Palladium Nanoparticles Supported on Poly(diallyl dimethyl ammonium chloride)-mesoporous Carbon as Catalysts for Nonylphenol Oxidation

Cui Ma, a Zhi-Xiang Zheng, a,b Juan-Juan Liu, a Jiang Li, a and Chun-Ming Wang a,b

a School of Basic Medical Sciences, Ningxia Medical University, 750001 Yinchuan, People’s Republic of China
b College of Chemistry and Chemical Engineering, Lanzhou University, 730030 Lanzhou, People’s Republic of China

Palladium nanoparticles were dispersed on the surface of poly (diallyl dimethyl ammonium chloride) - mesoporous carbon (Pd/PDDA-MC) composite as a catalytic for the environmental hormones nonylphenol (NOP) electrochemical oxidation. The Pd/PDDA-MC was characterized by transmission electron microscope (TEM), scanning electron microscopy (SEM), which indicated that the as-synthesized Pd nanoparticles were successfully dispersed on the surface of PDDA-MC nanocomposite. The electrochemical behavior of NOP was investigated on Pd/PDDA-MC modified GCE by cyclic voltammetry, differential pulse voltammetry. Electrochemical study has proved that the Pd/PDDA-MC nanocomposite showed excellent electro-catalytic activities toward the oxidation of NOP. The excellent reproducibility, stability and selectivity of the Pd/PDDA-MC modified GCE make it as a potential electrochemical sensor candidate for determination of environmental hormones in biology samples.

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Nonylphenols (NOP) is industrial surfactants and detergents, widespread in use for more than 40 years.1–3 It has been included among the group of organic compounds so-called “emerging contaminants”, due to their widespread use, persistence in the environment.4 NOP is an important environmental toxicant and potential endocrine disrupting chemical.5 NOP has a structure mimicking estradiol and has been reported to have xeno estrogenic effects. It has been shown not only inhibits the growth of the testes, but also affects the production and survival of sperms in rats.6 Administration of high dosage of NOP 500 mg/kg/day to newborn rats may cause disruption of the reproductive system and reproductive performance, reduction in the weight of epididymis and epididymal sperm density and testicular abnormalities.7 And its endocrine disrupting effect in the aquatic environment is particularly well documented.8,9 Recent studies have indicated NOP is ubiquitous in food stuffs, including fresh fruits and vegetables, human breast milk, livestock products and rice. Recently, many analytical methods, such as solid phase extraction (SPE),10 solid phase microextraction (SPME),11 liquid phase microextraction (LPME),12 gas chromatography,13 high performance liquid chromatography,14 different types of capillary electrophoresis,15 spectrophotometry,16 and electrochemical sensors17–21 for the determination of NOP in various environmental samples, but few research works for human body fluid have been reported.22,23 Among these analytical methods, electrochemical sensor should be a promising technique with the advantage of reliability, fast response, cheap instrument, low cost, simple operation, timesaving, high sensitivity, good selectivity and real-time detection in situ condition.

However, in our knowledge, direct detection of NOP using traditional electrochemical sensor is rare due to the poor response of NOP. In addition, NOP oxidation same as bisphenol A (BPA) also involves a relatively higher overpotential, which increases the interference of determination, leading to a low selectivity and sensitivity.24,25 So NOP determination based on electrochemical method is usually performed on modified electrodes. Therefore, it is still a challenge to investigate novel electrode modification material with high stability, good catalytic activity and excellent conductivity. Such as molecularly imprinted electrochemical sensor based on amine group modified graphene covalently linked electrode.26 Huang and his co-workers27 applied NOP-imprinted functionalized Au nanoparticles composites modified glassy carbon electrode for detection of NOP and calculated the detection limit was 0.32 μmol L−1. Zhang et al.28 proposed a sensitive and selective detection technique for NOP based on a sol–gel technology and multiwalled carbon nanotubes–Nafion functional layer modified the GCE, which the detection limit was 0.06 μmol L−1. Besides, other chemical modification electrodes for determination of NOP are also reported. Zhou et al.29 developed a graphene-chitosan composite film modified GCE, which prepared by in situ reduction. And the electrochemical sensor based on the thiol-β-cyclodextrin and graphene hybrid-modified gold electrode for the determination of NOP was proposed by the group of pro. Chen.30 And calculated the detection limit was 0.061 μmol L−1. And Zhou, et al.31 fabricated a novel electrochemical sensor for the determination of NOP based on a graphene-chitosan modified glassy carbon electrode and the detection limit was 0.0052 μmol L−1.

