



A novel poly(3,4-ethylenedioxythiophene)/iron phthalocyanine/multi-wall carbon nanotubes nanocomposite with high electrocatalytic activity for nitrite oxidation

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ABSTRACT

In the present work, the oxidative electrochemistry of nitrite on the poly(3,4-ethylenedioxythiophene)/iron phthalocyanine/multi-wall carbon nanotubes-(PEDOT/FePc/MWCNT) modified screen-printed carbon electrodes (SPCE) has been investigated. The parameters, such as overpotential, current density and rate constant at PEDOT/FePc/MWCNT-modified SPCE, were compared with an un-modified, FePc-, and FePc/MWCNT-modified SPCE for electro-oxidation of nitrite. As compared with the un-modified SPCE, an increase in the anodic peak current density (J_{pa}) (~100%) along with a decrease in the anodic peak potential (E_{pa}) of ~150 mV for electro-oxidation of nitrite at the FePc-modified SPCE was observed. When an under-layer of MWCNT was introduced onto FePc-modified SPCE, denoted as FePc/MWCNT-modified SPCE, and the number of FePc/MWCNT bilayer was optimized, the heterogeneous electron transfer rate constant (k) at FePc/MWCNT-modified SPCE was enhanced about 7.8 times as compared with that at FePc-modified SPCE. Moreover, as a layer of PEDOT film was electrodeposited onto the FePc/MWCNT-modified SPCE, denoted as PEDOT/FePc/MWCNT-modified SPCE, a significant increase in current response along with a remarkable decrease in E_{pa} were noticed. This can be attributed to the pre-concentration effect induced by the electrostatic interaction between the negatively charged nitrite and oxidized PEDOT film. On the whole, the PEDOT/FePc/MWCNT-modified SPCE greatly reduces the overpotential of ~330 mV along with 3.5 times enhanced the peak current density for the electro-oxidation of nitrite as compared with un-modified SPCE. The sensitivity and limit of detection ($S/N=3$) for the PEDOT/FePc/MWCNT-modified SPCE were found to be as $638 \text{ mA cm}^{-2} \text{ M}^{-1}$ and 71 nM, respectively. Notably, PEDOT/FePc/MWCNT-modified SPCE has a lower sensing potential than compared to several other modified electrodes. The developed sensor was also applied for the determination of nitrite in tap water sample.

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1. Introduction

Nitrite is ubiquitous within environment, food and physiological systems as it is commonly used as an additive in some foods. Moreover, nitrite has been reported as a human health-hazard since it can react with amines present in meat to produce carcinogenic nitrosamines [1]. Hence, it is necessary to develop a reliable and sensitive sensor to detect nitrite in food, drinking water and environmental samples.

Several techniques, including spectrophotometry [2], chemiluminescence [3], chromatography [4], and capillary zone elec-

trophoresis [5], have been developed for the determination of nitrite; some of them involve time-consuming and tedious procedures. The electrochemical technique is an appropriate alternative or a complementary choice, with respect to the mentioned techniques; it has been proved to be an inexpensive and effective way for quantitative determination owing to its intrinsic sensitivity, fast analysis, high selectivity and simplicity. The electrochemical oxidation of nitrite usually involves a large overpotential at the surfaces of the un-modified carbon electrodes, and therefore, the determination of nitrite tends to suffering interferences from other more oxidizable compounds. To overcome these problems, some electrochemically modified electrodes based on porphyrin [6], Pt nanoparticles [7], Nafion®/lead-ruthenate pyrochlore [8], and metallophthalocyanine [9] have been explored to lower the operating potentials for nitrite oxidation.

Due to their interesting redox properties, the transition metal phthalocyanine (MPC) complexes have been used as sensing mate-

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rials for the detection of some biologically and environmentally important compounds, such as nitrogen dioxide [10], H₂O₂ [11], nitrite [9,12], thiols [13,14], thiocyanate [15,16], and epinephrine [17]. The overpotential for nitrite oxidation at the MPc-modified electrodes is still rather high, and some modifications on the nature of the ligand of MPcs have been investigated to lower the overpotential [9] and detected nitrite at the sensing potential of ≥ 0.6 V (Ag/AgCl) in physiological pH. However, there is possibility to reduce overpotential of nitrite oxidation below 0.6 V by a making composite of MPc with PEDOT and MWCNT.

On the other hand, MWCNT have numerous attractive properties, such as promoting the electron transfer rate and electrocatalytic activity for a wide range of biologically and environmentally important species [18–20]. Their reaction rates and reversibility have been found to be superior to those of other carbon materials [21]. Recently, the electrocatalytic oxidation of nitrite on carbon nanotubes powder microelectrodes has been reported [22].

Conducting polymer (CPs) has been also attractive field of research for particularly sensing of biomolecules. Among CPs, the poly(3,4-ethylenedioxythiophene) (PEDOT) has received significant amount of attention as an electrode material in light emitting devices, electrochromic devices, polymer batteries [23,24]. In specifics, PEDOT has received particular attention for the electroanalytical application, e.g., detection of chemical [25] and biomolecules such as ascorbic acid [26], cysteine [27], etc. due to retaining of its electroactivity for wide range of pH.

