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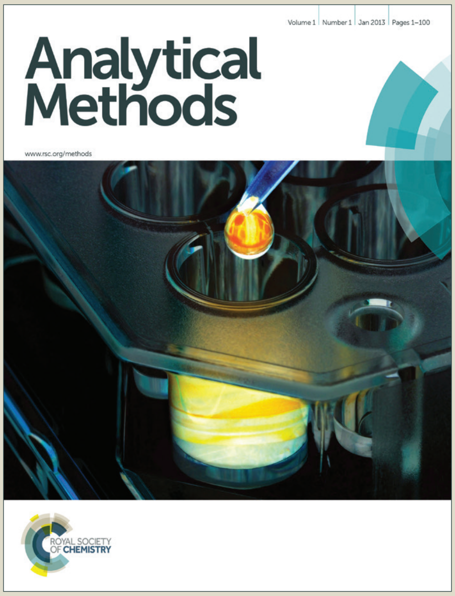

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Sensitive sensors for amperometric detection of nitrite based on carbon-supported PdNi and PdCo bimetallic nanoparticles

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Abstract

Carbon-supported PdNi (PdNi/C) and PdCo (PdCo/C) nanoparticles (NPs) were synthesized and modified on glassy carbon electrode (GCE) to fabricate highly sensitive amperometric nitrite sensors. Cyclic voltammetry (CV) and amperometric *i-t* curve were used to characterize the electrochemical behavior of the electrodes in the presence of nitrite. From the results, the PdNi/C and PdCo/C NPs modified electrodes both exhibited better electrochemical properties than commercial Pd/C catalyst with equal metal content (10%). The PdNi and PdCo sensors both exhibited remarkable sensitivity of 5.23 and 5.52 mA mM $^{-1}$ cm $^{-2}$, respectively. Interference studies showed that the modified electrodes exhibited excellent selectivity toward nitrite. In addition, the proposed sensors were applied to determine nitrite in several foods and moat water with satisfactory results.

Keywords:

Electrochemical sensor; PdNi/C; PdCo/C; Nanoparticle; Nitrite

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1. Introduction

Nitrite (NO_2^-), which extensively exists in the environment and is widely used in food preservation, has been proved that its excess level in the blood leads to haemoglobin oxidation [1, 2]. In addition, it can react with amine to form N-nitrosamines, many of which are known to be carcinogens. Due to the potential toxicity, it is quite necessary to determine nitrite for public health and environmental security [3]. Several techniques, including titrimetry [4], chemiluminescence [5], capillary electrophoresis [6], spectroscopic [7], chromatographic [8] and electrochemical methods [9] have been developed for nitrite determination. Compared to other methods, electrochemical techniques based on various modified electrodes are favoured owing to their high sensitivity, inherent simplicity, miniaturization, time saving and low cost [10]. However, the catalytic effect of many existing nitrite sensors were influenced by the complicated reduction products of nitrite [11]. Therefore, modified electrodes with suitable catalyst could not only overcome this shortcoming with an improved response, but also provided a means of improving sensitivity in analytical determinations [12].

Metal nanoparticles (NPs) possess extremely small size, a high specific surface area and unique physico-chemical characteristics and have been widely used for electrode materials [13-17]. The previous literature reported that the characteristics of noble metal and non-noble metals nanoparticles, especially catalytic property, were quite different from those of single noble metals [18]. The study of alloy electrodes is motivated primarily from the anticipation of a synergistic electrocatalytic benefit from the combined properties of the components of alloys [19]. Liu et al. reported an electrochemically co-deposited Pt NPs and Fe(III) on GCE and the sensitivity/selectivity of the sensor were prominent enhanced compared to Pt/C modified GCE [20]. Among those alloys, Pd-based catalysts, such as Pt-Pd [21], Au-Pd [22], Cu-Pd [23], Ni-Pd [16], have become a hot topic of interest because of their higher abundance and lower cost with other noble metal catalysts [16].

