

Electroanalytical Investigation of p-nitrophenol with Dual Electroactive Groups on a Reduced Graphene Oxide Modified Glassy Carbon Electrode

Honghong Rao^{1,*}, Weiming Guo¹, Huihui Hou², Hui Wang², Bo Yin², Zhonghua Xue² and Guohu Zhao¹

¹ College of Chemistry & Environmental Engineering, Lanzhou City University, Lanzhou, 730070, P. R. China.

² Key Laboratory of Bioelectrochemistry & Environmental Analysis of Gansu Province, College of Chemistry & Chemical Engineering, Northwest Normal University, Lanzhou, 730070, P. R. China.

*E-mail: rhhlab@hotmail.com, rh@nwnu.edu.cn

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Developing high selective and excellent sensitive electrochemical sensor for electrochemical active species with dual and multiple electroactive groups is very important in various analytical purposes. Here, on the basis of highly sensitive material of electrochemical reduced graphene oxide films modified glassy carbon electrode, the comparative study on the electrochemical sensing of p-nitrophenol (PNP) based on different current response signals offered by the reduction and oxidation process associated with nitro group and phenol group on PNP molecule was successfully demonstrated. By using cyclic voltammetry and chronoamperometry technique, a significant difference on the electrocatalytic and electrochemical detecting between nitro and phenol group of PNP molecule was pointed out. As a result, a remarkably apparent rate constant (κ , $6.79 \text{ M}^{-1}\text{s}^{-1}$) and a lower detection limit ($0.55 \mu\text{M L}^{-1}$) by electrochemical reduction process of nitro group was demonstrated, which strongly supporting the fact that the electroactive nitro group of PNP is more appropriate than the phenol group for the construction of sensitive electrochemical sensor.

Keywords: Electrochemical sensing; P-nitrophenol; Electrochemically reduced graphene oxide; Dual electroactive molecule; Glassy carbon electrode

1. INTRODUCTION

As is well-known, nitrophenols are widely distributed in nature such as in the soil and water environment as well as extensively used in the production of the synthesis of explosives, dyes, drugs and pesticides [1, 2]. Due to the characteristics of strong biorefractory and acute toxicity, nitrophenols have many toxic effects to the animals and human bodies, plants and aquatic lives. Therefore, most of

those compounds have been listed as important hazardous chemical by the environmental protection agency (EPA). Among these, PNP typically as an inter-mediate or a final product of organophosphorous pesticides [3], demonstrates high environmental impact on plants, animals and humans even at low concentration due to its persistence and toxicity as well as disease-associated physiological regulator on methemoglobinemia and fever [4]. Thus, it is clear that fabricating simple strategy for selective and sensitive determination of PNP and other nitrophenols such as chromatography [5, 6], UV-vis spectrophotometry [7], chemiluminescence [8], and electrochemical methods [9-14]. Among these methods, electrochemical methods based on chemically modified electrode have been well documented to be extremely attractive for various analytical purposes because of their cost-effective, high efficiency and simple operation [15-17]. Moreover, it usually carried out on low-cost apparatus (electrochemical station, glass electrolytic cell, electrodes, et al) within a short time (for example, several minutes for cyclic voltammetric scans), requiring no organic solvent (usually used in HPLC) and complex sample pretreatment [18-20].

As far as electrochemical sensor toward PNP determination, most researches were typically carried out on the basis of the electroreduction of electroactive nitro groups on the PNP molecule. However, as another electroactive group of PNP molecule, phenol groups may be oxidized at more positive potential, which also can be used to determine the PNP in the samples. Up to now, the use of an oxidation process of phenol groups on the PNP molecule for its electrochemical detecting has scarcely been reported so far. It may be attributed to the fact that PNP could be oxidated and resulted in forming a modified film on the substrate electrode surface due to the oxidation and polymerization process at more positive potential. However, it should be emphasized that the different electroactive group of a certain molecule would exhibit various electrochemical behaviour with its specific electrochemistry-readout in the oxidation or reduction process, which therefore would produce different detecting performance for the target. To date, the comparison of the electrochemical determination of PNP based on two kinds of electroactive species including nitro group and phenol group has been scarcely explored. On the other hand, with the increasing demand for the analytical purpose of ultra low amount analytes, various nanomaterials such as graphene [21-24] and its nanocomposites as unique and tempting sensing materials have exhibited many advantages because of their unique nanostructure as well as good capability of interface charge transport [25-29].

Herein, to verify the different sensing performance of various electrochemical measuring process originated from the nitro group and phenol group on PNP molecule, the electrochemical reduction graphene oxide (ERGO) films modified surface on glass carbon electrode surface was proposed as sensing substrate. The approach reported in this work not only shows that ERGO films can be easily achieved on a GCE surface from GO dispersions by electrochemical method through one-step electrodeposition technology, but also explores that the electrocatalytic activity and sensitivity of ERGO films towards p-nitrophenol (PNP) electrochemical reduction and oxidation associated with two kinds of electroactive groups of amino and phenol show a significant difference, which has promising applications for the electrochemical detection of PNP and its analogues with various electroactive groups.

