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Electrochemically Co-Deposition of Palladium Nanoparticles and Poly(1, 5-diaminonaphthalene) onto Multiwalled Carbon Nanotubes (MWCNTs) Modified Electrode and its Application for Amperometric Determination of Nitrite

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In this article, palladium nanoparticles (PdNPs) and 1, 5- diaminonaphthalene (1, 5-DAN) were electrochemically co-deposited onto multiwalled carbon nanotubes (MWCNTs) modified glassy carbon electrode (PdNPs-poly(1, 5-DAN)/MWCNTs/GCE). The morphology and properties of PdNPs-poly(1, 5-DAN)/MWCNTs/GCE were characterized by scan electron microscope (SEM), energy dispersive X-ray spectrum (EDX) and electrochemical techniques. The proposed sensor exhibited an excellent electrocatalytic performance for nitrite detection. The oxidation potential for nitrite detection at the fabricated sensors was decreased (0.792 V) and peak current was evidently improved, mainly due to the high synergistically catalytical effect of Pd nanostructures, poly(1, 5-DAN) and MWCNTs. The results revealed that the electrooxidation mechanism of nitrite was involved two electrons transfer in the irreversible reaction at the PdNPs-poly(1, 5-DAN)/MWCNTs/GCE. The oxidation peak current of nitrite was proportional to its concentration with the linear range of 0.25 μM ~ 0.1 mM by amperometry, and the limit of detection (LOD) was as low as 0.08 μM (S/N = 3). Furthermore, as-prepared sensors had good anti-fouling property, long-term stability and excellent practical ability, which was successfully applied to detect nitrite in real water samples and gained satisfactory recoveries of 97% ~ 105%.

Keywords: Palladium; Diaminonaphthalene; Synergistic effect; Electrooxidation

1. INTRODUCTION

Nitrite ion (NO_2^-) is a typical inorganic species, which has been extensively used in drinking water and vegetables as food additives and fertilizing agent for decades. High levels of nitrite may cause severe health problems such as blue baby syndrome, gastrointestinal tumors, and stomach cancer [1]. When absorbed into the bloodstream, nitrite ions interact with hemoglobin to produce methemoglobin and reduce the blood capacity to transport oxygen. Nitrite can also react with various amines to form N-nitrosamines, which are toxic and carcinogenic to humans [2]. According to the world health organization (WHO), the maximum permissible level of nitrite in drinking water is 3 mg/L. Therefore, the precise, sensitive determination of excessive nitrite ions is of great importance in food and environment.

Numerous analytical techniques have been developed for the determination of nitrite such as chemiluminescence [3], ion chromatography [4], spectrophotometry [5], capillary electrophoresis [6] and electrochemical methods [7, 8]. However, most of the traditional analytical methods are tedious procedure, complex pretreatment, high cost and not suitable for on-site detection [9]. Electrochemical techniques have gained great attention due to the low cost, possible miniaturization, high sensitivity, quick response, environmental-friendly property and feasibility in-field application [10, 11], which are encouraging for nitrite detection. Nevertheless, conventional naked electrodes (bare glassy carbon electrode, bulk metal electrode etc.) could not be used to detect nitrite with satisfactory results because of high working potential and electrode fouling [12, 13]. So many efforts are made for the design of stable, sensitive and reliable electrode materials for quantitative detection of nitrite ions.

Organic conducting polymer have received great attention for decades with a lot of potential applications due to their electrical conductivity, good environmental stability and ease of preparation [14]. Aromatic amine conducting polymers, as electrode materials, had unique ability to form stable complexes towards analytical targets [15]. Polydiaminonaphalene, including poly (1, 8-diaminonaphalene) and poly(1, 5-DAN), were acted as a kind of aromatic diamines and widely investigated for analytical application such as biosensors [16], heavy metals detection [17, 18], organic pollutants [19] and so on. Some electrode substrates or matrix, for example, carbon paste electrode, bare glassy carbon electrode, or naked platinum electrode, have been used to prepare polydiaminonaphalene for electro-analysis. However, the sensitivity and stability of the electrochemical sensors are not influentially enough for real applications [20, 21]. Therefore, suitable and excellent electrode platform was necessary to develop for immobilizing PDAN polymer.

Multi-walled carbon nanotubes (MWCNTs) were recognized as one of the promising active materials for the conductive supports due to the number of active sites, high conduction channels, wide potential window and good chemical stability, which can greatly increase the electrocatalytic oxidation/reduction at the surface of electrodes. In addition, intense efforts have been devoted to the incorporation of metallic nanoparticles into conductive polymers to improve their catalytic performance, and they can provide the strong electronic interactions between the nanoparticles and the polymer matrices [23]. In particular, Pd nanoparticles have been exploited for electroanalytical applications, which was attributed to its high electrocatalytic activity, chemical inertness to oxygen, low cost and environmental- friendly property [24]. To the best of our knowledge, there are no reports on the Pd nanopartilce and poly(1, 5-DAN) modified MWCNTs matrix for electrochemical sensing of nitrite.