PdNi and PdCo bimetallic catalysts have attracted much attention in recent years. This can be attribute to the following points (i) Ni and Co are important members of mixed-valence transition metal which have proven to have excellent properties in electrocatalysis [19]. (ii) Ni and Co were commonly used as alloy electro-catalyst for both anodic and cathodic reactions [24]. (iii) Ni, Co can not only results in alterations of both electronic and geometric parameters of Pd, but also together effects the chemisorption behavior of oxygenated species from the electrolyte in the potential region where unalloyed Pd surfaces are normally oxide covered [16, 25, 26]. (iv) Ni and Co also found to be efficient catalysts to decrease the poisoning effect of Pd-based catalysts [27]. (v) PdNi and PdCo catalysts seem to be more stable and comparative easy to prepare [28]. Thus, the electrocatalytic activities of PdNi and PdCo based bimetallic nanomaterials have been investigated in this work to achieve better electrochemical sensors with higher sensitivity, selectivity and stability.

To the best of our knowledge, electrochemical sensors for nitrite based on PdNi and PdCo bimetallic catalysts have not been reported yet. In this work, the PdNi/C and PdCo/C modified GCEs were fabricated and characterized to explore their catalytic activity for nitrite oxidation. The electrochemical behaviors of the PdNi/C and PdCo/C modified GCEs were investigated by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and amperometric *i-t* curve. Those materials exhibited excellent performance for nitrite electro-oxidation, such as high electrocatalytic activity, excellent sensitivity and good selectivity. The modified electrodes were used to determine nitrite in several real samples with satisfactory results. The PdNi/C and PdCo/C modified GCEs offer new opportunities for fast, simple, and sensitive analyses of nitrite.

2. Experimental

2.1. Reagents and materials

$PdCl_2$, $Ni(NO_3)_2$, $Co(NO_3)_2$ (Aldrich); oleylamine (OAm, technical grade, 70%, Aldrich); carbon black (Kejen EC 300J); acetic acid (ACS reagent, g 99.7%, Aldrich); Pd/C (10% Pd loading) were purchased and used as received. Nafion (5 wt. %) was purchased from Sigma-Aldrich. $NaNO_2$ was from the Chemical Reagent Company of

Tianjin Hongyan (China); 0.1 M phosphate buffer solution (PBS, pH 7.0) was employed as a supporting electrolyte. Rod GCEs were from the Chenhua Co. Ltd. (Shanghai, China). All kinds of pickled juice were commercially available. All other Chemicals and reagents for electrochemical measurements were of analytical grade and used without further purification. The deionized (DI) water for solution preparation was from a Millipore Autopure system (18.2 MΩ, Millipore Ltd., USA).

2.2. Preparation of PdNi/C and PdCo/C modified GCEs

2.2.1 Preparation of PdNi/C and PdCo/C

PdNi/C and PdCo/C were prepared according to our previous report [23]. Follow the steps outlined below, under an nitrogen (N_2) gas flow and magnetic stirring, 1:1 mol ratio of $PdCl_2$ and $Ni(NO_3)_2$ were dissolved in a solvent of OAm, were mixed in a reaction flask and degassed at room temperature and 110 ℃ for 0.5 h each. Then, raised to 220 ℃ at a rate of 10 ℃ and kept at this temperature for 1 h to complete the reduction. After cooling down to room temperature, the PdNi NPs were separated by adding ethanol and centrifugation. The PdNi NPs were washed thrice by a mixture of petroleum ether and ethanol and finally dispersed in hexane.

PdNi NPs (1 mg) as prepared in hexane (5 mL) were mixed with 10 mg of carbon black (Ketjen EC-600J) and sonicated for 3 h to load all the NPs on carbon. Then, the PdNi NPs were dried under a fume hood. The PdCo/C was prepared in the same way as PdNi/C.

