

Nano Composite of Palladium–Graphene Modified Electrode for Sensing of Hydrazine

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ABSTRACT

A sensitive hydrazine sensor fabricated by one-step electrodeposition of palladium–graphene nanocomposites (Pd–GENCs) on indium tin oxide (ITO) was demonstrated. Scanning electron microscope and energy dispersive X-ray spectroscopy showed the morphology and ingredient of Pd–GENCs. Experimental results of cyclic voltammetry, electrochemical impedance spectroscopy and chronoamperometry indicated that under the optimum conditions, the currents were dependent linearly on N_2H_4 concentrations in the range from 0.1 μM to 2.5 mM with a detection limit of 0.02 μM ($S/N = 3$) and sensitivity of 799.2 $\mu A\ mM^{-1}\ cm^{-2}$. And the response time of the sensor towards N_2H_4 is less than 3 s. Thus the research provided a new idea for small molecule detection.

Keywords: Sensor; Nano composite; Graphene; Palladium; Hydrazine

INTRODUCTION

In recent years, sensors have already permeated the extremely extensive functional areas such as industrial production, the space development, the ocean detection, environmental protection, resources investigation, medical diagnosis, biological engineering, and even cultural relic protection. During the electrochemical sensors, various materials are prepared to be nanostructure for application. Among those materials, nano composites develop so fast that they have been widely applied in sensors due to their special physical and chemical characteristics [1–3]. As a new type of the planar nano materials, graphene (GE) has aroused extensive interests due to its high surface area, excellent mechanical properties, super conductivity, chemical stability and wide potential window [4–6]. The composites of GE show better performance than single nanomaterials. Nowadays, GE is used for synthesizing nanocomposites via involved with other nanomaterials, as sensor material, it has great properties like photo–electrical effect, etc. And it also can prepare for detection of hydrogen peroxide [7], etc. Graphene oxide (GO) has good performance in the dissociation and layer, therefore, it is considered as a precursor to prepare suitable GE nano composite. More and more scientists dedicate to use GO as the

precursor for synthesize GE/ nano–metal and nano–metal oxide composites such as Au [8], Ag [9], Pt [10,11], Pd[12], Co[13], ZnO[14], etc. Using GE based materials as sensing platform for the detect emanation of Microcrystal–LR (MC–LR) [15], hydrogen peroxide [16] and glucose [17, 18] are fabricated. In the previous study, electro deposition of metal mingled GE firstly is prepared the pretreated grapheme oxide (GO) directly modified electrode, follow by electrochemically depositing metal on the modified electrode [19]. There has a research [20] indicates that the negatively charged GO sheets on positively charged surfaces from aqueous dispersion through electrostatic interactions.

Hydrazine (N_2H_4) detection is practically important in chemical products, medical products, agriculture chemical products, water treatment, photographing and photography products, and in producing medicine, foaming agent, etc [21–24]. In aqueous solution, the electrochemical behavior of N_2H_4 has been extensive research. But, the direct electrochemical oxidation of N_2H_4 need a relatively high over potentia because of kinetically sluggish towards electrode. Many affords have been made to lower the over potential by the modifying with nanomaterials[25], such as Pt[26],

Au[27], Ag[28], Cu[29], Co[30], Ni[31] and various chemical modified electrodes [32, 33]. Palladium is a kind of high catalytic activity, and relatively cheap precious metal. Nanopalladium (Pd), especially carbon supported Pd nanoparticles have been employed for the fabrication of non-enzymatic sensor [34–36]. And nano-Pd has already been used to detection ethanol [37,38], methanol[39], formic acid [40] etc. The application of indium tin oxide (ITO) electrodes has attracted increasing interest recently due to their prominent characteristics such as excellent optical transparency, high electrical conductivity, wide electrochemical working window, excellent substrate adhesion, and stable electrochemical and physical properties [41–43]. ITO film electrodes could also be available at a very low cost due to mass production given that they have been widely used in industrial applications.

In the present work, the N_2H_4 sensor is prepared by means of one-step electro deposition of Pd-GENCs on ITO electrode in ionic liquid Ethylene with ultrasonic wave assisted, and properties of the sensor are investigated. The research is expected to provide a new idea for small molecule detection.

