

POLY(THIOPHENE-3-ACETIC ACID)-PALLADIUM NANOPARTICLE COMPOSITE MODIFIED ELECTRODES FOR SUPERSENSITIVE DETERMINATION OF HYDRAZINE*

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Abstract A promising electrochemical sensor was fabricated by electrodeposition of Pd nanoparticles (PdNPs) on poly(thiophene-3-acetic acid) (PTAA)-modified glassy carbon electrode (GCE), forming a PdNPs/PTAA composites-modified GCE (PdNPs/PTAA/GCE). Scanning electron microscope (SEM) and electrochemical techniques were used for the characterization of these composites. It was found that the PdNPs/PTAA layer was very uniform. Electrochemical experiments showed that this proposed PdNPs/PTAA composites-modified electrode exhibited excellent electrocatalytic activity towards the oxidation of hydrazine. Under the optimum conditions, the proposed sensor can be applied to the quantification of hydrazine with a wide linear range from 8.0×10^{-9} mol/L to 1.0×10^{-5} mol/L with a low detection limit of 2.67×10^{-9} mol/L. The experiment results also showed that the sensor exhibited good reproducibility and long-term stability, as well as high selectivity with no interference from other potential competing species.

Keywords: Sensor; Hydrazine; Nanocomposites; Pd nanoparticles; Conducting polymer.

INTRODUCTION

Hydrazine is widely used as a fuel in rocket propulsion systems, also as pesticides, blowing agents, pharmaceutical intermediates, photographic chemicals and so on^[1]. Symptoms of acute exposure to high levels of hydrazine include irritation of eyes, nose, throat, temporary blindness, dizziness, nausea, pulmonary edema and coma in humans. Acute exposure can also damage the liver, kidneys and central nervous system of humans^[2–4]. Therefore, sensitive detection of hydrazine is practically important for environmental and biological analyses^[5].

Many analytical methods have been reported for the determination of hydrazine such as spectrophotometry^[6, 7], potentiometry^[8], titrimetry^[9], chemiluminescence^[10] and chromatography^[11]. However, the above methods have many disadvantages, including tedious and time-consuming multi-step procedures, interference resulting from impurities present in real samples and the high cost of equipment, reagent, and operator training. Fortunately, sensing technology offers the opportunity for portable, economical, sensitive, selective, rapid and cost effective methodologies. But direct electrochemical oxidation of hydrazine at the surface of noble metal electrodes such as mercury, silver, gold, platinum, nickel, rhodium and palladium is a slow electrode process requiring a large overpotential, which is the major barrier and still a great challenge for

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the determination of hydrazine by electrochemical methods. Therefore, modification of the electrode surface has been made to enhance the rate of electron transfer and minimize overpotential. A variety of redox mediators such as hematoxylin^[12], chlorogenic acid and its derivatives^[13, 14], carbon nanotubes^[15], acetylferrocene^[16], coumestan^[17], 4-pyridyl hydroquinone^[18] and various transition metal hexacyanoferrates^[19, 20] are an effective approach for improving the electron-transfer rate and minimizing overpotential. In spite of the relative good sensitivity and selectivity of chemically modified electrodes, the usage of these electrodes need a careful control of pH, because strong alkaline (pH > 9) conditions could lead to desorption from the electrode substrates^[15].

Nanoparticle-modified electrodes as novel chemically modified electrodes have attracted attentions in electroanalysis due to their higher sensitivity and lower detection limit. Compared to a macroelectrode, a nanoparticle-modified electrode has several main advantages such as high effective surface area, mass transport, catalysis and control over local microenvironment. Among other metal nanoparticles, PdNPs show higher electrocatalytic behavior for electrooxidation of hydrazine^[21]. Palladium has been deposited on a variety of substrates such as highly ordered pyrolytic graphite, glassy carbon electrode, carbon nanotube and boron-doped diamond. Although there have been many reports on electrooxidation of hydrazine on different substrates, the sensitive electrochemical determination of this analyte at a low overpotential with a well-defined signal is still highly challenging.