In the present work, we report electrocatalytic oxidation of nitrite using PEDOT/FePc/MWCNT-modified SPCE. In our previous work, electrocatalytic properties of PEDOT/MWCNT-modified SPCE have been investigated and significant decrease of overpotential was observed for the oxidation of nitrite [28], which is due to the electrostatic interaction between PEDOT film and nitrite ions. Though, PEDOT/MWCNT-modified SPCE has good sensitivity and lower detection limit, however, sensing potential for electro-oxidation of nitrite somewhat higher, which may invite interfering substance easily, than the present PEDOT/FePc/MWCNT-modified SPCE. Thus, it is an attempt to enhance properties like detection limit, sensitivity, and lower detection potential for oxidation of nitrite, by incorporating FePc onto PEDOT/MWCNT-modified SPCE. Notably, the PEDOT/FePc/MWCNT-modified SPCE has significant enhanced properties, such as sensitivity ($638 \text{ mA cm}^{-2} \text{ M}^{-1}$) and detection limit (71 nM), as compared with PEDOT/MWCNT-modified one (sensitivity: $140 \text{ mA cm}^{-2} \text{ M}^{-1}$; detection limit: $0.96 \mu\text{M}$). Moreover, as compared with PEDOT/MWCNT-modified SPCE [28], a further decrease in sensing potential (~ 100 mV) for PEDOT/FePc/MWCNT-modified SPCE was also obtained. Though there have been reports on the electrochemical detection of nitrite by MPc-modified electrodes [9,12,29–31], however, to the best of our knowledge, neither CPs/MPc/MWCNT- nor PEDOT/FePc/MWCNT-modified electrodes have been reported earlier for electro-oxidation of nitrite. Finally, the applicability of PEDOT/FePc/MWCNT-modified SPCE was investigated for the determination of nitrite in tap water.

2. Experimental

2.1. Chemicals and Instruments

Metal phthalocyanines (MPcs, M: Cu (II) (97%), Fe (III) (95%), Mn (II) (90%), Ni (II) (94%)) complexes, (2-hydroxypropyl)- β -cyclodextrin (H- β -CD), and 3,4-ethylenedioxythiophene (EDOT) were purchased from Sigma-Aldrich and used as received. All other chemicals were of analytical grade and used without further purification. 0.1 M solution of sodium nitrite solution was prepared by dissolution of sodium nitrite (Riedel-de Haën, 99%) in

pH 6 PBS solution. Multi-wall carbon nanotubes (MWCNT) were purchased from Nanotech Port Co. (Taiwan) and these MWCNT were produced via the chemical vapor deposition (CVD) method. The diameter and the length of the MWCNT are 40–50 nm and 3–5 μm , respectively. Deionized (DI) water was used throughout the work.

Electrochemical measurements were carried out at a CHI 440 electrochemical workstation (CH Instruments, Inc., USA) with a conventional three-electrode system. A three-electrode type of SPCE (Sensor R&D, Taiwan), with a geometric area of 0.071 cm^2 was used for the sensor preparation. The working electrode, reference electrode and counter electrode on the SPCE are carbon electrode, Ag/AgCl wire and carbon electrode, respectively. All electrochemical experiments were performed at room temperature and all the potentials are reported against the Ag/AgCl reference electrode.

2.2. Preparation of MPc, FePc/MWCNT, and PEDOT/FePc/MWCNT-modified SPCEs

MPc (M: Cu (II), Fe (III), Mn (II), Ni (II)) solutions with concentration of 2 mg mL^{-1} were prepared by dissolving MPcs in dimethylformamide (DMF) with the aid of ultrasonic oscillation. To prepare MPc-modified electrodes, $1 \mu\text{L}$ of the MPc solutions was drop-casted on the surface of the electrodes and was then dried at 60°C .

To prepare FePc/MWCNT-modified electrode, a MWCNT suspension with the concentration of 1 mg mL^{-1} was first prepared by suspending MWCNT in DMF solution with the aid of ultrasonication. After the preparation of suspension, $1 \mu\text{L}$ (one drop) of the MWCNT suspension was drop-casted on the surface of the electrodes and was then dried at 60°C . Thereafter, $1 \mu\text{L}$ of the FePc solution with concentration of 4 mg mL^{-1} were drop-casted on the surface of the electrodes and were then dried at 60°C . To optimize the number of FePc/MWCNT bilayer, the above-mentioned procedure was repeated for several times (up to 6). We also tried to prepare the suspension of the FePc and MWCNTs in order to drop-cast by single-step, however, precipitation occurred by direct mixing of FePc and MWCNTs.