2.2.2 Preparation of modified GCEs

Then the PdNi/C and PdCo/C as prepared were modified on GCEs by general drop-coating method. Before the modification, a GCE was polished with 1 and 0.05 μm α-Al_2O_3 powder, and then ultrasonically rinsed by ethanol and deionized water, dried in N_2 at room temperature. 20 mg PdNi/C was dispersed in 5 mL dimethylformamide (DMF) and 0.25 mL Nafion (0.25%, v/v, diluted from the 5% Nafion® solution) using high power ultrasonic to form PdNi/C dispersion. 20 μL PdNi/C suspensions were then dropped onto the GCE surface within five times. The electrode was subsequently dried under infrared lamp to finish the modification. Finally 10 μL Nafion (0.25%) solution was cast on the electrode surface to stabilize the PdNi/C film in aqueous solution. The PdCo/C modified GCE was made by the same method. Commercial Pd/C (10% Pd) catalysts was prepared as the same way and used for contrast experiment.

2.3. Apparatus

All the electrochemical measurements were carried out using a CHI 660D electrochemical workstation (CH Instruments, USA). A conventional three-electrode system, consisting of a modified GCE as the working electrode (working electrode area: 0.071 cm^2), and a saturated Ag/AgCl electrode as a reference electrode, a platinum wire as an auxiliary electrode, was employed. EIS was performed with the same three-electrode configuration in an electrolyte solution of 0.1 M KCl containing 0.01 M $[Fe(CN)_6]^{4-/3-}$, in a frequency range from 1 Hz to 100 kHz with an AC probe amplitude of 50 mV.

3. Results and discussion

3.1 Characterization of PdNi/C and PdCo/C

3.1.1 Structure characterization

Transmission electron microscopy (TEM) analyses show that the as-synthesized PdNi (Fig. S1A) and PdCo (Fig. S1B) alloy NPs are monodisperse, their diameters measured to be 3.6 ± 0.3 and 2.3 ± 0.3 nm, respectively. The XRD patterns (Fig. S1C) show that these bimetallic catalysts have the same face-centered cubic (fcc) structure as Pd. This indicates random distribution of the 3d transition metal (Co and Ni) atoms in the Pd lattice [25, 29] and proofs that the NPs possess a uniform alloy composition.

3.1.2. Electrochemical characterization

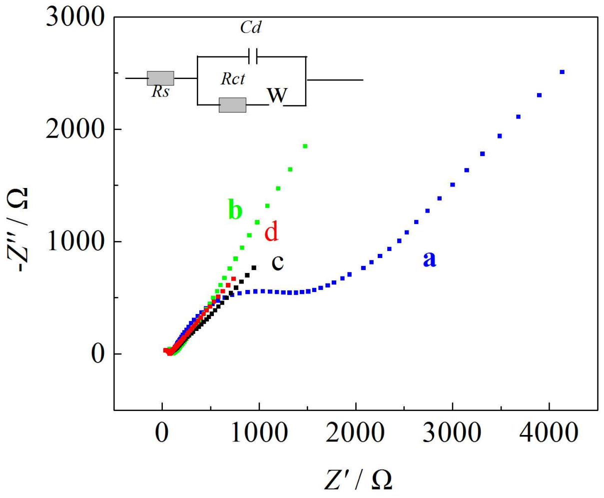

Fig. 1. Electrochemical impedance spectroscopy (EIS) of bare GCE (a), Pd/C (b), PdNi/C (c) and PdCo/C (d) modified GCEs in 0.1 M KCl electrolyte solution containing 0.01 M Fe(CN) $_6^{3-/4-}$.

EIS were employed for further characterization of the modified electrodes. Fig. 1 displayed the Nyquist plots of bare GCE (a), Pd/C (b), PdNi/C (c), and PdCo/C (d) modified GCEs at 250 mV. Generally, the semicircle portion observed at high frequencies in the Nyquist diagrams corresponds to the charge transfer limiting process, and the linear part at low frequencies corresponds to the diffusion process. The charge transfer resistance (Rct) value can be roughly measured as the semicircle diameter [30]. As seen in the EIS spectra, the bare GCE showed a large resistance (about 1363 Ω), which reflected slow electron transfer kinetics at bare GCE surface. Three almost straight lines can be observed for Pd/C (b), PdNi/C (c) and PdCo/C (d) modified GCEs, which indicated the greatly decreased of resistance and suggested that the electrode reaction was controlled by the diffusion process. This can be attributed to the good conductivity of the three kinds of metal materials. The Rct of PdNi/C (about 80 Ω) or PdCo/C (about 78 Ω) modified GCEs was lower than Pd/C (about 111 Ω), demonstrating an accelerated effect for the redox reaction of $[Fe(CN)_6]^{4-/3-}$. The possible mechanism will be showed in Section 3.2 later. This also indicated that the heterogeneous charge transfer capability of Pd NPs has been greatly enhanced by incorporating with Ni or Co NPs.

