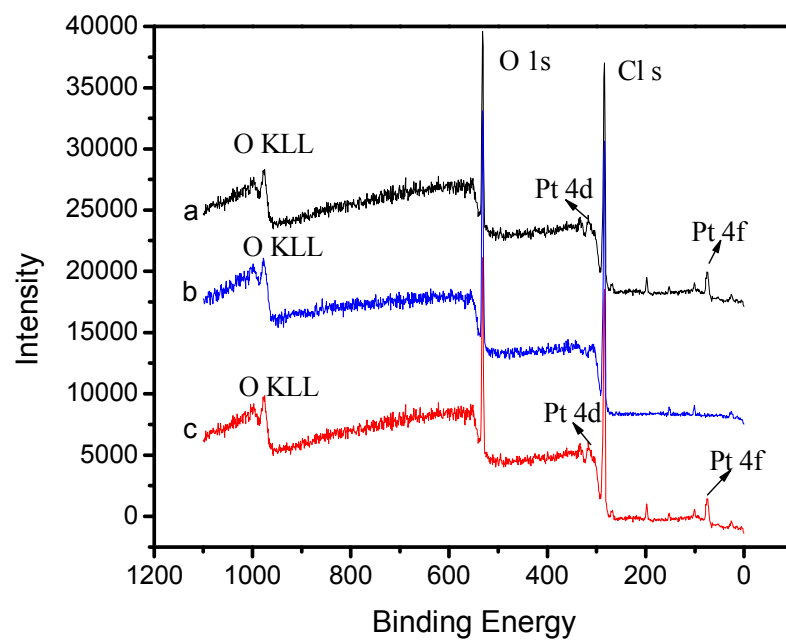
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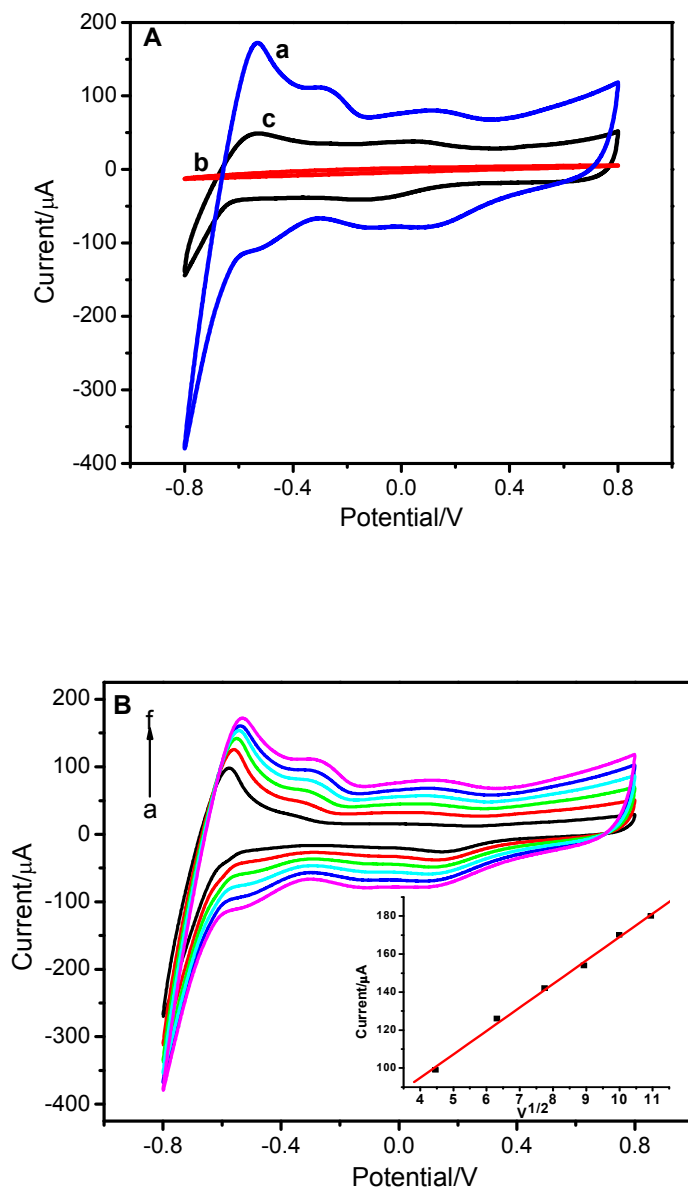
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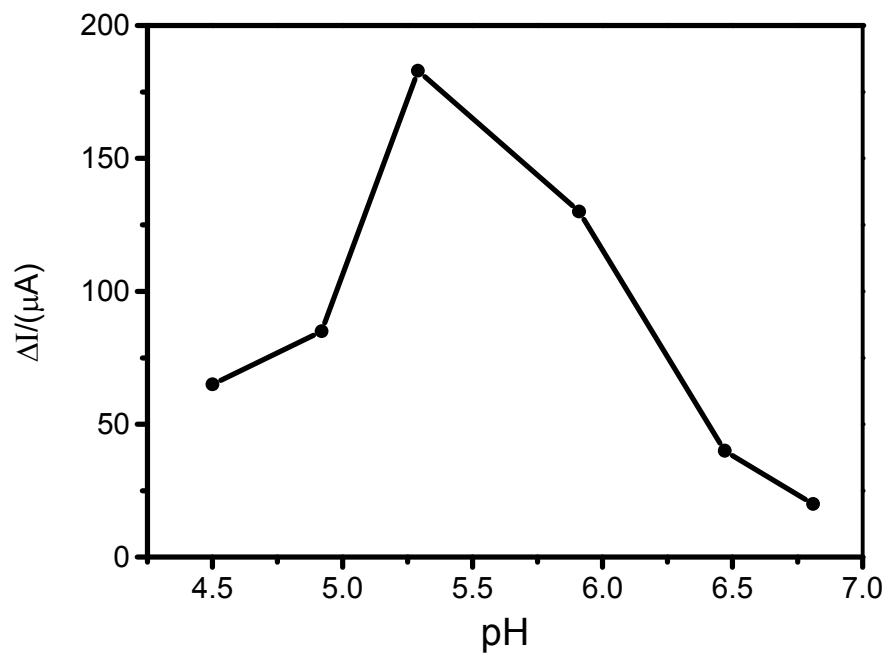