After optimizing the number of FePc/MWCNT bilayer, the PEDOT film was then electrodeposited onto FePc/MWCNT-modified SPCE by the cyclic voltammetric (CV) method. Typically, FePc/MWCNT-modified SPCE was scanned in aqueous solution containing 0.01 M EDOT, 0.5 mM (2-hydroxypropyl)- β -cyclodextrin and 0.1 M LiClO₄ in the potential range of 0 and 0.95 V at a scan rate of 50 mV s^{-1} for specific cycles. After electro-deposition of PEDOT, the resultant modified electrode, designated as PEDOT/FePc/MWCNT-modified SPCE, was treated with 0.1 M phosphate buffer solution (PBS, pH 6) by repeated cycling in the potential range of 0.3 – 0.9 V at the scan rate of 25 mV s^{-1} in order to obtain a stable background.

2.3. Amperometric detection of nitrite

For detection of nitrite by using PEDOT/FePc/MWCNT-modified SPCE, the suitable sensing potential in the limit current plateau region was determined by scanning the PEDOT/FePc/MWCNT-modified SPCE in the potential range between 0.2 and 0.6 V using the linear sweep voltammetry at a scan rate of 0.2 mV s^{-1} in 0.1 M PBS (pH 6) solution containing 0.5 mM nitrite. Considering the sensitivity and the steadiness of the PEDOT/FePc/MWCNT-modified SPCE, the suitable sensing potential was determined as 0.5 V (vs. Ag/AgCl). The determined sensing potential is $\sim 100 \text{ mV}$ lower than that reported in our previous study [28], which might be attributed to the electrocatalytic properties of FePc. The current densities in the concentration range between 2.5 and $200 \mu\text{M}$ were collected and calibration curve for nitrite was constructed.

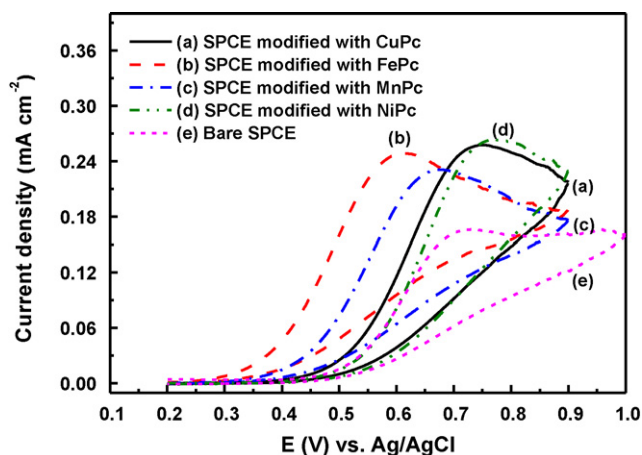


Fig. 1. Cyclic voltammograms of the un-modified SPCE and SPCE modified with metal phthalocyanines (MPCs, M: Cu, Fe, Mn, Ni). Measurements were carried out in 0.1 M PBS solution (pH 6) containing 0.5 mM nitrite at the scan rate of 25 mV s⁻¹. Concentration of MPC solution for film preparation: 2 mg mL⁻¹.

3. Results and discussion

3.1. Electro-oxidation behavior of nitrite at the MPC-modified SPCEs

Fig. 1 shows the CV responses of un-modified SPCE and MPC-modified SPCEs obtained in 0.1 M PBS solution (pH 6) containing 0.5 mM NaNO₂. It can be found that the MPC-modified SPCE showed higher current response to nitrite as compared with the un-modified SPCE. Besides, the potential for nitrite oxidation was affected by the nature of central metal of MPCs, which can be attributed to the redox activity of the central metal of MPCs [29]. By considering the peak current density (J_{pa}) and peak potential (E_{pa}), we chose the FePc as the most efficient electrocatalyst for the further experiments.

Fig. 2 depicts the CVs for the oxidation of nitrite at the FePc-modified SPCE in the PBS solution (pH 6) containing 0.5 mM nitrite at various scan rates. It can be found that (i) the relationship between the J_{pa} and square root of scan rate ($\nu^{1/2}$) was linear (the inset of Fig. 2(a)), indicating the oxidation of nitrite at the FePc-modified SPCE was diffusion-controlled, (ii) the peak potential (E_{pa}) shifts with the scan rate ($\log \nu$), indicating the irreversibility of the nitrite electro-oxidation process (see Fig. 2(b)), and (iii) Fig. 2(c) shows a plot of the current function ($I_p \nu^{-1/2}$) vs. ν , exhibited a typical shape indicative of a catalytic process composing of a one-electron transfer step followed by a chemical step [30].