Intrinsically conducting polymers (ICPs), especially ICPs substituted with the functional groups such as carboxylic groups or amino groups, are becoming increasingly popular in the development and application of biosensor. The ICPs substituted with the functional groups obtained by electrochemical synthesis can afford higher stability compared with those unsubstituted. Poly(thiophene-3-acetic acid) (PTAA), as one of ICPs substituted with the functional group, has high electrical conductivity, good environmental stability and excellent electrochemical activity. Recently, a number of studies have been reported on the immobilization of enzymes or DNA on PTAA matrix^[22, 23]. To the best of our knowledge, so far, there is no report on the electrodeposition of PdNPs on the surface of the electrosynthesized PTAA films for the determination of hydrazine.

In the present work, a simple and sensitive electrochemical sensor has been developed by preparation of PdNPs modified electrode using PTAA as the supporting material. The resulting PdNPs/PTAA film modified electrode showed excellent catalytic activity for the oxidation of hydrazine, which could be used as an effective sensor for the detection of hydrazine. Moreover, the proposed sensor was also used to determine hydrazine in real samples and obtained satisfied results.

EXPERIMENTAL

Reagents and Chemicals

Thiophene-3-acetic acid (TAA) was obtained from TCI. Lithium perchlorate trihydrate ($\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$), disodium hydrogen phosphate dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) and sodium dihydrogen phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) were purchased from Sinopharm Chemical Reagent Co. Ltd. Acetonitrile was obtained from Beijing Chemical Reagent Co. Ltd. Hydrazine was obtained from Tianjin Hengxing Chemical Preparation Company. The supporting electrolyte was 0.1 mol/L phosphate buffer solution (PBS) prepared with KH_2PO_4 and Na_2HPO_4 . All other chemicals were of analytical grade and used without further purification, and doubly distilled water was used throughout the experiments.

Apparatus

Scanning electron microscopy (SEM) analysis was performed using a JSM-5600LV microscope (JEOL, Ltd., Japan). The X-ray photoelectron spectroscopy (XPS) analysis was done with a K-Alpha XPS spectrometer (Thermo Fisher). Cyclic voltammetric and amperometric measurements were carried out on a potentiostat-galvanostat. A three-electrode cell (10 mL) was used with the modified glassy carbon electrode (GCE, 2 mm diameter) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum foil electrode as the counter electrode. All potentials were measured versus the SCE, and all experiments were carried out at room temperature.

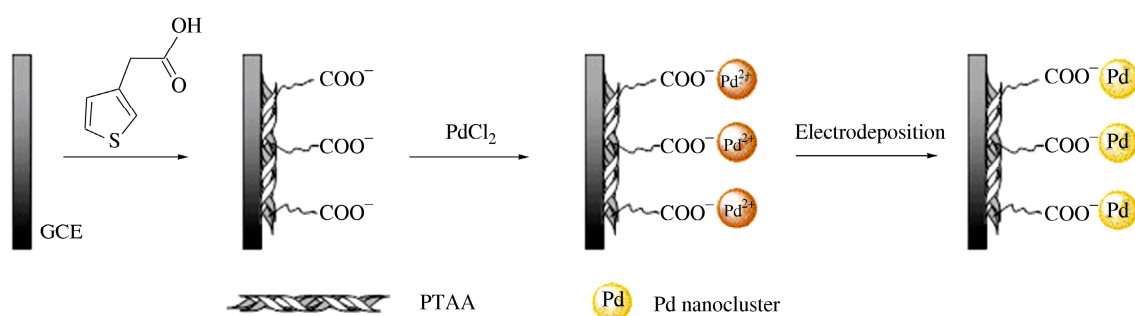
Fabrication of PdNPs/PTAA Composite Modified Electrode

Prior to modification, the bare GCE was polished with 0.3 μm and 0.05 μm alumina slurries. After each

polishing, it was rinsed with doubly distilled water, and ultrasonicated in ethanol and doubly distilled water for 5 min, successively, in order to remove any adsorbed substances on the electrode surface. Finally, it was dried under nitrogen atmosphere ready for use.

The PTAA modified GCE was prepared by the potentiostatical polymerization of 0.5 mol/L TAA at 2.2 V versus SCE for 90 s in 2 mL acetonitrile containing 0.1 mol/L LiClO₄. The as-obtained PTAA modified GCE was washed with deionized water to remove loosely monomer, supporting electrolyte and ions.