3.2 Electrocatalytic oxidation of nitrite

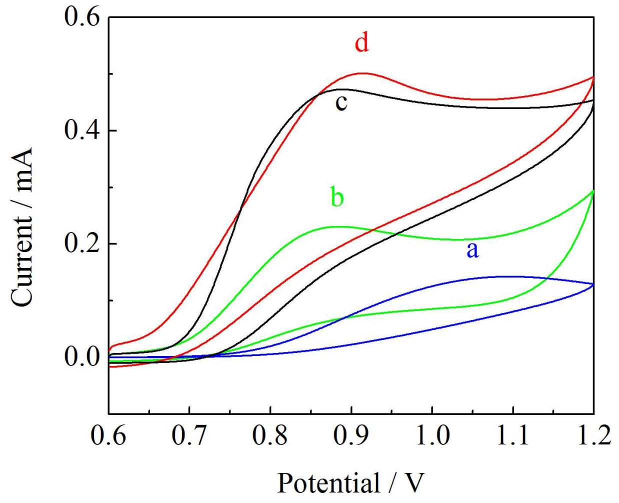

Fig. 2. Cyclic voltammograms of bare GCE (a), Pd/C (b), PdNi/C (c) and PdCo/C (d) modified GCEs in 0.1 M PBS (pH=7.0) containing 10 mM $NaNO_2$. Scan rate: 20 mV s^{-1}.

In order to investigate the electrocatalytic oxidation properties of nitrite with the PdNi/C and PdCo/C modified GCEs, cyclic voltammograms (CV) of nitrite at the different modified electrodes were recorded (Fig. 2). As seen, all of the electrodes exhibited an electrocatalytical oxidation response towards nitrite, but the CV at the GCE illustrated low and wide oxidation peak, which was due to its electro-inactive activity and worse antifouling properties. Compared with the bare GCE, a higher and less positive redox peak of Pd/C modified GCE appeared in Fig. 2, which could be interpreted as the Pd NPs, show electro-catalytic activity towards nitrite at some degree. It is worth point out that the PdNi/C and PdCo/C modified GCEs show well-defined, enhanced nitrite oxidation peak at 0.89 and 0.91 V, the overvoltage of nitrite oxidation was dramatically reduced at the PdNi/C and PdCo/C modified GCEs, were roughly 160 and 140 mV more negative than bare GCE, respectively. Compared with Pd/C modified GCE, the electrocatalytic oxidation responses to NO_2^- at PdNi/C and PdCo/C modified GCEs were much bigger, were about 3.3 and 3.5 fold higher than that of Pd/C modified GCE, respectively. The increasing of currents indicated their excellent electrocatalytic activity towards nitrite, which also demonstrated the synergistic effect of Pd-Ni and Pd-Co.

The probable nitrite oxidation processes on the surface of the PdNi/C and PdCo/C modified GCE are as follows:

$$Pd + H_2O \rightarrow Pd\text{-}O + 2H^+ + 2e^- \qquad (1)$$

$$Ni/Co \rightarrow Ni^{2+}/Co^{2+} + 2e^- \qquad (2)$$

$$2Ni^{2+}/Co^{2+} + Pd\text{-}O + 2H^+ \rightarrow 2Ni^{3+}/Co^{3+} + Pd + H_2O \qquad (3)$$

$$2Ni^{3+}/Co^{3+} + NO_2^- + H_2O \rightarrow 2Ni^{2+}/Co^{2+} + NO_3^- + 2H^+ \qquad (4)$$