Experimental Reagent and Materials

Choline chloride [$HOC_2H_4N(CH_3)_3Cl$] (ChCl) was purchased from Sino harm Chemical Reagent Co. Ltd. (Shanghai, China), High purity graphite powder was purchased from Shanghai Carbon Plant (Shanghai, China). Palladium chloride ($PdCl_2$) was got from Tianjin Yingda Sparseness and Noble Reagent Chemical factory (Tianjin, China). Phosphate buffer saline (PBS, pH 7.0 and 9.2 containing 0.1 M NaCl) was prepared for the experiments. All other chemicals were of analytical reagent grade and double-distilled water was used in all the experiments.

DL-180 ultrasonic cleaning machine (35 KHz, Zhejiang Haitian Electron Instrument Factory, China) was used to dissolve and form homogeneous solution. Indium tin oxide (ITO) electrode, before use, rinsed with double-distilled water, then sonicate treated in ethanol and double-distilled water for 5min, respectively. Then, the electrode was allowed to dry under nitrogen. A three-electrode cell controlled by EC 550 electrochemical workstation (Gaoss Union Technology Co., Ltd., Wuhan, China) and CHI660 electrochemical workstation (Chenhua Instruments, Shanghai, China). The three-electrode system,

where a standard saturated calomel electrode (SCE) served as reference electrode, a platinum wire electrode as the auxiliary electrode, and the prepared electrodes as the working electrode. Scanning electron microscopic (SEM) measurements were carried out on a scanning electron microscope (JEOL, JSM-6700F) at 15 kV. The chemical composition in samples was investigated by an energy dispersive X-ray spectroscopy (EDS) attached to JSM-6390A SEM. All the electrochemical experiments were conducted at room temperature (25 ± 2 °C).

Preparation of Pd-GE/ITO

Ionic liquid Ethaline was formed by continuous stirring and gentle heating of EG and ChCl (2:1) until a homogeneous, colorless liquid was formed [44]. GO was synthesized from graphite powder by a modified Hummers method [45].

The preparation of electrolyte solution: GO and $PdCl_2$ was dispersed in 1/15 M, pH 9.2 PBS, and ultra sonication-mixed for several minutes to form a homogeneous solution. Proportion able amount of Ethylene (H_2O : Ethylene = 9: 1) was added, ultra sonication-mixing to form a solution containing 0.1 mg mL^{-1} of GO and 0.8 mM $PdCl_2$. Water as employed to protect Ethylene during the electro deposition [46].

The preparation of Pd-GE: the electrochemical deposition of Pd-GENCs on the ITO was performed in the above electrolyte solution from –1.5 to 0.5 V for 10 circles at the scan rate of 10 mV s^{-1} . During electro deposition process, ultrasonic wave was irradiated onto the solution. For comparison, electro deposition was also conducted at the same condition without $PdCl_2$ and GO to prepare GO/ITO and Pd/ITO. The temperature of the solution was controlled at 25 ± 0.1 °C using a water bath. Prior to experiments, the solution was deoxygenated with high purity nitrogen gas.

RESULTS AND DISCUSSION

Characterization of Pd-GE

The morphology of Pd-GE formed on the surface of ITO was observed by SEM. The Fig. 1B showed that the Pd with grains like-shape which the size of nanospheres were uniform distribution with a diameter about 80 nm (Fig. 1A), combining well with graphene film and the practical size became much smaller than the pure nano-Pd, and the surface was relative uniform. The EDS pattern further revealed that the product was composed of C and Pd (Fig. 1C),

suggesting that Pd–GENCs was synthesized successfully. The reason, as previous reported [24], was that GO with the negative charge combined

effectively with Pd²⁺ with the positive charge through electrostatic attraction.

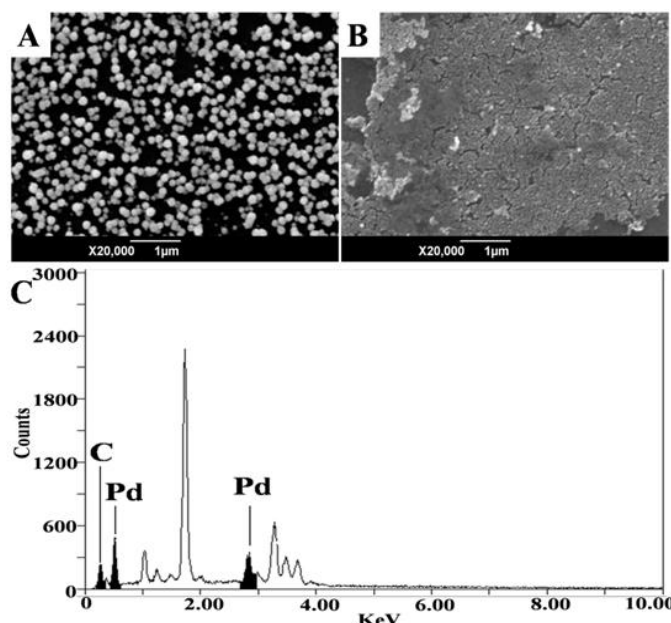


Fig1. SEM images of Pd(A), Pd–GENCs(B); EDS of Pd–GENCs(C).