The PdNPs was electrochemically deposited on the PTAA modified GCE by the potentiostatical deposition of 0.2 mmol/L PdCl₂ at an applied potential of −0.14 V versus SCE for 120 s in 1 mol/L H₂SO₄ solution. The fabricated composite modified electrode was washed with distilled water to remove residual acid and ions (Scheme 1). The obtained modified electrode was denoted as PdNPs/PTAA modified GCE.



Scheme 1 The construction process of the PdNPs/PTAA modified GCE

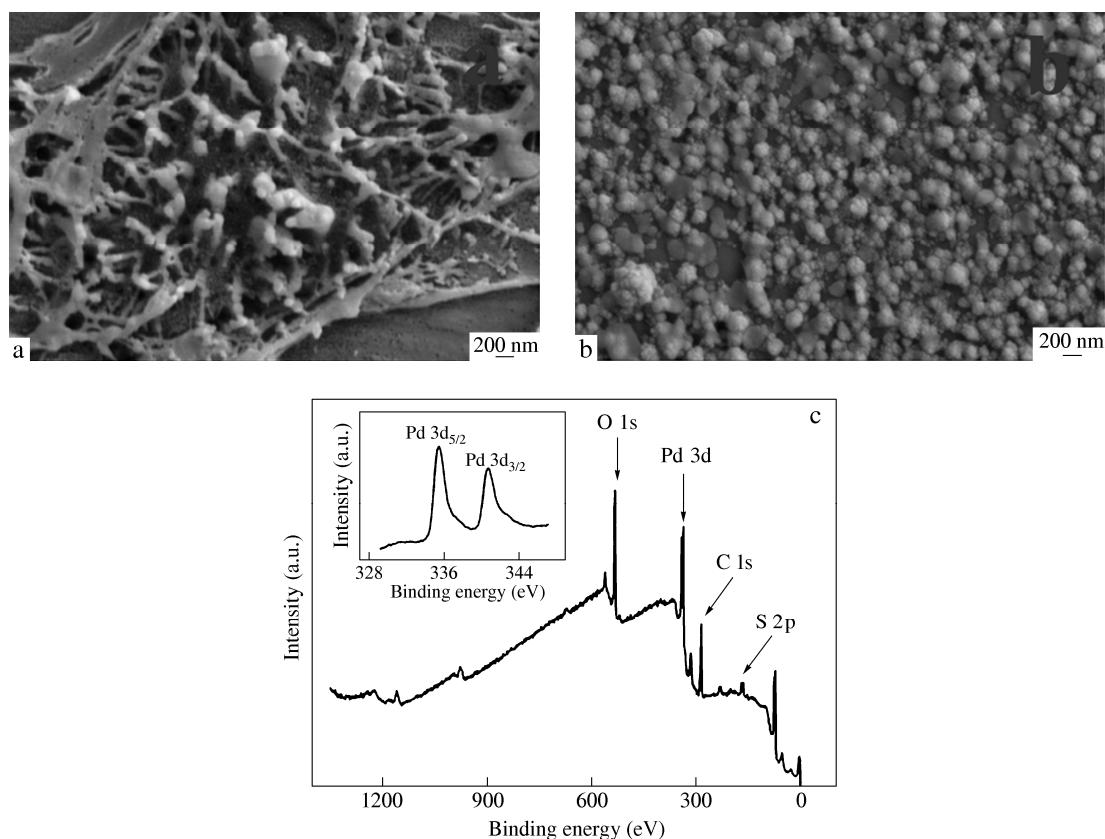


Fig. 1 SEM images of PTAA (a) and PdNPs/PTAA (b); (c) XPS spectrum of PdNPs/PTAA Inset, XPS region of Pd 3d

RESULTS AND DISCUSSION

Surface Morphology of Modified Electrode

The morphology of the PdNPs/PTAA film was characterized by SEM technique. Figure 1(a) shows that PTAA emerges as fibers and dispersed very well on the ITO substrate, which provides a three dimensional medium and net-like structure to facilitate the homogenous distribution of PdNPs. As shown in Fig. 1(b), a relatively high-coverage of ordered monolayer of PdNPs without agglomeration is found on the surface of the PTAA, in which there is a higher density of carboxyl groups. The particles are roughly spherical in shape and the average size of the particles is about 150 nm.