$$Pd\text{-}O + NO_2^- \rightarrow Pd + NO_3^- \qquad (5)$$

Inactive oxide Pd-O often existed on the Pd surface and it may hindered the oxidation of Pd. Appropriate alloying of Pd with Ni or Co facilitate desorption of oxygen species from Pd-O by the electrochemical oxidation of Ni^{2+} to Ni^{3+} or Co^{2+} to Co^{3+} (Eq. (3)). So the “clean” Pd could take part in reaction (Eq. (1)) afresh. The Ni^{2+} or Co^{2+} regenerated by the oxidation of NO_2^- (Eq. (4)), which can be used to “clean” the Pd-O surface again (Eq. (3)). The electrochemical catalysis of the PdNi/C and PdCo/C modified GCEs was enhanced by the synergistic effect of Pd and Ni/Co.

For evaluating the electrochemical catalysis of the PdNi/C and PdCo/C modified GCEs toward nitrite oxidation, linear sweep voltammetry curves were obtained with increasing concentrations of the analyte. Fig. S2 illustrated a series of linear sweep voltammetry curves of PdNi/C and PdCo/C modified GCEs in the presence of different concentrations of nitrite ranging from 0 to 14 mM in 0.1 M PBS solution, and the correlation between the oxidation peak intensity and nitrite concentrations were shown in insets of Fig. S2. As is obvious, the anodic peak current increased constantly with increasing nitrite concentrations, and the plot was linear up to a concentration of 14 mM. The linear regression equations were expressed as:

$$I\ (mA) = 0.0441 + 0.0376\ C(NaNO_2)\ (mM)\ (R^2 = 0.9961),\ (PdNi/C\ modified\ GCE),$$

$$I\ (mA) = 0.0434 + 0.0396\ C(NaNO_2)\ (mM)\ (R^2 = 0.9970),\ (PdCo/C\ modified\ GCE).$$

3.3 Effect of pH on the determination of nitrite

The effect of pH on the oxidation peak potential and oxidation peak current of nitrite at the PdNi/C (a) and PdCo/C (b) modified GCEs were also investigated by CV (Fig. S3). The trends of the two sensors were similar. The oxidation peak potential decreased when the pH increased from 5.0 to 7.0 and kept a stable value from 7.0 to 10.0 in Fig. S3a. It is apparent that the highest peak current was obtained in PBS at the pH of 7.0. The same change lows could be found in the Fig. S3b. Therefore, the pH of 7.0 was chosen for the analytical experiments.

3.4. Amperometric response of nitrite

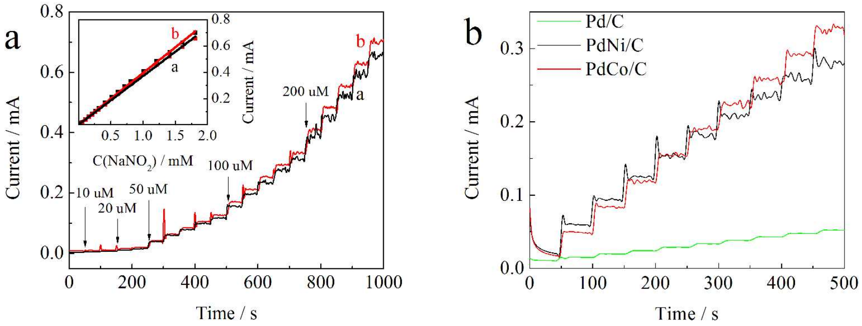

Fig. 3. (a) Amperometric response of PdNi/C (a) and PdCo/C (b) modified GCEs in stirred 0.1 M PBS (pH=7.0) with successive additions of nitrite. The applied potentials are both 0.90 V; the inset is the plot of electrocatalytic current of nitrite versus its concentrations. (b) The amperometric response of Pd/C, PdNi/C and PdCo/C modified GCEs at 0.90 V, respectively, with a dropwise addition of 0.2 mM $NaNO_2$ per 50 s in 0.1 M PBS (pH=7.0).