Besides the modification materials mentioned above, there has been significant interest in the development of one such novel carbon material, such as mesoporous carbon (MC). The first synthesis of MC material was described in the patent literature in 1969. This material has been intensively studied with regard to technical applications as catalysts and catalyst support. MC would be an ideal electro-catalyst support in electrochemical sensor and fuel cell electrodes due to its high surface area, high conductivity, tunable pore size, interconnected pore network, and tailorable surface properties.32 So, MC catalysts could open the door for new catalytic processes.33

In addition, for the platinum is resource scarcity and costly, in an effort to reduce the cost of catalysts used for small molecular organic oxidation, attention has shifted to non-Pt materials such as Palladium. Palladium nanostructures and its nanocomposite are drawing increasing attention in recent years due to its lower cost, higher abundance, and proven electro catalytic effect on small organic molecules. It is essential to prepare Pd nanostructures containing nano-sized particles on suitable substrates to exploit the high surface area and to volume ratio and enhance catalytic activity. Therefore, the preparation of Pd nanostructures, whether a solution based or coated on suitable substrates, is of considerable interest among various research groups.34

In this paper, we used a novel and highly effective polyelectrolyte functionalization method for MC using poly(diallyldimethylammonium chloride) (PDDA) which is a water-soluble quaternary ammonium and strong polyelectrolyte as reported previously.35 Pd nanoparticles were then in situ synthesized on PDDA-MC via the electrochemical reduction process. After that, a stable, sensitive and selective analytical method to determine NOP in urine, fast, and inexpensive way was constructed. The working electrode used was glassy carbon electrode modified with a kind of Pd/PDDA-MC nanocomposite by physical adsorption.
Experimental

Reagents and instruments.—Poly(diallyl dimethyl ammonium chloride) (PDDEA), polystyrene-block-polyethyleneoxide (PVP), Sodium dodecyl sulfate (SDS), PdCl₂ and Triblock copolymer F127 (PEO106-PPO70-PEO106) were purchased from Sigma-Aldrich Co. LLC. The other reagents were obtained from Shanghai Chemical Co., Ltd. (Shanghai, China). All chemicals were analytical grade without further purification. All chemical solutions were prepared with deionized water purified via Milli-Q unit. Chemical solution was bubbled with high pure N₂ gas for 10 min to remove oxygen before the electrochemical measurement. The PBS buffer solution (0.1 M) was prepared from Na₂HPO₄ and NaH₂PO₄, the pH adjusting was regulated with NaOH.

And NOP stock solutions of 0.01 M were stored at room temperature. All chemical reagents were obtained from Shanghai Chemical Co., Ltd. (Shanghai, China). It indicated that this material has abundant mesoporous structure, and it have the uniform distribution pore size. Nitrogen adsorption and desorption isotherms were measured on MC using Barrett–Joyner–Halenda (BJH) method. The surface morphology of MC was investigated via transmission electron microscope (TEM, Tecnai G2 F30, FEI, USA), Raman spectra were acquired using a Renishaw inVia Microscope with a 514.5 nm Argon laser at 50% power with a 50° aperture.

Then the mixture was continuously stirred at 60°C for another 24 h. The final product was collected by sedimentation separation and filtration, washed with water and dried in air. The obtained sample was calcined at 700°C for 3 h in nitrogen flow to obtain mesoporous carbon.