2. EXPERIMENTAL

2.1 Materials and Apparatus

Graphene oxide (GO) was provided by Nanjing XFNANO Materials Tech Co., Ltd., (Nanjing, China). P-nitrophenol and other chemicals were of analytic grade and purchased from Sigma-Aldrich. Milli-Q water was used throughout and all measurements were performed at room temperature. Cyclic voltammograms (CVs), chronoamperometry and differential pulse voltammetry (DPVs) were recorded on a CHI660 electrochemical station (CHI Instruments Inc., USA.) with a bare and the corresponding ERGO films modified glassy carbon electrode (GCE) as working electrode, Ag/AgCl (saturated KCl) and Pt as reference and auxiliary electrode, respectively. Electrochemical impedance spectroscopy (EIS) results were achieved by a VMP2 Multi-potentiostat (Princeton Applied Research, USA) with 5 mV amplitude. The employed ERGO modified electrode was characterized by scanning electron microscopy (SEM, Zeiss, Oberkochen, Germany) and Raman (Renishaw) with a HeNe Laser excitation at 633 nm.

2.2 Preparation and Methods

Graphene oxide as received was dispersed in Milli-Q water by using ultrasonication. Prior to electrochemical reduction, a bare GCE was firstly polished with 0.3 and 0.05 μM alumina powders, followed the treatment of sonication respectively using acetone, ethanol, and water. ERGO films modified GCE were obtained by using cyclic voltammetric reduction at a given potential window after the immersing of a bare GCE into buffer solution containing GO dispersions with N_2 bubbling and magnetic stirring. For raman characterization, the ERGO samples on the electrode surface were collected through consecutive ultrasonication. All electrochemical measurements were recorded by immersing the ERGO films modified GCE into 0.2 M PBS (pH=7) solution containing different concentrations of PNP within given potential range.

3. RESULTS AND DISCUSSION

As well known, cyclic voltammetry (CV) as a conventional electrochemical method, were extensively used to produce various electropolymer films on the electrode substrate [30]. To achieve a high sensing substrate, CV technology was proposed to produce stable ERGO films on a GCE surface according to previous works [31-34]. The electrochemical reduction and electrodeposition of GO from its homogenously dispersed solution onto an electrode surface were confirmed by using SEM and Raman spectroscopy. As clearly in Fig. 1a, the bare GCE displays a smooth surface nature. After modified with ERGO films, Fig. 1b, a great change on the electrode surface was underwent and typical morphological characteristics of ERGO films with clearly crumpled and wrinkled as well as flake-like structure were well presented.

On the other hand, to further verify the formation of ERGO films offered by CV method, raman spectroscopy was employed for distinguishing the ordered and disordered crystal structures

[32]. Fig. 1c shows the typical *D* and *G* mode peak associated with GO and ERGO on the different electrode surface. As well known, where *G* band can be assigned to the E_{2g} phonon of C sp^2 atoms, while *D* band is a breathing mode of κ -point phonons of A_{1g} symmetry [35]. As clearly, *G* and *D* band of pristine GO respectively with a strong and weak peak at 1352 and 1595 cm^{-1} is well displayed. Furthermore, ERGO films obtained by CV method demonstrate two typical *D* and *G* bands with strong peaks. Interestingly, compared with that of GO, the intensity of *D* bands increases and *G* bands decreases significantly, respectively, suggesting that the successfully deoxygenation in ERGO can be successfully achieved [36] and, also indicating that the as-proposed method to be an effectively strategy to gain ERGO films on the GCE surface, resulting in achieving a ERGO modified electrode.

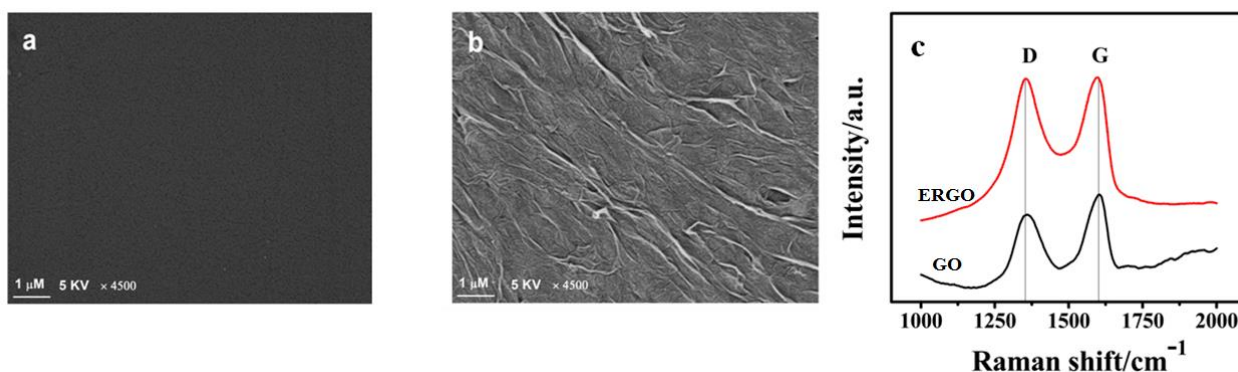


Figure 1. SEM images of bare glassy carbon electrode (a) and electrochemical reduced graphene oxide films modified glassy carbon electrode (b), Raman spectra of pristine graphene oxide and as-prepared electrochemical reduced graphene oxide sample.