Fig. 3a showed a typical steady state amperometric responses of the PdNi/C and PdCo/C modified GCEs with the successive addition of nitrite into the continuously stirred solution of 0.1 M PBS at the applied potential of 0.90 V. Clearly, the electrodes exhibited a fast and sensitive response to the changes of nitrite concentration. Their response reached 95% of the steady-state value within about 2 s after the addition of nitrite. It was obvious that the amperometric current increases with the successive addition of nitrite. The response current of PdCo/C modified GCE was little higher than that of PdNi/C sensor. The calibration curves of the PdNi/C and PdCo/C modified GCEs were shown in the inset of Fig. 3a. The good linear relationships for PdNi/C (i(mA) = 0.3693 C($NaNO_2$) + 0.0028, R^2= 0.9988) and PdCo/C (i(mA) = 0.3899 C($NaNO_2$) + 0.0054, R^2= 0.9990) modified GCEs were exhibited and their concentrations in the range of 10 μM to 1.8 mM, both with a detection limit of 0.5 μM based on S/N= 3. The sensitivities were calculated to be 5.23 and 5.52 mA mM^{-1} cm^{-2} for PdNi/C and PdCo/C modified GCEs, respectively. The amperometric responses of the PdNi/C, PdCo/C and Pd/C modified GCEs at 0.90 V for successive additions of $NaNO_2$ were compared in Fig. 3b. The Pd/C modified GCE showed much less current response, whereas the PdNi/C and PdCo/C modified GCEs yielded significantly larger current responses, which was consistent with the results of Fig. 2. The performances of the proposed sensors were compared with the other sensors for nitrite detection, which were listed in Table 1. The PdNi/C and PdCo/C modified GCEs both have much higher sensitivity than most of other previous sensors. These results indicated that the proposed PdNi/C and PdCo/C modified GCEs were excellent platform for the detection of nitrite.

3.5. Interference experiment

Several possible substances were added into the PBS at 0.90 V to examine whether they interfered with the determination of nitrite using PdNi/C and PdCo/C modified GCEs, respectively. As shown in Fig. 4, when 0.2 mM nitrite was added into the PBS solution the current significantly increased with great response. But when 0.20 mM interfering species (various organic and inorganic interfering species normally found in food and biological samples, such as Potassium Sorbate (PS), Sodium Benzoate (SB), Glucose, Fructose, Lactose, Sucrose, UA, Glycine, NaCl) were added, no interference was observed at 0.90 V for PdNi/C and PdCo/C modified GCEs, respectively. Therefore, the PdNi/C and PdCo/C modified GCEs both exhibited good selectivity for the determination of nitrite. These results indicated that

Table 1

Comparison of analytical performance of our proposed PdNi/C and PdCo/C sensors toward nitrite with other published sensors.

Electrode material	Methods	Linear range (μM)	Detection limit (μM)	Sensitivity (mA mM^{-1} cm^{-2})	Reference
CR-GO/GCE	Amperometry	8.9- 167	1	0.376	[31]
Au- Fe(III) NPs modified GCE	Amperometry	0.3- 150	0.2	1.84	[20]
Au– Pt NPs	Amperometry	70- 1200	2	0.396	[32]
GR-CS/Au NPs GCE	Amperometry	1- 380	0.25	4.35	[33]
Cobalt nanoflowers	Amperometry	100- 2150	1.2	0.087	[34]
Pt NPs/Au electrode	Amperometry	10- 1000	5	3.53± 0.05	[14]
AuNPs/CLDH/GCE	Amperometry	1- 191	0.5	2.33	[35]
NPGL/GCE	Amperometry	1- 1000	—	1.04	[36]
Hb/PLE	DPV	10- 220	5	0.068	[37]
GR-MWCNTs/FeNPs nanocomposite	Amperometry	0.1- 1680	0.076 (±1.3)	0.697	[38]
Mn(II)-complex-modifie CPE	CV	5- 1860, 1860- 15500	0.8	0.244, 0.032	[39]
nano-Al2O3-film-modified GCE	Amperometry	0.05- 1.2, 1.2- 1100	0.01	2.348, 0.473	[40]
GC/poly-TBO-SWCNT	Amperometry	1- 4000	0.37	0.0843	[41]
PdNi/C modified GCE	Amperometry	10- 1800	0.5	5.23	This work
PdCo/C modified GCE	Amperometry	10- 1800	0.5	5.52	This work

the PdNi/C and PdCo/C modified GCEs exhibited highly specific to $NaNO_2$ in the presence of various substances. Furthermore, the current response becomes stable in less than 2 s, which indicates a significantly rapid response of the sensors towards $NaNO_2$.