Preparation of the working electrode.—A glassy carbon electrode was polished to a mirror finish with 1.0 µm, 0.3 µm and 0.05 µm alumina suspension successively. The polished electrode was washed with ethanol/water solution (1:1, V/V) and then ultrasonicated in ultrapure water each for 5 min. After that, the electrode is ready to serve as a substrate for the working electrode. The electrodes for the electrochemical measurements were fabricated by dispersing 1.0 mg of PDDEA-MC in 1.0 mL ultra-pure water and then sonicating for 0.5 h. 8.5 microliters of the suspension were dropped on the glassy carbon electrode and the solvent was evaporated at room temperature. The modified electrode denoted as Pd/PDDEA-MC/GCE.

Experiment method.—The electrochemical experiments were carried out in an electrochemical cell with a three-electrode configuration with a CHI660C electrochemical workstation (CHI., USA). Pd/PDDEA-MC supported on GCE were as a working electrode. The Pt wire and a saturated calomel electrode (SCE) served as a counter electrode and reference electrode.

Results and Discussion

Here we present the preparation and characterization of PDDEA-functionalized mesoporous carbon (PDDEA-MC) by a simple synthetic method. The PDDEA-MC, SDS-MC, and PVP-MC composite was prepared by the same method, respectively. The result indicated that the PDDEA-MC can be easy form a steady aqueous dispersion which attributes to PDDEA could bind with negatively charged MC to prevent the aggregation of MC through electrostatic repulsion. As illustrated in Scheme 1, during the functionalization process, NaCl salt is added to allow the PDDEA chain to adopt a random configuration, thus leading to positively charged Pd precursors chains on the surface of PDDEA-MC via electrostatic interaction. The subsequent reduction by electrochemical reduction process gives Pd nanoparticles with uniform distribution. After that, a stable, sensitive and selective analytical method to determine NOP in urine, fast, and inexpensive way was constructed.

Characterization of Pd/PDDEA-MC.—Fig. 1a shows the TEM images of MC. It indicated that this material has abundant mesoporous structure, and it have the uniform distribution pore size. Nitrogen adsorption and desorption isotherms were measured on MC using Barrett–Joyner–Halenda (BJH) method to evaluate their surface structural properties and pore size distribution (PSD) curves. Fig. 1b shows the nitrogen adsorption-desorption isotherms and pore size distribution of MC. It can be seen that the isotherms of all nanocomposite displayed a type-IV isotherm with an H₂ hysteresis loop, indicative of mesoporous materials. The hysteresis loop of nitrogen adsorption and desorption isotherms present to the high-pressure area, which show that MC have narrow pore size distribution. Both nitrogen
Figure 1. TEM images of MC (a), Nitrogen adsorption-desorption isotherms for MC (b), inset of (b) is DFT pore size distribution curve of the as-prepared MC. Raman spectrum (d) of the obtained Pd/DDA-MC (c). TEM images of Pd/DDA-MC hybrids (c).

adsorption and desorption isotherms agree with the results depicted in the TEM diagram.

As shown inset of Fig. 1b, the MC exhibits a sharp peak at 7.4 nm, suggesting that the composites have a relative narrow pore size distribution with a multipore structure. Figs. 1a and 1b proved that there are many mesoporous pores in these carbon skeletons. An average pore diameter about 7.4 nm was calculated according to density functional theory (DFT) method.41 MC possesses a BET surface area of 806.06 m²/g, a total pore volume of 1.474 cm³/g.

The original host of MC was characterized by Raman spectroscopy in Fig. 1d, Raman spectroscopy has historically played an important role in the structural characterization of carbon and carbon-based materials.42 The most prominent features in the Raman spectra of MC materials are the so-called G band appearing at 1582 cm⁻¹, the D band at about 1350 cm⁻¹.43 Defects in graphitic materials are important for improving the performance of carbon-based materials for practical applications. Defects often improve the performance of carbon materials.44 The D band is often referred to as the “disordered” band and G band as the “ordered” graphitic band. Therefore, the relative intensity of the D band and G band (I_D/I_G) is indicative of the graphitization degree.45 (I_D/I_G = 3.35, the I_D and I_G value is the peak intensity of D-peak and G-peak, respectively). The higher I_D/I_G ratio of MC indicates a much more disordered graphitic structure and many active sites on the surface of MC.46 It shows favorable catalysis for some sample. Energy dispersive spectroscopy (EDS) X-ray maps of the Pd/PDDA-MC indicated that Palladium crystallites were loading on the surface of PDDA-MC composite.