Electrochemical properties of Pd–GE/ITO

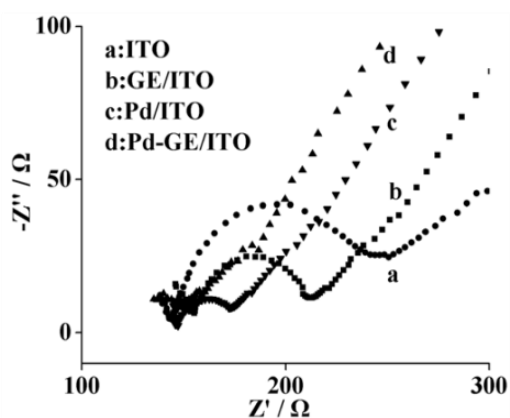


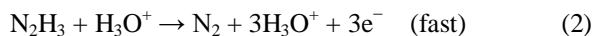
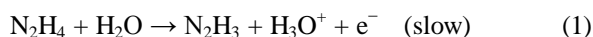
Fig2. EIS plots for the ITO (a), GE/ITO (b), PdNPs/ITO (c) and the Pd–GENCs/ITO (d) in a solution of 1.0 mM [Fe(CN)₆]^{3-/4-} + 0.1 M KCl as the supporting electrolyte. The frequencies swept from 10⁵ to 10⁻² Hz.

Electrochemical impedance spectroscopy (EIS) is an effective method for probing the whole procedure in preparing modified electrodes, which can provide information on the impedance changes accompanying the stepwise electrode modification process. The diameter of the semicircle in the Nyquist plot equals the electron-transfer resistance (R_{et}), which is related to the electron-transfer kinetics of the redox probe at the electrode surface. Fig. 2 displayed the EIS of the ITO, GE/ITO, Pd/ITO, and Pd–GE/ITO in 1.0 mM [Fe(CN)₆]^{3-/4-} containing 0.1 M KCl. The R_{et} of the Pd/ITO (Fig. 2 curve c) and the GE/ITO (Fig. 2 curve b) was obviously smaller

than that of the ITO (Fig. 2 curve a), demonstrating that Pd nanospheres had formed and attached to the electrode and GE in the modified electrode promote the electron transfer of the ITO. The R_{et} of the Pd–GE/ITO (Fig. 2 curve d) was greatly smaller than that of the GE/ITO and the Pd/ITO, indicating the successful conformation of Pd–GENCs. The Pd–GE/ITO was improved that it had the good conductivity performance for its synergic effect [47].

Fig. 3A, an anodic peak was observed by the ITO (red curve) and it displayed a very low background in the working potential range with 5.0 μM N₂H₄. The Pd/ITO (green curve) had an obviously peak relative to the GE/ITO (black curve) and the ITO which was contributed to the catalysis of Pd. In the same concentration conditions, Pd–GE/ITO (blue curve) electrode response curve was much larger than the Pd/ITO. The increase of the anodic current at more positive potential was similar which was ascribed to the intrinsic characteristics and synergic effect of Pd–GENCs immobilized on the electrode surface. For the electrode modified with Pd–GENCs, that which was Pd–GE/ITO (Fig. 3B) without N₂H₄, and when the same concentration of N₂H₄ was added to blank 0.1 M, pH 7.0 PBS, a significant increase in the anodic peak current was observed accompanying the decrease of cathodic peak current, demonstrating a typical electro catalytic reduction process of N₂H₄ by Pd–GENCs. According to a previous

report [48], the mechanism of N_2H_4 oxidation as follows:



The electro catalytic of N_2H_4 on the Pd–GE/ITO was controlled by diffusion of the analytes in bulk solution.