In this present work, we report that amperometric determination of nitrite was carried out by PdNPs and poly(1, 5-DAN) co-decorated onto MWCNTs modified glassy carbon electrode. The PdNPs-poly(1, 5-DAN)/MWCNTs electrode exhibits excellent electrocatalytic activity for nitrite detection, and the wide linear range of 0.25 μM ~ 0.1 mM and low detection limit (LOD) of 0.08 μM were achieved. The practical ability, anti-interferences, stability and reproducibility were also evaluated. The experimental results demonstrated the excellent performance of PdNPs-poly(1, 5-DAN)/MWCNTs modified electrode for the detection of nitrite.

2. EXPERIMENTAL

2.1 Regents and materials

Palladium chloride, 1, 5- DAN were bought from Sigma-Adlrich (Sigma-Adlrich, USA). $NaNO_2$, $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, KCl, N, N-dimethyl formamide (DMF) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). MWCNTs were obtained from Pioneer Nanotechnology Co. (Nanjing, China), and were functionally carboxyl-pretreated before use [22]. The supporting electrolyte was used for phosphate buffer solution (PBS) prepared by 0.1 M KH_2PO_4 and 0.1 M K_2HPO_4 with different pH. All the chemicals were of analytical reagent grade and used without further purification. Electrochemical experiments were performed in N_2 atmosphere at room temperature.

2.2 Apparatus

All the electrochemical experiments were carried out using CHI760 E electrochemical workstation (Shanghai Chenhua Co., China) with a conventional three-electrode cell. A modified glassy carbon electrode (GCE) of 3 mm diameter was used as working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as reference electrode and counter electrode, respectively. The morphological characterization and composition of the composite materials were examined using a field emission scanning electron microscope with an energy dispersive X-ray spectrum (S-4800, Japan).

2.3 Preparation of PdNPs-poly(1, 5-DAN)/MWCNTs modified GCE

A bare glassy carbon electrode was polished carefully to a mirror-like surface with 0.05 µM alumina aqueous slurry, then successively washed in an ultrasonic cleaner with nitric acid (1:1), anhydrous ethanol and distilled water, respectively. The GCE was dried out for use. Next, 2.0 mg MWCNTs were dispersed in 1 mL DMF with the aid of ultrasonic agitation to give 2.0 mg/mL black suspension. 5 µL of MWCNTs solution was cast on the surface of fresh GCE and then the solvent DMF was evaporated to form a MWCNTs-modified GCE (MWCNTs/GCE).

Pd nanoparticles and poly(1, 5-DAN) were electrochemically co-deposited at the MWCNTs/GCE. Briefly, the resulting MWCNTs/GCE was immersed in the electrochemical cell containing 0.25 mM 1, 5-DAN and 0.05 mM $PdCl_2$ in the 0.1 M HNO_3 solution. The co-electrodeposition of Pd nanoparticles and poly(1,5-DAN) was done by 20 successive cyclic voltammetry in the potential range of -0.2 to 1.2 V at a scan rate of 50 mV/s. The resulting electrode was gently rinsed with water and dried at room temperature. For comparison, the poly (1, 5-DAN)/MWCNTs/GCE or PdNPs/MWCNTs/GCE were electropolymerized independently by the same procedure without Pd or 1.5-DAN solution.

2.4 Electrochemical measurement

Cyclic voltammetry was carried out for nitrite detection in the potential of -0.2 V ~ 1.2 V at a scan rate of 50 mV/s. Low concentration of nitrite was detected by amperometry, which was performed at an applied potential of 0.80 V in 0.1 M PBS (pH 4.5) solution under stirring conditions.