Morphologies of Pd nanoparticles deposited on PDDA-MC have been characterized by TEM. Fig. 1c shows the typical TEM images of as-synthesized hybrids. It is clearly seen that PDDA-MC are uniformly decorated by the nanosized Pd particles with very few aggregations, and the average particle size of Pd nanoparticles between 2.0-7.0 nm, indicating a strong interaction between PDDA-MC support and particles. Highly dispersed metal nanoparticles on supports with larger surface areas have advantages in catalytic activity and sensor sensitivity. Therefore, Pd/PDDA-MC hybrids should be a potential material for use in future nanotechnology.

Characterization of electrochemical behavior of Pd/PDDA-MC/GCE. — The electrochemical responses of [Fe(CN)₆]³⁻/⁴⁻ (1:1) at the sensors was studied using cyclic voltammetry (CV) to illustrate the electrochemical properties of Pd/PDDA-MC sensor. Fig. 2a showed the cyclic voltammograms of GCE, PDDA-MC/GCE, and Pd/PDDA-MC/GCE obtained in 5.0 mM [Fe(CN)₆]³⁻/⁴⁻ (1:1) solution containing 0.1 M KCl. A bare GCE showed a couple of well-defined redox peak with peak-to-peak separation (ΔEp) of 70 mV. When the electrode was coated with Pd/PDDA-MC, an increase in peak currents (Ip) was observed. It indicated that the Pd/PDDA-MC could increase the electron transfer rate between electrode surface and [Fe(CN)₆]³⁻/⁴⁻.

Compared with bare GCE and PDDA-MC/GCE, the peak currents of Pd/PDDA-MC/GCE increased dramatically. The results indicated that Pd/PDDA-MC modified GCE could greatly increase the electron transfer rate of [Fe(CN)₆]³⁻/⁴⁻. This electro-catalytic activity toward [Fe(CN)₆]³⁻/⁴⁻ could be due to the unique electronic properties of Pd/PDDA-MC which accelerates electron transfer rate via improved conductivity and the high specific surface area of Pd/PDDA-MC. Simultaneity, The interface confinement effect of MC contributes to stabilize the active center of Pd catalyst.47

For further characterization of the modified electrode, the electrochemical impedance spectroscopy (EIS) was used. Fig. 2b presented the Nyquist diagrams of bare GCE (curve a), PDDA-MC (curve b), and Pd/PDDA-MC (curve c) in 5.0 mM [Fe(CN)₆]³⁻/⁴⁻ (1:1) containing 0.10 M KCl. It can be seen that a well-defined semi-circle at higher frequencies was obtained at the bare GCE and a very small semi-circle was observed at Pd/PDDA-MC/GCE. It indicated that the electron transfer resistance decreased when GCE was modified with Pd/PDDA-MC composite, which facilitated the electron transfer of [Fe(CN)₆]³⁻/⁴⁻. It should be caused by the good conductivity of Pt/PDDA-MC which weakening a resistance into the electrode/solution system. In brief, a conclusion can be made from the Nyquist diagram of the modified electrode.
Fig. 2. Cyclic voltamograms of Pd/PDDA-MC/GCE (curve a), PDDA-MC/GCE (curve b), GCE (curve c) in 5.0 mM [Fe(CN)₆]⁴⁻/[Fe(CN)₆]³⁻ + 0.10 M KCl (Fig. a). Nyquist plots of bare GCE (curve a), PDDA-MC/GCE (curve b) and Pd/PDDA-MC/GCE (curve c) in 5.0 mM [Fe(CN)₆]⁴⁻/[Fe(CN)₆]³⁻ + 0.10 M KCl, with an AC voltage of 5 mV amplitude in a frequency range from 0.1 Hz to 100 kHz under a 0.18 V open circuit potential (Fig. b).