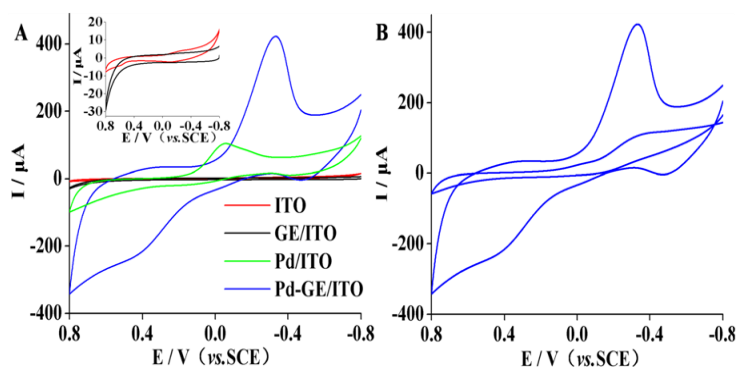


Fig3(A). CVs of the ITO (red line), GE/ITO (black line), Pd/ITO (green line) and the Pd–GENCs/ITO (blue line) with N_2H_4 of $5.0 \mu M$. (B) The Pd–GENCs/ITO with $5.0 \mu M N_2H_4$ or without in $0.1M$, $pH 7.0$ PBS at the scan rate of $100 mV/s$.

The Influence of the Potential Applications

Effect of applied potential for the determination of N_2H_4 was investigated at different potentials ranging from 0 to 0.50 V. At the applied potentials from 0 to 0.25 V, the electro oxidation response of N_2H_4 increased and reached a peak plateau. From 0.25 to 0.50 V, the response of the electrode gradually decreased. Moreover, the baseline current of the signal became unstable above 0.25 V. As a result, optimal potential at 0.25 V was finally chosen as the applied potential throughout all the amperometric measurements.

As shown in Fig. 4, the different modified electrode had the different amperometric responses for the same concentration of N_2H_4 in $pH 7.0$ PBS at 0.25 V. From the Fig. 4A, we could see that the Pd–GE/ITO had great electrochemical response than others when added the same concentration of N_2H_4 step by step, Fig. 4B showed the corresponding calibration curve of the steady–state current versus N_2H_4 concentration. As shown, the proposed sensor got the biggest signal response for the sensitive determination of N_2H_4 , and had good linear relationship

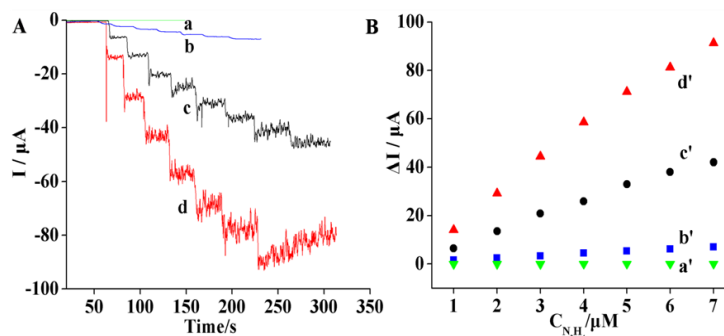


Fig4(A). Amperometric responses of the ITO (a), GE/ITO (b), Pd/ITO (c), and the Pd–GENCs/ITO (d) at $0.25 V$ (vs. SCE) upon successive addition of the same concentration of N_2H_4 in $0.1 M$, $pH 7.0$ PBS; (B) The linear relationship between the concentration of N_2H_4 and response current.

Amperometric Detection of Hydrazine

Fig. 5A illustrated a typical current–time curve of the sensor upon the addition of an aliquot concentration of N_2H_4 into a continuous stirring $pH 7.0$ PBS at 0.25 V. The 95% of steady–state current could be obtained less than 3 s by using the modified electrode, revealing the faster response of the sensor. At low N_2H_4 concentration, the diffusion of N_2H_4 to the electrode surface was

negligible. However, the increasing of N_2H_4 concentration affected the normal diffusion of new analyte molecules to the electrode surface. At the concentration that was higher than $660.5 \mu M$, there was a leveling off in the electrochemical response. Accordingly, as shown in Fig. 5B, the linear response obtained for N_2H_4 sensing at the Pd–GE/ITO was divided into two parts: (1) from 0.1 to $660.5 \mu M$, the linear regression equation

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was $I (\mu\text{A}) = -0.7992 C (\mu\text{M}) -13.63$ ($r = 0.9986$) with a sensitivity of $799.2 \mu\text{A mM}^{-1} \text{cm}^{-2}$ and a detection limit of $0.02 \mu\text{M}$ ($S/N = 3$); (2) from $660.5 \mu\text{M}$ to 2.5 mM , the linear regression

equation was $I (\mu\text{A}) = -0.3771 C (\mu\text{M}) -329.1$ ($r = 0.9926$) with a sensitivity of $377.1 \mu\text{A mM}^{-1} \text{cm}^{-2}$.