3. RESULTS AND DISCUSSION

3.1 SEM and EDX characterization of PdNPs-poly(1, 5-DAN)/MWCNTs/GCE

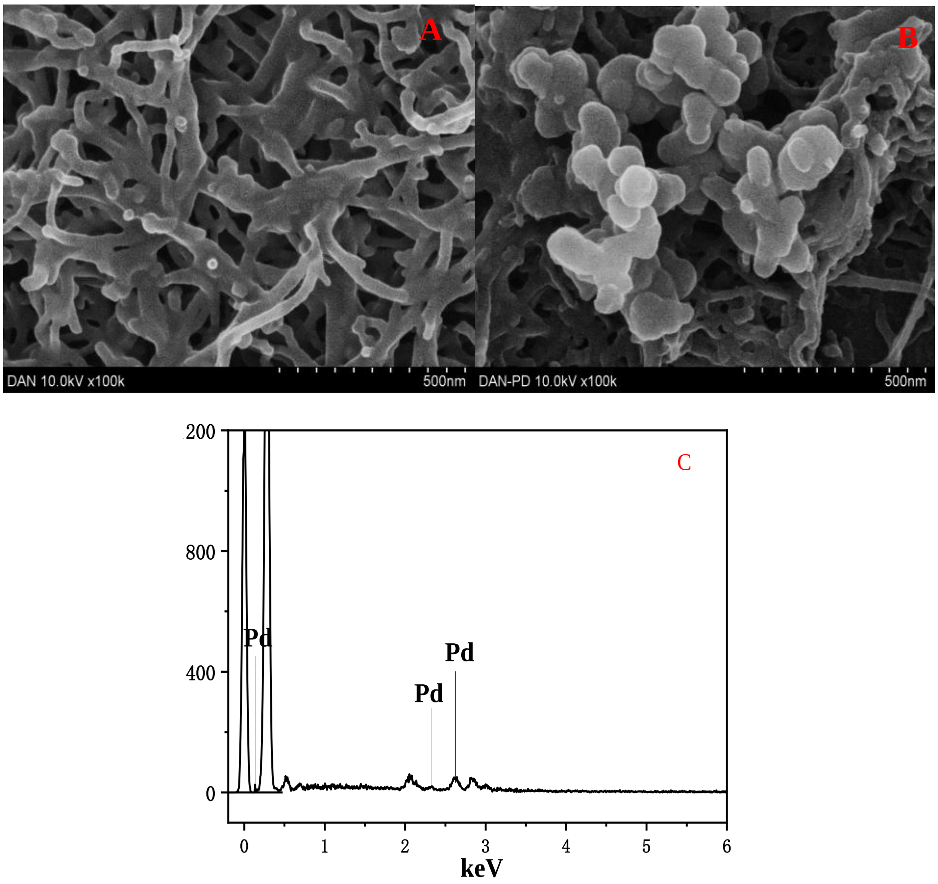

Figure 1. SEM of (A) poly(1, 5-DAN)/MWCNTs/GCE and (B) PdNPs-poly(1, 5-DAN)/MWCNTs/GCE; (C) EDX of PdNPs-poly(1, 5-DAN)/MWCNTs/GCE

Figure 1 displays the SEM images of (A) poly(1, 5-DAN)/MWCNTs/GCE and (B) PdNPs-poly(1, 5-DAN)/MWCNTs/GCE. It can be clearly seen that the distribution and thickness of poly(1, 5-DAN) film was relatively homogeneous over the surface of MWCNTs (Figure 1A).

Pd nanoparticles were incorporated into the poly(1, 5-DAN) film, and both of them were decorated on the tubular networks of MWCNTs (Figure 1B). The presence of PdNPs was further confirmed by EDX analysis and the result was shown in Figure 1C.

3.2 Electrochemical characterization of PdNPs-poly(1, 5-DAN)/MWCNTs/GCE

Figure 2 displays the cyclic voltammograms of (a) bare GCE, (b) MWCNTs/GCE, (c) PdNPs/MWCNTs/GCE and (d)PdNPs-poly(1, 5-DAN)/MWCNTs/GCE in 5 mM $[Fe(CN)_6]^{3-/4-}$ and 0.1 M KCl solution at 50 mV/s. As can be seen in Fig.2a, well-defined redox peaks of $[Fe(CN)_6]^{3-/4-}$ were obtained at the bare GCE, which revealed that the GCE surface was satisfactory through pretreatment. After MWCNTs modified GCE (b), the peak currents of $[Fe(CN)_6]^{3-/4-}$ were obviously increased at the MWCNTs/GCE. Moreover, when PdNPs were electropolymerized onto the MWCNTs/GCE, the redox peaks of $[Fe(CN)_6]^{3-/4-}$ were improved further at the PdNPs/MWCNTs/GC. However, when PdNPs and poly(1, 5-DAN) were co-deposited on the MWCNTs/GCE, the PdNPs-poly(1, 5-DAN)/MWCNTs/GCE exhibited largest peak current signal and best electrochemical response in $[Fe(CN)_6]^{3-/4-}$ solution. According to Randles-Sevcik equation [25]:

$$I_p = 2.69 \times 10^5\, AD^{1/2}\, n^{3/2}\gamma^{1/2}\, C$$

where n is the number of electrons participating in the redox reaction, A is the area of the electroactive area (cm^2), D is diffusion coefficient of the molecule in solution (cm^2/s), and γ is the scan rate of the potential perturbation (V/s).