For a totally irreversible diffusion-controlled system, the electron transfer coefficient (α), and the number of electron transfer involved in the rate-determining step (n_α) can be found using Eq. (1) [31]:

$$E_p = \frac{2.3RT}{2(1-\alpha)n_\alpha F} \log \nu + K \quad (1)$$

where K is a constant, ν is the scan rate, and all other parameters have their conventional meanings. By using the slope in Fig. 2(b), $(1-\alpha)n_\alpha$ can be estimated as 0.428, suggesting the rate-determined step involves one-electron transfer as the value of α ranges between 0.3 and 0.7 [32]. According to Eq. (1), the heterogeneous electron transfer rate constant, k , can be obtained from the intercept of Fig. 2(b). It can be shown that [31]:

$$K = E^0 + \frac{RT}{(1-\alpha)n_\alpha F} \left[0.78 + \frac{2.3}{2} \log \left(\frac{(1-\alpha)n_\alpha F D}{k^2 RT} \right) \right] \quad (2)$$

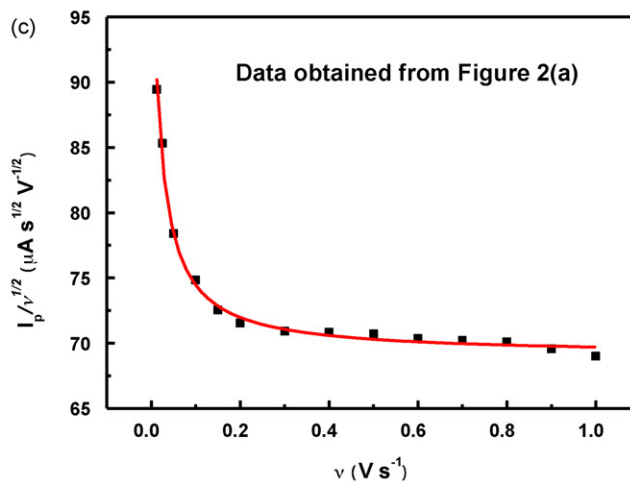
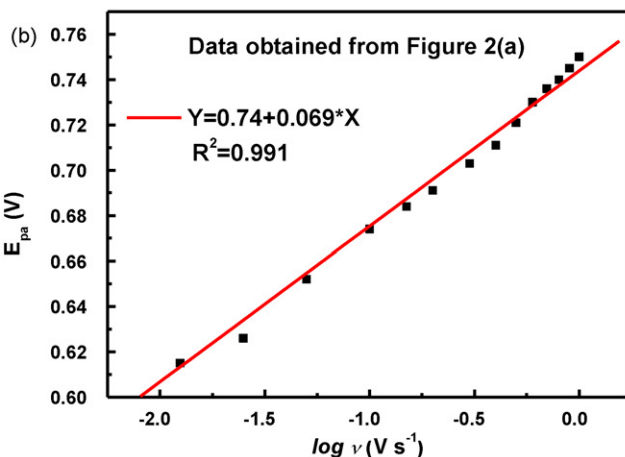
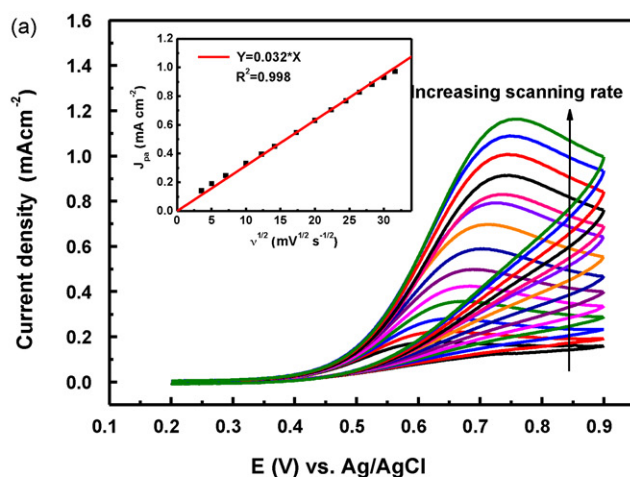


Fig. 2. (a) Cyclic voltammograms of the FePc-modified SPCE in 0.1 M PBS solution (pH 6) containing 0.5 mM nitrite at various scanning rates (ν) from 12.5, 25, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900, and 1000 mV s⁻¹. Inset: plot of J_{pa} vs. scan rate (ν), (b) plot of E_{pa} vs. $\log(\nu)$, and (c) $I_p/\nu^{1/2}$ vs. ν . Concentration of FePc solution for film preparation: 2 mg mL⁻¹.

where E^0 is the formal potential (0.59 V vs. SCE [33]), D is the diffusion coefficient of nitrite (2.1×10^{-5} cm² s⁻¹ [34]), and the remaining parameters have their conventional meanings. The rate constant k was calculated as 0.0074 cm s⁻¹, which is close to the value reported for the FePc derivative (0.0064 cm s⁻¹) [31]. Furthermore, the total number of electron transferred (n_t) in the process for the nitrite electro-oxidation can be calculated from Eq. (3) [32]:

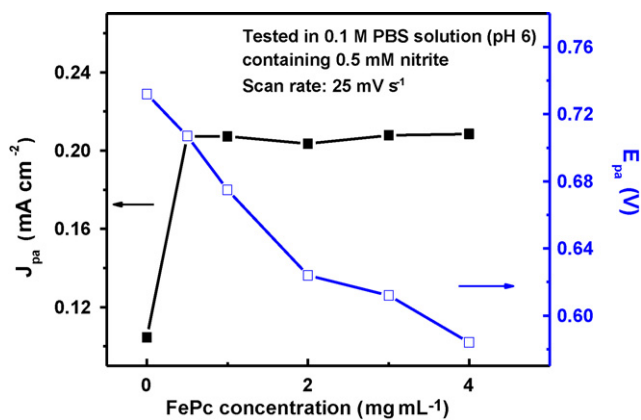
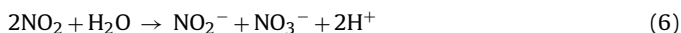
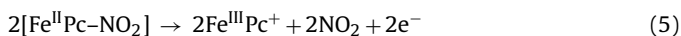
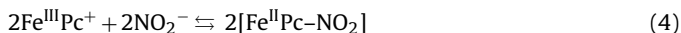


Fig. 3. The effect of the concentration of FePc solution for film preparation on the peak current density (J_{pa}) and peak potential (E_{pa}). The solid square and the hollow square in the figure represent the peak anodic current density and peak anodic potential, respectively. Measurements were carried out in 0.1 M PBS solution containing 0.5 mM nitrite at the scan rate of 25 mV s⁻¹.

$$J_{pa} = 2.99 \times 10^5 n_t [(1 - \alpha)n_\alpha] C_0 D^{1/2} \nu^{1/2} \quad (3)$$

where C_0 is the bulk concentration of nitrite (0.5 mM) and the remaining parameters have their conventional meanings. The value of n_t was estimated to be about 2, suggesting that nitrate (NO_3^-) is the most likely product of the reaction.

From the above analyses and evidence from the literature [29,35], the mechanism for the nitrite oxidation on the FePc-modified SPCE is proposed as follows:



The formation of the adduct ($[\text{Fe}^{\text{II}}\text{Pc}-\text{NO}_2]$), due to the electronic coupling between Fe^{3+} in FePc complex and nitrite [34], was proposed as the nitrite activation step. After forming an adduct, it undergoes electrochemical oxidation to form $\text{Fe}^{\text{III}}\text{Pc}^+$ and NO_2 , followed by rapid disproportionation of NO_2 into NO_2^- and NO_3^- [35]. Different mechanism [36] has been proposed for the detection of nitrite using nanoFePc with the oxidation state of Fe in FePc being 2⁺, and the number of electron transfer is 1. However, according to the literature [29], the electro-oxidation of nitrite starts from the formation of the adduct of nitrite and FePc, followed by a rate-determining one-electron transfer step. The adduct formation was resulted from the electronic coupling between Fe^{3+} in FePc complex and nitrite. In our case, the oxidation state of Fe in FePc is 3⁺, and therefore we proposed the mechanism similar to that proposed by the literature [29] for the detection of nitrite.

The optimum concentration of FePc was determined for oxidation of nitrite by just drop-casting it on SPCE. As shown in Fig. 3, a significant shift in E_{pa} was noticed toward the negative side as the FePc concentration was increased from 0 to 4 mg mL⁻¹. It should be noted that as the FePc concentration was higher than 4 mg mL⁻¹, FePc precipitated. As a result, FePc concentration of 4 mg mL⁻¹ was chosen for later experiments.

3.2. Electro-oxidation behavior of nitrite at the FePc/MWCNT- and PEDOT/FePc/MWCNT-modified SPCEs

Since MWCNTs have some important properties, such as high surface-area-to-volume ratio, facilitating electron transfer [18–20], and good electrocatalytic properties to nitrite [22], an under-layer of MWCNTs was introduced to the FePc film with an intention of increasing the active surface and facilitating the electron transfer

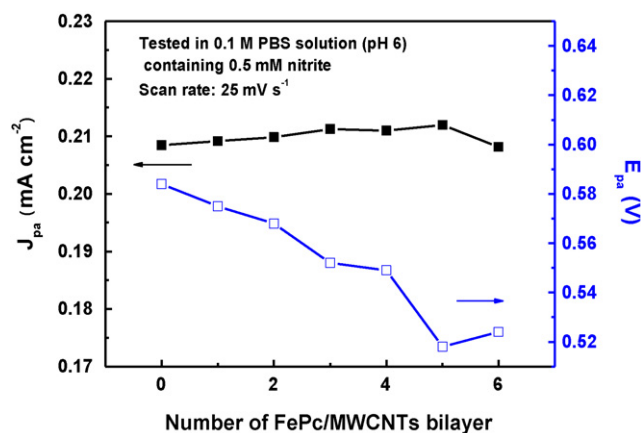


Fig. 4. The effect of the number of FePc/MWCNT bilayer on the peak current density (J_{pa}) and peak potential (E_{pa}). The solid square and the hollow square in the figure represent the peak anodic current density and peak anodic potential, respectively. Measurements were carried out in 0.1 M PBS solution (pH 6) containing 0.5 mM nitrite at the scan rate of 25 mV s⁻¹. Concentration of FePc solution for film preparation: 4 mg mL⁻¹.