Fig. 2, that the Pd/PDDA-MC sensor exhibits more excellent properties, may be attributed to the specific and mesopores structure and the Pd/PDDA-MC greatly improves the active area of the sensor surface.

Cyclic voltammetric behaviors of NOP.— Fig. 3 showed cyclic voltamograms of Pd/PDDA-MC (a), PDDA-MC (b), GCE (c) in presence of 0.10 mM NOP in 0.1 M PBS at pH 9.0, scan is 20 mV/s. No redox peak was observed at GCE without NOP. The same phenomenon was also obtained at PDDA-MC/GCE and Pd/PDDA-MC/GCE. From this, it can be concluded that Pd/PDDA-MC is electro-inactive in the selected potential region. When 0.10 mM NOP was added into 10 mL PBS, only a small oxidation peak of NOP was observed at bare glassy carbon electrode. However, a significant enhancement in anodic current was achieved at the modified electrode, which suggests that Pd/PDDA-MC is an effective mediator in the electrocatalytic oxidation of NOP. It attributes to the high specific surface area and adsorptive capacity of PDDA-MC. Moreover, no corresponding reduction peak of NOP was observed at both electrodes, indicating that the oxidation reaction is totally irreversible.

pH effects.— The effect of the buffer solution on the sensor response was tested in four different buffer solutions (Na₂SO₄, NaClO₄, HAc-NaAc, phosphate buffer solution (PBS), acetate, citrate, and borate) with the concentration of 0.10 M. When the PBS was used, the baseline was steady and high sensitivity was obtained. In this sense, the PBS was chosen. The effect of the pH value of PBS on the peak current and potential response of Pd/PDDA-MC/GCE to 0.10 mM NOP was investigated in the pH range from 2.0 to 13.0. The peak potential was shifted negatively with the increase of solution pH. The relationship between the oxidation peak potential and pH was shown in Fig. 4a. A linear shift of $E_{pa}$ toward negative potential with an increasing pH indicates that protons are directly involved in the oxidation of NOP. It obeys the following equation: $E_{pa}$ (mV) = 1.0479 - 0.0635 pH ($R = -0.9988$). A slope of $-63$ mV/pH suggests that the number of electron transfer is equal with that of hydrogen ions taking part in the electrode reaction. So the electrochemical reaction mechanism is described as in Scheme 2.

The oxidation peak current gradually decreased with an increasing pH value from 2.0 to 8.13. However, when the pH further increased to 10.67, the oxidation peak current conversely increased that was shown in Fig. 4b. Therefore, considering the sensitivity of the determination of NOP, a pH value of 9.0 was chosen for the subsequent analysis experiments.

Effects of scan rate.— Fig. 5a showed the cyclic voltammograms of 1.0 mM NOP at Pd/PDDA-MC/GCE with different scan rate. It can be seen that with the increase of the scan rate, the oxidation peak currents increased gradually. As shown in Fig. 5b, the peak current increased linearly with the scan rate in the range of 5–150 mV/s and can be expressed as following: $I_{pa}$ ($\mu$A) = 8.773 + 0.2029$\nu$ (mV/s) ($R = 0.9995$). It indicates that the oxidation of NOP on Pd/PDDA-MC/GCE is an adsorption-controlled process, which can be used to pre-concentrate micro-quantity of NOP onto the surface of Pd/PDDA-MC/GCE for quantitative analysis. In this work, the scan rate was chosen as 20 mV/s.