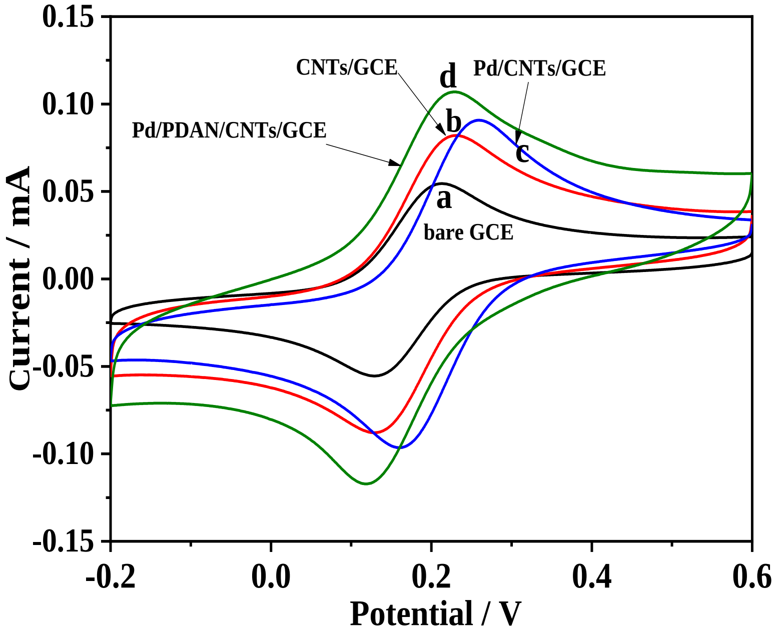

Figure 2. Cyclic voltammograms of (a) bare GCE, (b) MWCNTs/GCE, (c) PdNPs/MWCNTs/GCE, and (d) PdNPs-poly(1, 5-DAN)/MWCNTs/GCE in 5 mM $[Fe(CN)_6]^{3-/4-}$ containing 0.1 M KCl solution with a scan rate of 50 mV/s.

The $[Fe(CN)_6]^{3-/4-}$ redox system exhibits a heterogeneous one-electron transfer ($n = 1$). C is equal to 5 mM, and the diffusion coefficient (D) is $(6.7 \pm 0.02) \times 10^{-6}$ cm^2/s. The average values of the electroactive areas for optimized MWCNTs/GCE, PdNPs/MWCNTs/GCE and PdNPs-poly(1, 5-DAN)/MWCNTs/GCE were 0.107 cm^2, 0.118 cm^2 and 0.145 cm^2, respectively. It confirmed that the as-prepared electrode had the highest electroactive area, which was beneficial for their electrochemical performance. MWCNTs, as a good substrate and platform, provided higher specific surface area for the co-electrodeposition of PdNPs and poly(1, 5-DAN), and enabled much electron conducting pathway through MWCNTs tube-like networks for the enhancement in electron transfer process. In addition, PdNPs were incorporated into the matrix of poly(1, 5-DAN), which resulted in enhancing conductivity at the composites modified electrode. Therefore, the electrocatalytic performance of the proposed method was remarkably enhanced due to the synergistically catalytical effect of Pd nanostructures, poly(1, 5-DAN) and MWCNTs.

3.3 Electrochemical oxidation of nitrite

Figure 3 compares the CV curves of (a, e) PdNPs-poly(1, 5-DNA)/MWCNTs/GCE, (b) bare GCE, (c) MWCNTs/GCE and (d) poly(1, 5-DAN)/MWCNTs/GCE in the absence (a) and (b → e) presence of 3 mM $NaNO_2$ in 0.1 M PBS (pH 4.5) solution at a scan rate of 50 mV/s. As can be seen in Figure 3, no electrochemical redox reaction was occurred at the PdNPs-poly(1, 5-DAN)/MWCNTs/GCE in the absence of nitrite (blank solution (a)). The oxidation of nitrite occurred at the bare GCE (b) with a wide peak and the peak potential was E_{pa} = 0.90 V. In comparison with bare GCE, both of MWCNTs/GCE (c) and poly(1, 5-DAN)/MWCNTs/GCE (d) exhibited increased oxidation peak currents of nitrite, and the oxidation peak potentials negatively shifted to 0.81 V and 0.796 V, respectively.