between FePc and the SPCE, thus improving the electrocatalytic properties of the FePc-modified SPCE. As shown in Fig. 4, after introducing a layer of MWCNT, a shift in E_{pa} to the negative side and an increase in J_{pa} were noticed. Besides, when the number of FePc/MWCNT bilayer was increased from 1 to 5, J_{pa} slightly increased and E_{pa} shifted about 60 mV to the negative side. However, the FePc/MWCNT composite film became unstable physically and fell off easily as the bilayer number was greater than 5, resulting in lower J_{pa} and higher E_{pa} . Note that in order to get the optimal sensing performance, in terms of E_{pa} and J_{pa} , of the FePc/MWCNT-modified SPCE, it is necessary to adjust the number of FePc/MWCNT bilayer. However, the structure of the resultant composite film became complex and increased the build-up time for electrode preparation. Nevertheless, the modified electrode with FePc/MWCNT bilayer of 5, designated as (FePc/MWCNT)₅-modified SPCE, was chosen for further experiments.

In our previous report [28], the sensor response to nitrite was improved by electrodepositing a layer of PEDOT film onto the unmodified SPCE, which can be attributed to the pre-concentration effect induced by the electrostatic interaction between the oxidized PEDOT film and nitrite ions. In this work, we do not specifically investigate the pH effect because our previous work [28] indicated that the CV response of the PEDOT/MWCNT-modified electrode is insensitive to pH ranging from 6 to 8. With an intention to enhance sensor response, PEDOT film was electrodeposited onto the (FePc/MWCNT)₅-modified SPCE, designated as PEDOT₁/(FePc/MWCNT)₅-modified SPCE, and results are shown in Fig. 5. As shown in Fig. 5(a), a significant increase in J_{pa} and a remarkable shift in E_{pa} to the negative side were noticed as a layer of PEDOT film was deposited onto the (FePc/MWCNT)₅-modified SPCE. In addition, smaller E_{pa} along with slightly higher J_{pa} was observed for nitrite electro-oxidation at the PEDOT₁/(FePc/MWCNT)₅-modified SPCE than those at the PEDOT₁/(MWCNT)₅-modified SPCE, which is indicative of the electrocatalytic role of FePc playing in facilitating this electrochemical process. Compared to other MPc-modified electrodes [37–39], the E_{pa} obtained in this work is much lower. To optimize the amount of PEDOT deposited onto the (FePc/MWCNT)₅-modified SPCE, we controlled the amount of PEDOT in terms of the cycle number during electropolymerization. As seen in Fig. 5(b), it can be found that as the cycle number was increased from 1 to 2, J_{pa} further increased. However, as the cycle number was further increased (>2), J_{pa} decreased and E_{pa} shifted to the unfavorable side. While the

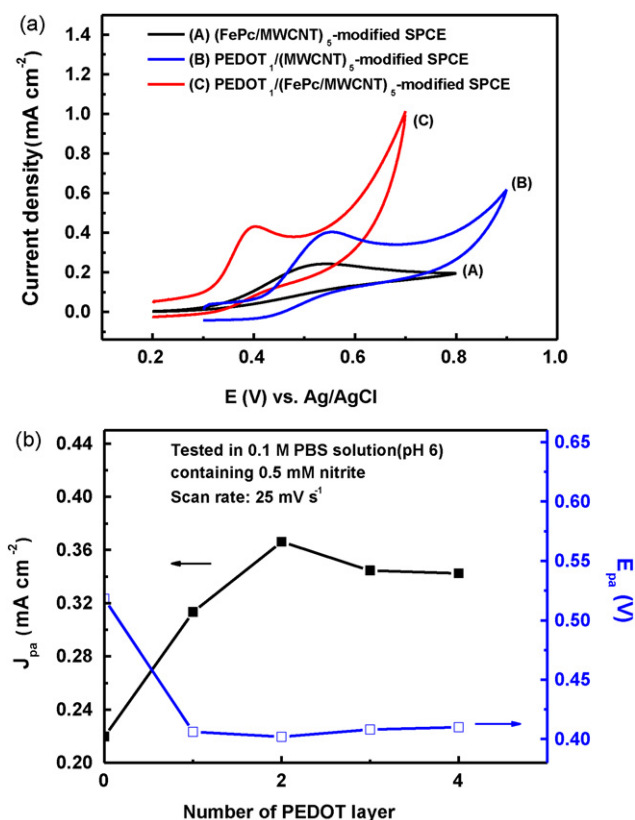


Fig. 5. (a) Cyclic voltammograms of the (FePc/MWCNT)₅, PEDOT₁/(MWCNT)₅ and PEDOT₂/(FePc/MWCNT)₅-modified SPCEs with PEDOT film electropolymerized for 1 cycle in 0.1 M PBS solution (pH 6) containing 0.5 mM nitrite. Scan rate: 25 mV s⁻¹. (b) The effect of the cycle number for the electro-deposition of PEDOT film on the peak current density (J_{pa}) and peak potential (E_{pa}). The solid square and the hollow square in the figure represent the peak anodic current density and peak anodic potential, respectively. Measurements were carried out in 0.1 M PBS solution (pH 6) containing 0.5 mM nitrite at the scan rate of 25 mV s⁻¹.

electrostatic interaction was enhanced by increasing the amount of PEDOT film, the diffusion barrier for nitrite increased simultaneously, and therefore the advantageous effect of electrostatic interaction between PEDOT was greatly reduced at greater amount of PEDOT deposited. Therefore, the amount of PEDOT obtained at 2 cycles was found to be optimal number for electrocatalytic oxidation of nitrite. The resultant modified electrode was designated as PEDOT₂/(FePc/MWCNT)₅-modified SPCE.