With increase of scan rate, $E_{pa}$ shifted positively, a linear relationship can be obtained in the range of 5–350 mV/s. The equation

$$\text{C}_9\text{H}_{19}^- - \text{H}^+ + \text{e}^- \rightarrow \text{C}_9\text{H}_{19}^- + \text{H}^-$$

Scheme 2. The electrochemical reaction mechanism of NOP
can be expressed as $E_{pa} \text{ (mV)} = 0.0373 \ln \nu \text{ (mV/s)} + 0.2175$ ($R = 0.9948$). For an adsorption-controlled and irreversible electrode process, according to Laviron\textsuperscript{48} based on the Eq. 1.

$$E_p = k_0 + \frac{RT}{nF} \ln \nu$$

$E_p$ is defined by the following equation: where $\alpha$ is transfer coefficient, $k_0$ is standard rate constant of the reaction, $n$ is electron transfer number involved in the ratedetermining step, $\nu$ is scan rate, and $E_0$ is formal potential. Other symbols have their usual meanings. Thus, the value of $\alpha$ can be easily calculated from the slope of $E_{pa} - \ln \nu$. In this work, the slope is 0.037. Therefore, the value of $\alpha$ was calculated to be 1.28 (taking $n = 1$, $T = 298$, $R = 8.314$, and $F = 96485$). So, the number of $\alpha$ in the electro-oxidation of NOP is 0.694.

**Effects of accumulation potential and time.**— The relationship between peak current and scan rate in Effects of scan rate section indicates that the rate-determining step is the adsorption step during the oxidation of NOP on Pd/PDDA-MC. Hence, the accumulation can improve the amount of NOP on the electrode surface, and then obviously improve the determining sensitivity. The effects of accumulation time and accumulation potential were shown in Fig. 6. The effect of accumulation potential ranging from $-0.40$ to $0.40$ V was investigated in Fig. 6a, while the accumulation potential shifted from $-0.40$ to $0.0$ V, the oxidation peak current increased remarkably. Then, the decreased oxidation peak current was obtained under more positive accumulation potential. Therefore, an accumulation potential of $0.0$ V was selected as an optimum accumulation potential for determination of NOP. Meanwhile, the effect of accumulation time ranging from 50 to 800 s on the oxidation peak currents of $0.10$ mM NOP was studied under the optimum accumulation potential described above. The oxidation peak current increased gradually with extending accumulation time in the range of 50–600 s. As the obvious increase of oxidation peak current was seen in Fig. 6b, more and more NOP accumulated on the Pd/PDDA-MC surface. Afterwards, the peak current increased much slightly as further increasing the accumulation time. Considering both sensitivity and work efficiency, the optimal accumulation time of 600 s was employed in the further experiments.

**Calibration curve and Interference.**— The determination of NOP concentration using Pd/PDDA-MC/GCE was performed with DPV shown in Fig. 7. The results showed that the anodic peak current ($I_{pa}$)
was proportional to NOP concentration in the range of $3.0 \times 10^{-7}$ to $3.5 \times 10^{-5}$ M, the linear regression equation can be expressed as $I_{pa} \ (\mu A) = 17.554 + 0.4251 \ c \ (\mu M)$ ($R = 0.9888$), and in the range of $3.5 \times 10^{-5}$ to $8.0 \times 10^{-4}$ M, the linear regression equation can be expressed as $I_{pa} \ (\mu A) = 1.1856 + 0.9964 \ c \ (\mu M)$ ($R = 0.9885$). The detection limit was $1.25 \times 10^{-7}$ M ($S/N = 3$). The relative standard deviation (RSD) of 10 times determination for $2.0 \times 10^{-5}$ M is 1.47%, shown an excellent reproducibility of the modified electrode.

The anodic current of NOP has no significant change at the proposed electrode after its preparation for four weeks, indicating the excellent stability of Pd/PDDA-MC.