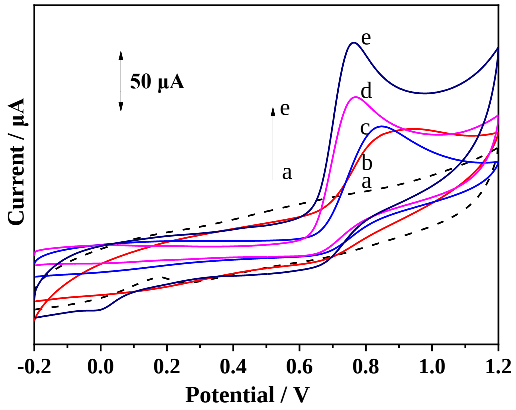

Figure 3. cyclic voltammograms of (a, e) PdNPs-poly(1, 5-DAN)/MWCNTs/GCE, (b) bare GCE, (c) MWCNTs/GCE and (d) poly(1, 5-DAN)/MWCNTs/GCE in the absence (a) and presence (b → e) of 3 mM nitrite in the PBS (pH 4.5) solution with a scan rate of 50 mV/s.

Furthermore, when PdNPs and poly(1, 5 DAN) co-deposited on the MWCNTs/GCE, PdNPs-poly(1, 5-DAN)/MWCNTs/GCE displayed the largest peak current for the nitrite detection, and the peak potential was negatively shifted to 0.792 V, indicating that electrochemical oxidation of nitrite can be carried out more easily. This enhancement in the peak current and decrement in peak potential can be also attributed to the high electroactive area resulting from the synergistic effect of PdNPs, poly(1, 5-DAN) and MWCNTs, which were in agreement with CVs experiment in $[Fe(CN)_6]^{3-/4-}$ solution.

In order to investigate the reaction kinetics, the effects of scan rate on the oxidation of peak potential and current were evaluated by cyclic voltammetry at different scan rates. Figure 4 A represents the typical CVs of 3 mM $NaNO_2$ in 0.1 M PBS (pH 4.5) at the PdNPs-poly(1, 5-DAN)/MWCNTs/GCE at the different scan rates from 10 mV/s to 200 mV/s. The oxidation peak currents increased linearly with the square root of the scan rate, and the calibration equation was $y = 7.624x + 28.77$ ($R^2 = 0.9906$), which indicated that the involved electrochemical reaction was controlled by the diffusion step. The oxidation peak potential (E_p) was shifted to more positive values with the increase of scan rate, which confirmed the irreversible behavior for the oxidation process of nitrite. The peak potential was proportional to the logarithm of scan rate and the linear regression equation was indicated as $y = 0.067x + 0.709$ ($R^2 = 0.9925$). According to Laviron's equation [25], the electron transfer number (n) is calculated as the following equation:

$$E_{pa} = E^{0'} + \left(\frac{RT}{anF}\right)\ln\left(\frac{RTk^0}{anF}\right) + 2.30\left(\frac{RT}{anF}\right)\log v \ (1)$$

where a is the electron transfer coefficient, n is the number of electrons transferred, $E^{0'}$ is the formal potential, v is the scan rate. R, T and F have their conventional meanings. The n value was calculated to be 1.8 (about 2), when a is taken 0.5 in totally irreversible reaction. It means that the oxidation mechanism of nitrite involves two electrons transfer at the PdNPs-poly(1, 5-DAN)/MWCNTs/GCE, as shown in Eqs (2) and (3) [26, 27]:

$$2NO_2^- \leftrightarrow 2NO_2 + 2e \quad (2)$$

$$2NO_2 + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+ \quad (3)$$

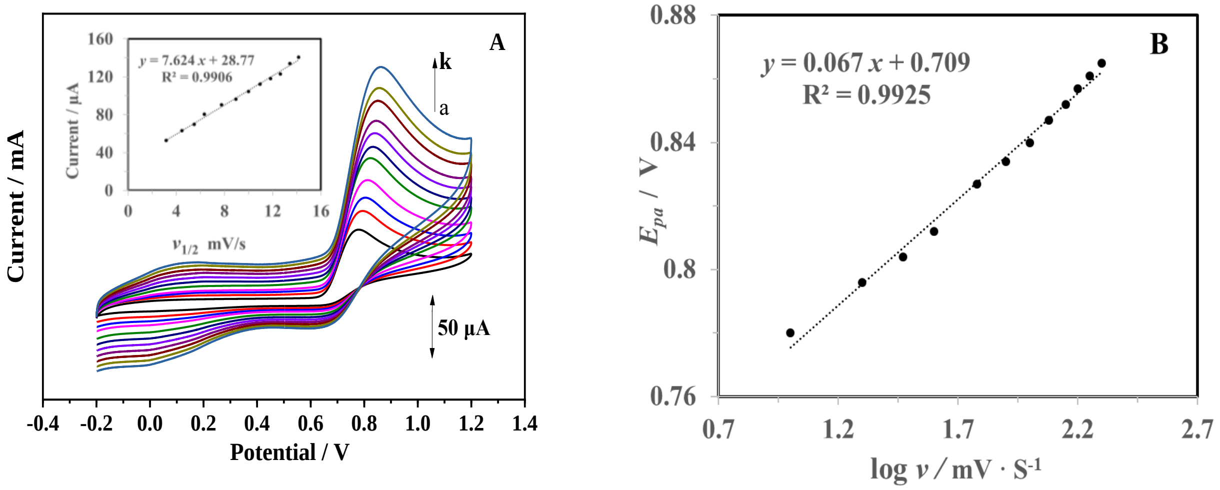

Figure 4. Cyclic voltammograms of PdNPs-poly(1, 5-DAN)/MWCNTs/GCE in 0.1 M PBS (pH 4.5) containing 3 mM $NaNO_2$ at different scan rates (a → k: 10, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200 mV/s); Inset is the plot of oxidation peak current versus $v^{1/2}$. (B) The calibration curve of peak potential versus log v.

3.4 The effect of pH

The influence of pH on the electrochemical behavior of nitrite was very important, therefore, the electrochemical properties of nitrite at the PdNPs-poly(1, 5-DAN)/MWCNTs/GCE was studied at different pH values ranging from 3.0 to 7.0. The peak currents of nitrite increased by increasing pH from 3.0 to 4.5, but then decreased with pH ranging from 5.0 to 7.0. A high sensitivity of nitrite was observed in pH 4.5 than that of other pH. In strong acidic media (pH < 4), nitrite was not stable, which may undergo the following conversion of NO_2^- to NO and NO_3, as shown in Eq. (4): $2H^+ + 3NO_2^- \rightarrow 2NO + NO_3^- + H_2O$ [28]. When pH was above 5.0, the electrocatalytic oxidation of nitrite became more difficult due to shortage of protons [29], and the catalytic peak currents were also decreased. Therefore, pH 4.5 was chosen as an optimum for the further studies.

3.5 Amperometric determination of nitrite

Under the optimum conditions, amperometry was employed to investigate the electrochemical response of nitrite at the proposed PdNPs-poly(1, 5-DAN)/MWCNTs/GCE. Figure 5 displays amperometric i-t curve for successive additions of nitrite containing 0.1 M PBS (pH 4.5) at an applied potential of 0.80 V under stirring condition. The oxidation current was proportionally linear to the concentration of nitrite in the range of 0.25 μM ~ 100 μM with linear regression equation ($y = 0.021\,x + 0.129$, $R^2 = 0.9971$). The limit of detection was calculated as 0.08 μM ($S/N = 3$), which was far below the guidance level of nitrite ions (3 mg/L) prohibited by the World Health Organization (WHO).

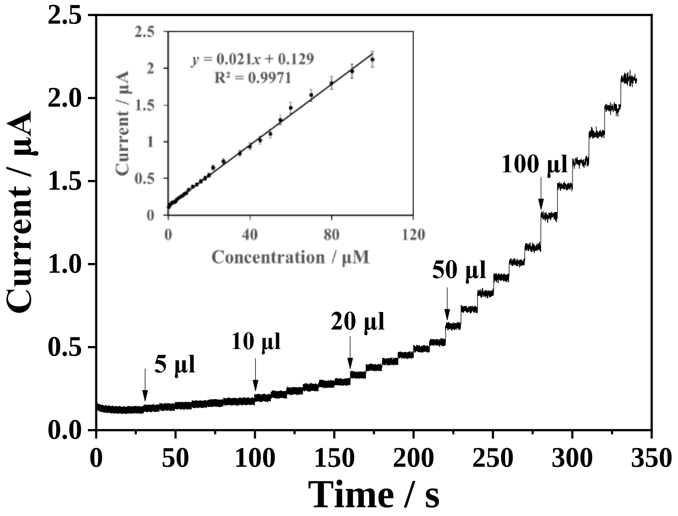

Figure 5. The current-time responses of PdNPs-poly(1, 5-DAN)/MWCNTs/GCE with the successive addition of different concentration of nitrite in 0.1 M PBS (pH 4.5) at an applied potential of 0.8 V; Inset is calibration plot of amperometric current versus nitrite concentration.