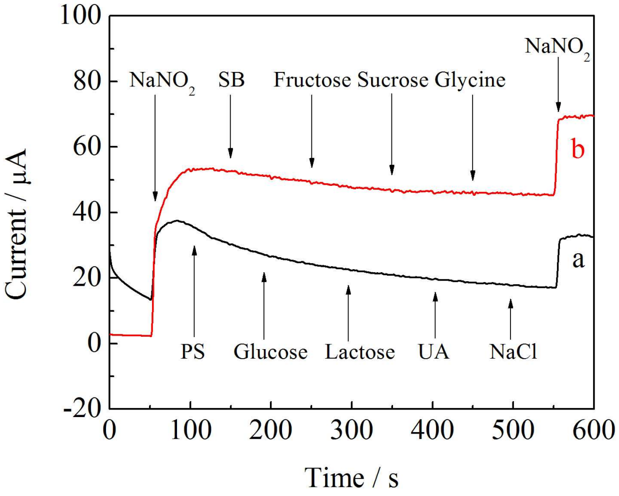

Fig. 4. Interference test of the PdNi/C (a) and PdCo/C (b) sensors in 0.1 M PBS (pH=7.0) at 0.90 V with 0.2 mM $NaNO_2$ and other interferents as indicated.

3.6 Reproducibility and stability

In order to investigate the stability of the PdNi/C or PdCo/C modified GCEs, electrochemical experiments were repeatedly performed 10 times with the modified electrodes in the solution containing 100 µM nitrite. The relative standard deviations (% *RSD*) were 3.2% and 3.5% for PdNi/C and PdCo/C modified GCEs, respectively. Furthermore, the stability of PdNi/C and PdCo/C modified GCEs were also investigated. After the electrodes were used for approximately 40 times during 20 days, only a small decrease of current sensitivity (about 10%) for 100 µM nitrite were observed.

3.7 Analysis of real sample

Table 2. Determination of NO_2^- in real samples.

Sample	Nitrite (mM)	
	PdCo/C	PdNi/C
Pickled cabbage 1's sour juice	1.30	1.39
Pickled cabbage 2's sour juice	1.14	1.22
Pickled bamboo shoot's sour juice	3.74	3.79
Pickled chicken wing's sour juice	2.95	2.94
Moat water	0.10	0.09

The *RSD* values for determination were less than 3.9% for $n = 3$.

To evaluate the ability of the sensor for routine analysis, the sensors were applied to the determination of NO_2^- in real samples. Under constant stirring, the nitrite sensors were immersed in 50 mL 0.1 M PBS at 0.90 V for PdNi/C and PdCo/C modified GCEs, respectively. After stabilization of the background current, injection of 1 mL of the real sample was carried out, followed by successive injections 100 μL 0.1 mM nitrite solution. The results are close to the values of ingredient lists. The concentrations of nitrite in the real samples were calculated from the standard addition method and the final results were displayed in Table 2.

4. Conclusions

Two sensors for nitrite determination based on PdNi and PdCo NPs were presented. The PdNi/C and PdCo/C modified GCEs exhibited excellent electrocatalytic activity to nitrite oxidation and suitable for determination of nitrite. The methods exhibited wider linear range and higher sensitivity. Then they were successfully used in the analysis of several real samples. Furthermore, the PdNi/C and PdCo/C modified GCEs offered opportunities to build up more sensitive, more selective and lower cost fabrication sensors for the detection of nitrite.

Acknowledgments

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