Some common uric acid, urea, Vc, dopamine, glucose, phenolic complexes (phenol, hydroquinone, hydroxyphenol, pyrocatechol, 4-nitrophenol) and inorganic ions were tested to check their levels of interference in NOP determination by DPV in simulate urinary. Among the selected organic interferents, phenolic compound, methanol, and ethanol have no response in the selected potential range. 80-fold concentration of uric acid, urea, Vc, dopamine, glucose, L-cysteine, histidine, phenolic complexes have no influence on the signals of 0.25 mM NOP with deviations below 8.6%. Otherwise, some inorganic ions such as 350-fold concentrate on of Mg$^{2+}$, Ca$^{2+}$, Cu$^{2+}$, Fe$^{3+}$, Al$^{3+}$, SO$_4^{2-}$, PO$_4^{3-}$ and NO$_3^{-}$ have no influence on the determination of NOP. These results indicate that Pd/PDDA-MC have a selective reactivity to NOP.

**Real samples analysis.—** The proposed Pd/PDDA-MC/GCE was applied for determination of the NOP in human urine. Fig. 8 showed the DPV curves of 9 mL (pH 9.0) PBS and 1 mL human urine without any treatment in the absence (a) and presence (b) of NOP. It was found that only an anodic peak of NOP at 0.45 V was obtained, with an estimated concentration of $4.0 \times 10^{-6}$ M. The result indicated that the modified electrode has high selectivity and sensitivity of the determination of the NOP in human urine, the Pd/PDDA-MC/GCE was a hopeful sensor for the determination of the NOP in physiological solution.

Table 1 compares the analytical figures of merit of the Pd/PDDA-MC/GCE electrode for NOP determination to those for other electrode materials. it appears that the present detection range are somewhat lower than those previously reported.

As the NOP was not detected in human urine, the accuracy of the method was evaluated by performing a recovery test after spiking the samples. The standard addition method was used for...
ward NOP with good electrode stability in the solution. This new Pd/PDDA-MC/GCE electrode can provide a good electrochemical sensing platform for NOP and thus it is expected to have widely potential applications in real sample analysis.

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Table I. performance comparison of the proposal biosensor for NOP detection with other sensors (using differential pulse voltammetry).

| Sensor                  | Linear range (µM) | Detection limit (µM) | References |
|-------------------------|-------------------|---------------------|------------|
| Pd/PDDA-MC              | 0.3-800           | 0.125               | This work  |
| IL/GR                   | 0.5-200           | 0.058               | 18         |
| GR-CS/GCE               | 0.01-40           | 0.005               | 19         |
| CTAB/CP                 | 0.1-25            | 0.01                 | 20         |
| GH-DNA/GCE              | 0.05-4            | 0.01                 | 21         |

Table II. NOP in human urine (n = 5).

| Sample no. | Added (×10−5M) | Detected (×10−5M) | RSD (%) | Recovery (%) | Bias (%) |
|------------|----------------|-------------------|---------|--------------|----------|
| 1          | 0.50           | 0.517             | 1.65    | 103.4        | +3.4     |
| 2          | 1.00           | 0.978             | 1.50    | 97.80        | −0.22    |
| 3          | 2.00           | 2.098             | 1.36    | 104.9        | +4.9     |

Calculating the NOP concentrations. Table II presented the results obtained for five parallel measurements. The recovery of sample solution of different concentration NOP is between 97.0% and 105%, and with a less relative standard deviation (RSD) less than 1.7%, the results indicating that the sensor might be sufficient for practical applications.

Conclusions

In this work, we have demonstrated the PDDA-MC nanocomposite synthesized by a facile self-assembly process. A simple Pd/PDDA-MC modified GCE sensor has been fabricated to investigate the electrochemical behavior of NOP. This study has indicated that Pd/PDDA-MC exhibits novel electrocatalytic activity toward NOP oxidation. The obtained results revealed that determination of the NOP in urine can be easily performed using the Pd/PDDA-MC/GCE and the modified electrode had dramatically enhanced electrocatalytic activity to

Figure 8. The DPV curves of 9 mL (pH 9.0) PBS buffer solution and 1 mL human urine without any treatment in the absence (curve a) and presence (curve b) of NOP.
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