Table 1 summarizes the parameters of E_{pa} , J_{pa} , and k for the electro-oxidation of nitrite at the FePc-, (FePc/MWCNT)₅-, and PEDOT₂/(FePc/MWCNT)₅-modified SPCEs. The electron transfer rate constants for (FePc/MWCNT)₅- and PEDOT₂/(FePc/MWCNT)₅-modified SPCEs were estimated from the intercepts of Fig. S1(a) and (b) along with Eq. (2). As compared with FePc-modified SPCE, the electron transfer rate constant, k , was

Table 1

Values of E_{pa} , J_{pa} , and k for the electro-oxidation of nitrite at un-modified SPCE, FePc/SPCE, (FePc/MWCNT)₅/SPCE, and PEDOT₂/(FePc/MWCNT)₅/SPCE, respectively. Measurements were carried out in 0.1 M PBS (pH 6) solution containing 0.5 mM nitrite at the scan rate of 25 mV s⁻¹.

Electrodes	Parameters		
	E_{pa} (mV)	J_{pa} (mA cm ⁻²)	k (cm s ⁻¹)
Un-modified SPCE	732	0.104	–
FePc-modified SPCE	584	0.209	0.007
(FePc/MWCNT) ₅ -modified SPCE ^a	520	0.214	0.055
PEDOT ₂ /(FePc/MWCNT) ₅ -modified SPCE ^b	380	0.366	0.162

^a With FePc/MWCNT bilayer number of 5.

^b With PEDOT layer number of 2 and FePc/MWCNT bilayer number of 5.

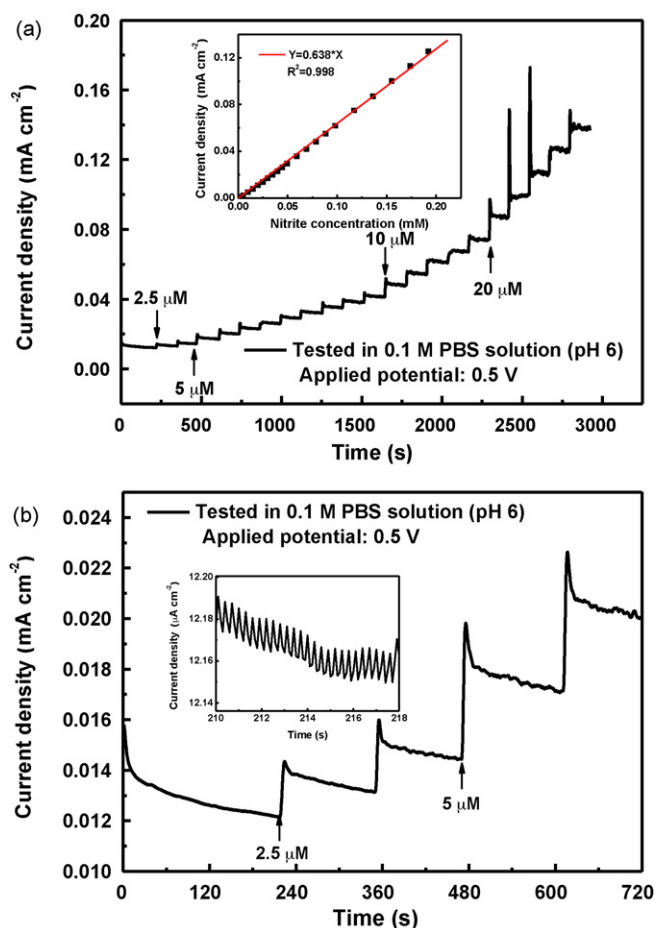


Fig. 6. (a) The amperometric current responses of the PEDOT₂/(FePc/MWCNT)₅-modified SPCE to various nitrite concentrations in 0.1 M PBS solution (pH 6) at an applied potential of 0.5 V vs. Ag/AgCl. Resulted calibration curve for nitrite is included as the inset. (b) Enlarged current density-time curve in (a). The noise level also shown in the inset of (b).

significantly enhanced (~8 times) by modifying the SPCE with optimal number of FePc/MWCNT bilayer. Besides, k was further enhanced from 0.055 to 0.162 cm s⁻¹ after electrodepositing 2 layers of PEDOT onto the (FePc/MWCNT)₅-modified SPCE. The enhancement in the electron transfer rate constant could be attributed to the synergetic effect of the high conductivity and catalytic effects of MWCNT and pre-concentration effect induced by the electrostatic interaction between conductive PEDOT and nitrite ions.