The electrochemical properties of PdNPs/poly(1, 5-DAN)/MWCNTs for nitrite detection were comparable to those of AuNPs/PRhB/CNTs/GCE reported by our groups [30]. Nevertheless, palladium is cheaper and easily obtained than gold. The PdNPs and poly(1, 5-DAN) composites can be co-deposited onto the CNTs surface by a facile and one-step electrochemical polymerization, which provide a simple and environmental-friendly method for preparation of PdNPs/poly(1, 5-DAN)/CNTs/CGE. The LOD, sensitivity and linear response range of the reported sensor were superior to or comparable with other those of nitrite sensors previously reported, the results were summarized in Table 1. The results also proved that the PdNPs-poly(1, 5-DAN)/MWCNTs composites modified electrode as prospective materials was deserved to promote for nitrite detection.

Table 1. Results of the present study compared with previous reports of various electrodes for nitrite sensing

Electrode	Method	Linear range	LOD	Sensitivity	Ref.
AuNPs/PRhB/CNTs [c]	i-t DPV	0.02 ~ 5.00 µM 1 ~ 10 mM	6.7 nM	87.58 µA •L• mM^{-1}	[30]
Pd/SWCNTs [d]	DPV	2 ~ 238µM 283 ~ 1230 µM	0.25 µM	417 µA mM^{-1} 192 µA mM^{-1}	[31]
PdCo/CNF [e]	DPV	0.4 ~ 30 µM 30 ~ 400 µM	0.2 µM	----	[32]
Au-Pd/rGO [f]	i-t	0.05 ~ 1000 µM	0.02 µM	-----	[33]
ERGO-Pd [g]	i-t	0.04 ~ 108 µM	15.64 nM	7.672 µA µM^{-1} cm^{-2}	[34]
GC/poly-TBO [h]-SWCNT	i-t	0.001 ~ 4 mM	0.37 µM	84.3 mA M^{-1}	[35]
CTAB-GO [i] /MWCNT	DPV	5 ~ 800 µM	1.5 µM	102.7 µA mM^{-1}	[36]
GR-MWCNTs /FeNPs [j]	DPV	0.1 ~ 1680 µM	0.076 µM	0.697 µA µM^{-1} cm^{-2}	[37]
GO-MWCNT-PMA -Au [k]	DPV	0.2 µM ~ 0.01 mM	0.67 µM	483.51 µA mM^{-1} cm^{-2}	[38]
GNPs/MWCPE [l]	SWV	0.05 ~ 250 µM	0.01 µM	0.4177 µA L µM^{-1}	[39]
Au-MOF-5/GC [m]	CV	5.0 µM ~ 65 mM	1.0 µM	0.23 µA µM^{-1} cm^{-2}	[40]
Porphyrin/MOF-525	i-t	20 ~ 800 µM	2.1 µM	95 µA mM^{-1} cm^{-2}	[41]
PdNPs-poly(1, 5-DAN)/MWCNTs	i-t	0.25 µM ~ 0.1 mM	0.08 µM	708.27 µA mM^{-1} cm^{-2}	This work

c: gold nanoparticles/polyrhodamine B/CNTs

d: Single-walled carbon nanotube;

e: PdCo alloy nanoparticles-embedded carbon nanofiber;

f: Au-Pd nanostructures supported on reduced graphene oxide;

g: Reduced graphene/Pd nanocomposite;

h: Poly(Toluidine Blue O);

i: Graphene oxide;

j: Iron nanoparticles;

k: Gold nanoparticle decorated functionalized graphene oxide-carbon nanotube;

l: MWCNTs modified carbon paste electrode with gold nanoparticles;

m: Gold nanoparticles incorporated zinc based metal-organic framework.

3.6 Selectivity, stability and reproducibility

Selectivity is a very important factor for sensors, and the influence of common interfering ions along with nitrite has been examined by the amperometry test to evaluate the efficacy of the present sensor. Figure 6A shows the amperometric response of the PdNPs-poly(1, 5-DNA)/MWCNTs/GCE for successive additions of different ions and nitrite. It can be seen clearly that 50-fold concentration of Cu^{2+}, Mg^{2+}, Ca^{2+}, NH_4^+, F^-, SO_4^{2-}, $H_2PO_4^{2-}$, HCO_3^-, CO_3^{2-} and NO_3^- ions showed negligible current responses at the PdNPs-poly(1, 5-DNA)/MWCNTs/GCE, and as-prepared electrode has a good selectivity for nitrite detection in the presence of a 50-fold excess of interferents. The operational stability was further evaluated at the PdNPs-poly(1, 5-DNA)/MWCNTs/GCE by amperometry and the results were shown in Figure 6B. The amperometric current response of nitrite was about 97% of its initial current response when continuously run up to 2000 s, indicating that the proposed composites electrode had a good operational stability for nitrite detection. The reproducibility of as-prepared composites electrode was examined for 15 successive determination of 25 µM nitrite at the same electrode, and the relative standard deviation (RSD) was 2.13%. Taking 10 different electrodes for 25 µM nitrite detection, and the RSD was 4.53%, The results clearly showed that the fabricated PdNPs-poly(1, 5-DNA)/MWCNTs/GCE had excellent selectivity, comparable stability and reproducibility for the electrochemical detection of nitrite.