This nanostructured film could extremely enhance the active surface area and might be very important to promote electron transfer. Consequently, the resulting modified electrode exhibited an excellent electrocatalytic capability towards the oxidation of hydrazine.

The existence of PdNPs/PTAA nanocomposite was also analyzed by XPS. Figure 1(c) shows the XPS pattern of S 2p, O 1s and C 1s and proves the PTAA exists as simple substance. As it also can be seen from the XPS spectra, the Pd 3d_{5/2} and 3d_{3/2} lines appear at 335.8 and 341.1 eV, respectively, showing the existing of Pd(0). These support the conclusion that PdNPs/PTAA nanocomposite has been successfully electrodeposited on GCE.

Characterization of Modified Electrode

Electrochemical impedance spectroscopy (EIS) can offer information on the impedance changes of the electrode surface during the modification process. Nyquist plots of the bare GCE, PTAA modified GCE and PdNPs/PTAA modified GCE are shown in Fig. 2 with the real part (Z_{re}) on the X-axis and the imaginary part (Z_{im}) on the Y-axis. The Nyquist plot includes a semicircle part and a linear part. The semicircle part corresponds to the charge-transfer-limited process, and the diameter of the semicircle is related to the charge-transfer resistance (R_{ct}) of the modified layer, while the linear part is formed by the diffusion control of the reactant species. The increase or decrease in the R_{ct} values exactly characterizes the modification of the electrode surface^[24, 25]. According to Fig. 2, the R_{ct} values of the bare GCE, PdNPs/PTAA modified GCE and PTAA modified GCE, are 238, 756 and 1227 Ω , respectively. The R_{ct} values of the PTAA modified GCE (Fig. 2, curve b) were much larger than those of the bare GCE (Fig. 2, curve a), indicating that PTAA films were electrodeposited on the surface of the bare GCE. However, the R_{ct} values of the PdNPs/PTAA modified GCE (Fig. 2, curve c) were much smaller than those of the PTAA modified GCE (Fig. 2b), this was because PdNPs were electrodeposited on the surface of the PTAA modified GCE, which resulted in the conductivity enhancement of the obtained PdNPs/PTAA composite films. The result also confirmed that PdNPs was successfully electrodeposited on the surface of the PTAA modified GCE.

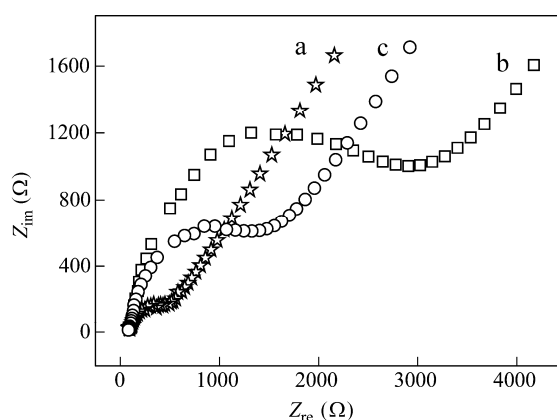


Fig. 2 EIS of bare GCE (a), PTAA modified GCE (b), and PdNPs/PTAA modified GCE (c) in 5.0 mmol/L $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) containing 0.1 mol/L KCl

Electrocatalytic Behaviors of Modified Electrode

In order to evaluate the electrocatalytic activity of the PdNPs/PTAA modified GCE toward the oxidation of hydrazine. Electrochemical behaviors of the bare GCE (a), PTAA (b) and PdNPs/PTAA (c) modified GCE toward the oxidation of hydrazine were investigated in 0.1 mol/L PBS (pH 7.0) containing 0.5 mmol/L hydrazine by cyclic voltammetry (Fig. 3). It can be seen that the bare GCE (a) has no catalytic activity to hydrazine. The PTAA modified GCE (b) only displayed slight catalytic activity to hydrazine. In contrast, a well-formed sharp catalytic oxidation peak at 0.117 V was observed at the PdNPs/PTAA modified GCE. In addition, a control experiment was also carried out in hydrazine-free 0.1 mol/L PBS. No visible oxidation peak is observed at the PdNPs/PTAA modified GCE in blank 0.1 mol/L PBS solution (Fig. 3, curve c'), which further validates the conclusion that the oxidation peak (Fig. 3, curve c) arises from hydrazine oxidation. Such excellent catalytic activity of PdNPs/PTAA might be attributed to the synergistic reaction of PTAA and PdNPs. The well-distributed PdNPs on the surface of PTAA with a high density would provide more active sites for the catalytic redox reaction and greatly increase the electrocatalytic activity.