3.3. Amperometric detection of nitrite

The calibration curve for nitrite was constructed by measuring the current change after the addition of nitrite with specific con-

Table 2

The determination of nitrite concentration in tap water sample by comparing the proposed method and the Griess method.

Sample/method	Actual value (μM)	Added (μM)	Value found after adding	RSD ^b (% , $n=3$)	Recovery ^c (% , $n=3$)
Tap water/Griess method	N.D. ^a	50	51.5	2.1	103
Tap water/electrochemical detection (this work)	N.D.	50	50.8	2.3	102

^a Not detectable.^b Relative standard deviation.^c Concentration found after adding 50 μM of nitrite/50 μM of nitrite.

centration and shown in Fig. 6. Note that the current density in the calibration curve is the one which has already subtracted the background current density; therefore, it starts from zero. It can be found that the current density increases linearly with the increase in nitrite concentration. Besides, from the slope (inset of Fig. 6(a)), the sensitivity for the PEDOT₂/(FePc/MWCNT)₅-modified SPCE was found to be 638 mA cm⁻² M⁻¹. Fig. 6(b) shows the enlarged current density–time curve present in Fig. 6(a). From the inset of Fig. 6(b), the background noise level was determined to be about 0.15 $\mu\text{A cm}^{-2}$. Based on signal-to-noise ratio of 3, the limit of detection (LOD) for the PEDOT₂/(FePc/MWCNT)₅-modified SPCE was estimated and was found to be 71 nM. It should also be noted that the limit of detection for the PEDOT/FePc/MWCNT-modified SPCE is comparable with or lower than that obtained with other CNT-based modified electrodes [28,40–46]. Besides, the LOD for our proposed method is below the maximum admissible level ($\sim 3 \mu\text{M}$) of nitrite in drinking water established by the European Community [47]. This implies that the proposed method is applicable for the detection of nitrite in drinking water. Moreover, the modified electrode also showed a good repeatability for nitrite determination since the relative standard deviations of 3.5 and 2.8% were obtained by carrying out five consecutive chronoamperometric measurements using 5 and 20 μM nitrite, respectively. In addition, the reproducibility for the fabricated sensor, determined by testing five electrodes in 0.1 M PBS solution (pH 6) containing 20 μM of nitrite is 7.6%.

The interference effect of the foreign ions on the determination of nitrite was examined by addition of various ions into the PBS solution (pH 6) containing 0.5 mM nitrite and the results are summarized in Table S1. It can be found that most anions did not show any interference effect during the determination of nitrite by using PEDOT₂/(FePc/MWCNT)₅-modified SPCE. However, 10-fold concentration of SO₃²⁻ ion shows serious interference.

It is worth comparing our PEDOT₂/(FePc/MWCNT)₅-modified SPCE, in terms of sensing potential, with other modified electrodes used for the electro-oxidation of nitrite. Our PEDOT₂/(FePc/MWCNT)₅-modified SPCE has relatively lower sensing potential as compared with that of the electrode modified with PPy/SWCNT (0.75 V vs. SCE, pH 5.5) [48], oxotitanium Pc (0.6 V vs. Ag/AgCl, pH 7.4) [9], Fe (III) poly-3-aminophenyl porphyrin (0.75 V vs. SCE, pH 7.4) [49], or thiazadiazole (0.84 V vs. Ag/AgCl, pH 7.4) [50]. As a result, PEDOT₂/(FePc/MWCNT)₅-modified SPCE does not suffer from interference from foreign ions.

3.4. The real sample analysis

Finally, the present PEDOT₂/(FePc/MWCNT)₅-modified SPCE was examined for real sample analysis in tap water and our results were compared with Griess method. For Griess method, typically equal volumes of 1 \times Griess reagent (Sigma–Aldrich) and tap water sample were mixed and incubated for 15 min. Thereafter, the concentration of nitrite was determined by reading the absorbance at 540 nm. The obtained results, both by an electrochemical method and the Griess method, were summarized in Table 2. It can be found that the results obtained by our method are in good agreement with those obtained by the Griess method. It should be noted that the original nitrite concentration is undetectable by both methods,

which is simply because tap water sample contains too low concentration of nitrite. Also, for the detection of nitrite using our modified electrode, the tap water (0.5 mL) has added in the buffer solution (7.5 mL), therefore the nitrite concentration of tap water was further diluted (~ 8 times) in this step. As a result, we added 50 μM of nitrite in tap water sample and recorded the results as “value found after adding”.

4. Conclusion

The PEDOT/FePc/MWCNT-modified SPCEs were fabricated and their application to amperometric detection of nitrite was investigated. Thanks to the synergistic effect of the redox properties of FePc along with the promoted electron transfer rate by introducing MWCNT and PEDOT, the overpotential for nitrite electro-oxidation was significantly reduced at the PEDOT/FePc/MWCNT-modified SPCE as compared to the un-modified SPCE. Besides, the current response to nitrite was also significantly enhanced. The lower operating potential and practical detection limit (~ 71 nM) allow the PEDOT/FePc/MWCNT-modified SPCE for practical use.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.08.010.

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