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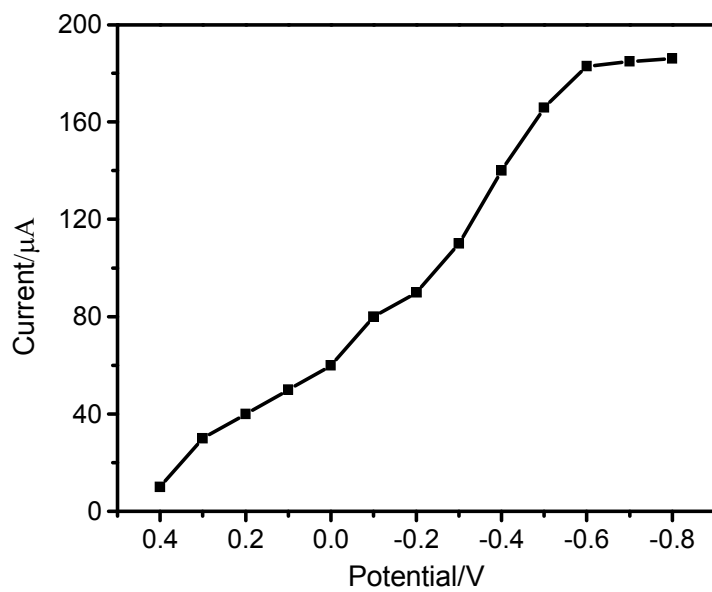
Fig.8

Fig.9

A graphical and textual abstract for the Table of contents entry

A novel ion imprinted electrode with high sensitivity and specific recognition to Pt(IV) was obtained by *in-situ* polymerization.