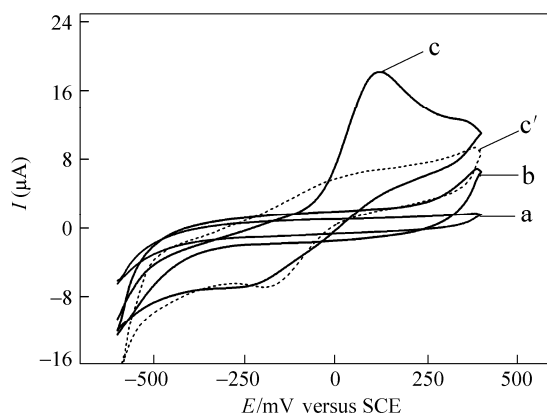


Fig. 3 Cyclic voltammograms of the bare GCE (a), PTAA (b) and PdNPs/PTAA (c' and c) modified GCE in the N_2 -saturated PBS (0.1 mol/L, pH 7.0) in the absence (c') and presence of 0.5 mmol/L hydrazine (a, b and c) Scan rate: 100 mV s^{-1}

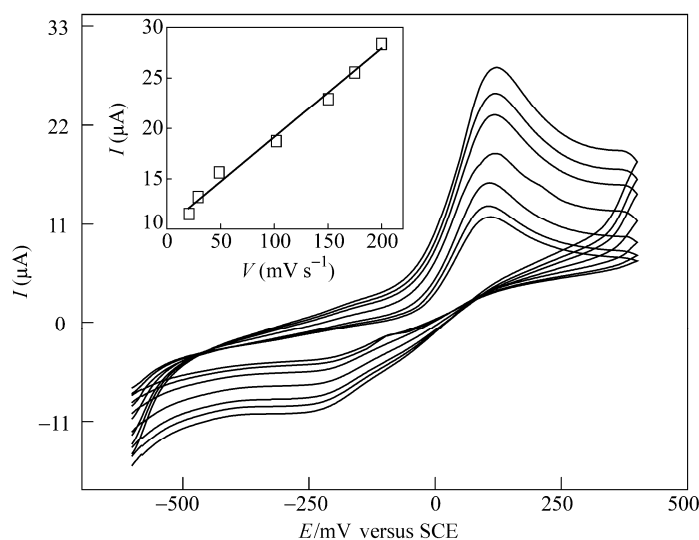


Fig. 4 Cyclic voltammograms of the PdNPs/PTAA modified GCE recorded in 0.1 mol/L PBS (pH 7.0) containing 0.5 mmol/L hydrazine at different scan rates (inner to outer): 0.02, 0.03, 0.05, 0.1, 0.15, 0.175, and 0.2 V s^{-1}

The inset shows the dependence of the redox peak currents on the square root of scan rates.

The effect of scan rate on hydrazine oxidation of PdNPs/PTAA modified GCE was also studied. Figure 4 shows the CVs of PdNPs/PTAA modified GCE recorded in 0.1 mol/L PBS containing 0.5 mmol/L hydrazine under the scan rate from 20 mV s^{-1} to 200 mV s^{-1} . It can be seen that the peak potential shifted slightly toward positive direction with increasing the scan rate. And the peak currents of hydrazine oxidation were linearly proportional to the square root of the scan rate ($v^{1/2}$) as shown by the inset of Fig. 4. It indicates that the electrochemical reaction rate is fast and the oxidation of hydrazine on the PdNPs/PTAA modified GCE is a typical diffusion-controlled process.

Optimization Conditions for the Sensor

It is well known that the applied potential strongly affects the amperometric response of a sensor. We have systemically investigated the impact of applied potentials on the amperometric response of the PdNPs/PTAA modified GCE to hydrazine. Amperometric response was performed by varying the potential of the PdNPs/PTAA modified GCE between -0.05 V and 0.3 V in the presence of 0.5 mmol/L hydrazine. As shown in Fig. 5, the current response increased with the increase of applied potential. When the potential reached 0.15 V , the current response almost became steady. In addition, high potential would oxidize some interfering species which were stable under relatively low potential. Thus, 0.15 V was chosen as the optimal potential for amperometric hydrazine sensing.