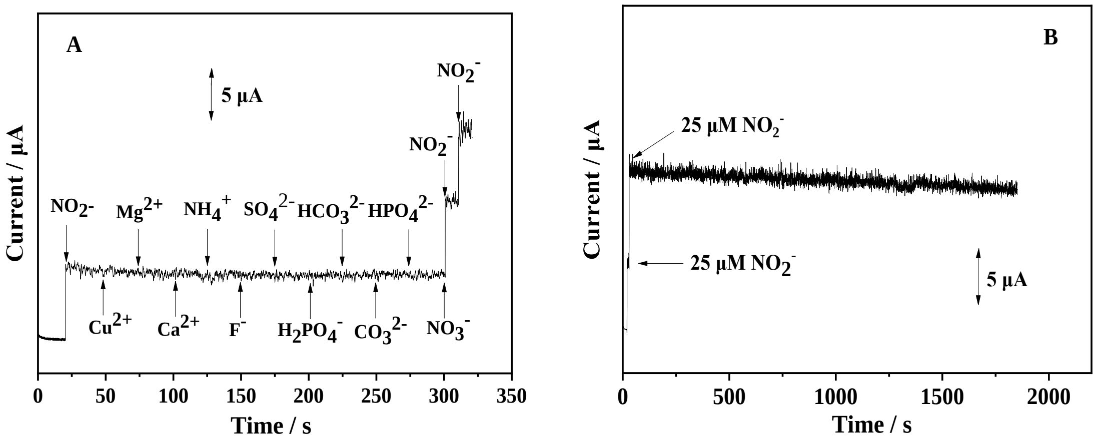

Figure 6. (A) Amperometric response of PdNPs-poly(1, 5-DAN)/MWCNTs/GCE for addition of 25 µM nitrite and 1.25 mM Cu^{2+}, Mg^{2+}, Ca^{2+}, NH_4^+, F^-, SO_4^{2-}, $H_2PO_4^{2-}$, HCO_3^{2-}, CO_3^{2-} and NO_3^{2-} into continuously stirred PBS. (B) Amperomitric i-t response up to 2000 s of PdNPs-poly(1, 5-DAN)/MWCNTs/GCE for 25 µM nitrite in 0.1 M PBS (pH 4.5) solution under stirring conditions.

3.7 Determination of nitrite in real samples

To demonstrate the practical ability of the present composites modified electrode, the detection of nitrite in different water samples was performed by amperometry. After the water samples were filtered, and the known concentration of nitrite was spiked into the water samples. A standard additions method was adopted to calculate the recovery [35, 36]. The results of recoveries from different water samples were summarized in Table 2. It can be clearly observed that the developed composites electrode had satisfactory recoveries in the range of 97% ~ 105% in water samples, which implied that the fabricated sensor was promoting to detect nitrite in real water.

Table 2. Determination of nitrite in real water samples at the PdNPs-poly(1, 5-DAN)/MWCNTs/GCE by amperometry (*n* = 3)

Sample	Added (µM)	Found (µM)	Recovery (%)	RSD (%)
Tap water	1	0.97	97	4.87
	2	1.96	98	3.96
	4	4.07	101.7	2.84
Lake water	1	1.05	105	4.95
	2	1.98	99	3.51
	4	4.06	102	3.64
Drinking water	1	1.03	103	4.62
	2	1.97	98.5	3.59
	3	2.96	98.6	3.28

4. CONCLUSION

In summary, a relatively simple and novel electrochemical platform was developed by palladium nanopartilces and poly(1, 5-DAN) co-deposited onto MWCNTs modified glassy carbon electrode. The PdNPs-poly(1, 5-DAN)/MWCNTs electrode exhibited excellent electrocatalytic activity toward the oxidation of nitrite, which showed high electroactive area and fast electron transfer due to the high synergistic effect of PdNPs, conducting polymer and MWCNTs. It showed wide linear range from 0.25 µM to 0.1 mM with low detection limit of 0.08 µM for nitrite detection. The fabricated composite electrode also displayed many advantages, such as operational stability, good anti-interferences, and acceptable reproducibility, and it can be successfully applied in analysis of nitrite in real samples with satisfactory results. This study may provide new method and opportunity in the field of electrochemical sensing for nitrite detection in environment and food control.

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