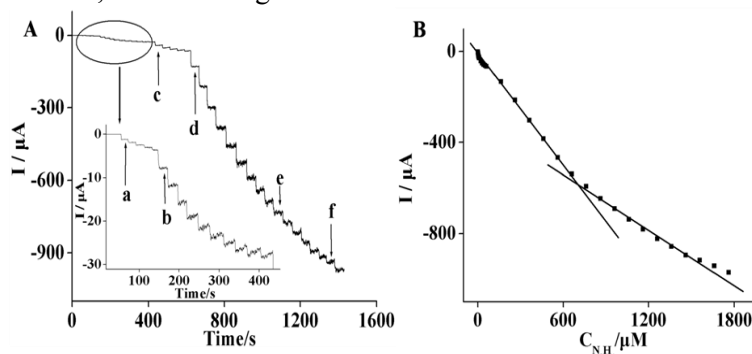


Fig5(A). Amperometric responses of the Pd–GE/ITO at 0.25 V (vs. SCE) upon successive addition of 0.1 μM (a), 1.0 μM (b), 10.0 μM (c), 100.0 μM (d), 1.6 mM (e) and 2.2 mM (f) N₂H₄ in 0.1 M, pH 7.0 PBS. Inset: Amplification figure. (B) Plot of peak current vs. N₂H₄ concentration.

Table1. Comparisons of the responses of some N₂H₄ sensors constructed based on different modified electrodes.

Sensor	Line range(μM)	Detection limi(μM)	Sensitivity (μAmM ⁻¹ cm ⁻²)	Ref.
Nano-copper oxide/GCE	0.1-600.0	0.03	94.2	49
RuON-GCE	2.0-268.3, 268.3-417.3	0.15	-	50
PtNPs/ZnO/GCE	0.5-1300.0, 1300.0-6000.0	0.2	110.0	26
HTP-MWCNT-CPE	1.0-20.0, 20.0-1000.0, 1000.0-6000.0	0.13	12.6	51
Mn(II)complex/MWCNTs/GCE	1.0-1050.0	0.5	38.0	52
PANI-Ag/GCE	20.0-90.0	-	-	53
PdNPs-PANI-GCE	40.0-800.0	0.06	0.5	48
GNPs/Ch/GCE	0.5-500.0, 500.0-9300.0	0.1	89.1	54
BiHCF/CCE	7.0-1100.0	3.0	4.2	55
PSS-GE/GCE	3.0-300.0	1.0	-	56
Pd-GE/ITO	0.1-660.5, 660.5-2500.0	0.02	799.2	This work

(RuON: ruthenium oxide nanoparticles; PtNPs: platinum nanoparticles; HTP: 4-hydroxyl-2-(triphenylphosphonio) phenolate; MWCNTs: Multi-walled carbon nanotubes; PANI: polyaniline nanowires; PdNPs: palladium nanoparticles; GNPs: gold nanoparticles; Ch: choline; BiHCF/CCE: bismuth hexacyanoferrate/carbon ceramic electrode; PSS: poly (sodium styrenesulfonate).)

The comparison between previously reported chemically modified electrodes for the determination of N₂H₄ was listed in Table 1. As seen, the designed Pd–GE/ITO exhibited relatively lowest detection limit, highest current sensitivity and wider linear range with two linear segments. The excellent sensor could be attributed to the composite structure of Pd–GENCs film, which had synergic effect toward N₂H₄ oxidation.

Repeatability and Stability of the Sensor

The repeatability and stability of the Pd–GE/ITO were also studied in the linear range of N₂H₄. The relative standard deviation (RSD) was 2.1% for five successive measurements of 5.0 μM N₂H₄ in PBS. The current response in

PBS containing 5.0 μM N₂H₄ showed no obvious change after 30 cycles, thereafter decreasing slowly with the increase of numbers of cycles. The storage stability of the sensor was also investigated. The amperometric measurements were measured using the same electrode and it retained above 95% of its initial response when stored at 4°C for 4 weeks.

CONCLUSIONS

In this study, the N₂H₄ sensor had been successfully prepared. The sensor exhibited a simple fabrication and good electro catalytic activity for N₂H₄ with the wide linearity, excellent low detection limit and high sensitivity. This might

be caused by synergic effect of carbon materials and metallic nano composites. The research provided a new idea for small molecule detection. The further work is on our schedule.

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