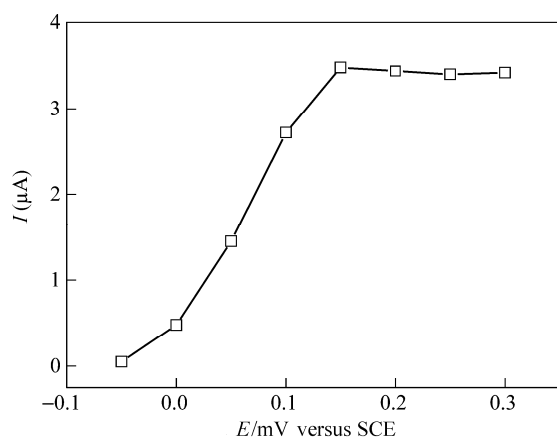


Fig. 5 Effect of working potential on the amperometric response of the sensor at different applied potentials measured in a pH 7.0 PBS containing 0.5 mmol/L hydrazine

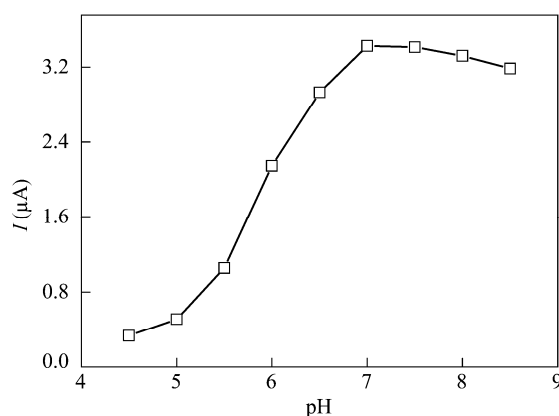


Fig. 6 Influence of pH on the amperometric response of the sensor in the presence of 0.5 mmol/L hydrazine in PBS at the potential of 0.15 V

The electrocatalytic oxidation of hydrazine is dependent on solution pH. Therefore, it is necessary to optimize the pH value for efficient electrocatalysis of its oxidation. Figure 6 presents the pH dependence of the amperometric response of 0.5 mmol/L hydrazine in the pH range 4.5–8.5. It can be seen that the current increased as the pH changed from 4.5 to 7.0, following by a large decrease in the pH range of 7.0–8.5. The maximum response was obtained at pH 7.0. Therefore, pH 7.0 PBS was used as the electrolyte in subsequent experiments.

Amperometric Determination of Hydrazine

The amperometric response of the PdNPs/PTAA modified GCE to successive additions of hydrazine was further evaluated under the optimized experimental conditions. Figure 7 shows the typical current-time dynamic response of PdNPs/PTAA modified GCE towards hydrazine. The electrode responded quickly to the change of hydrazine concentration and reaches about 95% of the steady-state current within 8 s, and the amperometric signal shows linear correlation to hydrazine concentration in the range from $8.0 \times 10^{-9} \text{ mol/L}$ to $1.0 \times 10^{-5} \text{ mol/L}$ with a correlation coefficient of 0.998. Beyond this concentration range, the calibration curve deviates from

linearity. The detection limit was found to be 2.67×10^{-9} mol/L (S/N = 3). This result suggests that the hydrazine concentration could be easily detected at very low concentrations using the amperometric method.

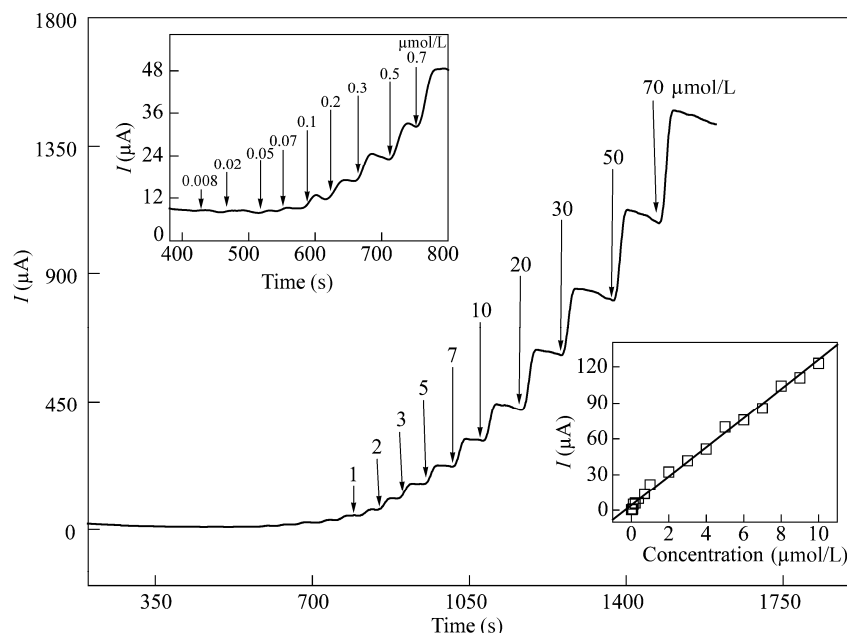


Fig. 7 The typical current-time dynamic response of the PdNPs/PTAA modified GCE towards various concentrations of hydrazine
Inset: the calibration curve for hydrazine detection

Reproducibility and Stability of the PdNPs/PTAA Modified GCE

The reproducibility and repeatability of the developed sensor were determined. In a series of 8 sensors prepared in the same way, a relative standard deviation (R.S.D.) of 3.6% was obtained towards 0.1 mmol/L hydrazine, indicating the reliability of the method. A set of 10 different amperometric measurements for 0.1 mmol/L hydrazine with a single sensor yield a R.S.D. of 3.5%.

The stability of the hydrazine sensor was explored. The proposed sensor was stored in air at ambient conditions. The response to 0.1 mmol/L hydrazine was tested each week, after 35 days of storage, the response of the sensor only decreased by 2.2% compared to the initial response, which shows the long-term stability.

Interference Study

The influence of various species on the determination of hydrazine (0.1 mmol/L) was studied under optimum conditions. The tolerance limit was defined as the maximum concentration of the interfering species that cause an error less than 5% for determination of 0.1 mmol/L hydrazine. The results are given in Table 1 and show very good selectivity for the PdNPs/PTAA modified GCE.

Table 1. Interference study for the determination of 0.1 mmol/L hydrazine under optimized conditions

Species	Maximum tolerable concentration ratio
Na^+ , K^+ , NH_4^+ , CH_3COO^- , PO_4^{2-} , SO_4^{2-} , glucose, lactose, fructose, NO_3^-	1000
CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, Ca^{2+}	100
Mg^{2+} , Ba^{2+}	75

Real Sample Analysis

To illustrate the feasibility of the sensor in practical analysis, distilled water sample and drinking water sample from different sources were spiked with different standard concentrations of hydrazine. Then a known amount of the prepared sample solutions was added to the supporting electrolyte solution, followed by a series of additions

of standard solutions of hydrazine (standard addition method) and analyzed under optimized conditions using the amperometric technique. The satisfactory results summarized in Table 2, indicate that the sensor can be used efficiently for the determination of hydrazine in sample analysis.

Table 2. Results of quantitative determination of hydrazine in different water samples spiked with a known quantity of hydrazine

Sample	Hydrazine added ($\mu\text{mol/L}$)	Hydrazine found ^a ($\mu\text{mol/L}$)	Recovery (%)
Distilled water	10	10.2	102
Drinking water	10	9.8	98

^a Average of three determinations

CONCLUSIONS

A simple and sensitive electrochemical sensor for detection of hydrazine was fabricated by construction of PdNPs on the surface of PTAA monolayer. The PdNPs/PTAA film provided a porous structure with large effective surface area, which could act as electron transfer medium and promote charge transfer. The sensor showed the maximal electrocatalytic ability for the oxidation of hydrazine. Meanwhile, the resulted sensor exhibited extremely fast amperometric response. The detection limit was down to 1×10^{-9} mol/L with a very wide linear range from 8.0×10^{-9} mol/L to 1.0×10^{-5} mol/L. Moreover, this proposed method was applied to the determination of hydrazine in real samples with satisfactory results.

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