As mentioned above, ERGO films modified electrode could be successfully gained by a simple yet effective CV method. To investigate the electrochemical behaviours of two electroactive groups of PNP molecule, the electron transport on such a modified electrode was need to be verified so as to confirm the good electrocatalysis capability of the proposed sensing substrate in our strategy. To demonstrate, the electrochemical behaviour of the redox couple of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ on the bare and modified electrodes was investigated by using CV and DPV, respectively. As shown in Fig. 2a, a pair of redox wave of bare GCE (curve I) are well displayed. Clearly, the anodic and cathodal peak currents of the probe indicate a low sensitive response of bare GCE toward the electrochemical probe. However, after modified with ERGO coating, the currents of probe peak remarkably increase, further indicating that ERGO films modified on the electrode surface effectively accelerate the electron transfer process between the probe molecules and electrode surface. Furthermore, the electrical conductivity of ERGO modified electrode was further investigated by using electrochemical impedance spectroscopy (EIS). As seen in Fig. 2b, semicircles in the high frequency region as well as straight line in the low frequency region for both two electrodes are well exhibited. As clearly, the decrease on the diameter of the semicircle reflects the decrease of the interfacial charge-transfer resistance of ERGO modified electrode. All these results demonstrate that the proposed ERGO films exhibit a good enhancement for the electron transport on the interface between the modified electrode

surface and the solution, which would be more useful for the electrochemical investigation involved various analytical purposes toward the target with dual electroactive groups.

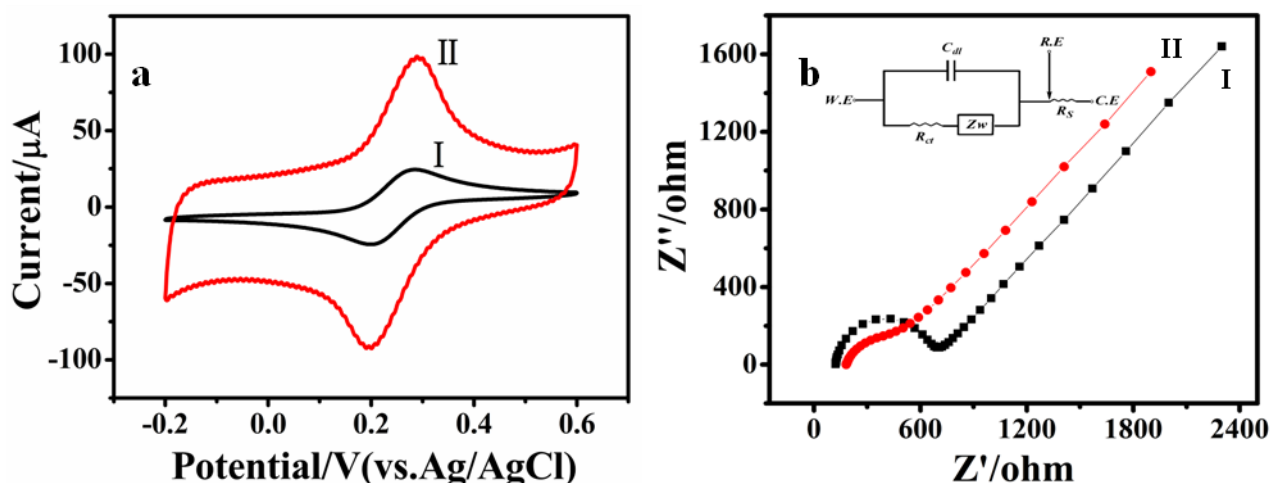


Figure 2. (a) Cyclic voltammograms of bare (curve I) and electrochemical reduced graphene oxide films modified glassy carbon electrode (curve II) and (b) Electrochemical impedance spectroscopy curves of bare (curve I) and electrochemical reduced graphene oxide films modified glassy carbon electrode (curve II) in 0.1 M KCl containing 1 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ at a scan rate of 5mV s^{-1} . Insert is employed equivalent circuit model.

Fig. 3 shows the cyclic voltammograms of 1.0 mM PNP at bare and ERGO films modified electrode in 0.2 M PBS (pH=7). As a unique molecule with different electroactive groups of nitro and phenol species described above, typical CVs of the electrochemical reduction of PNP molecule obtained at bare and ERGO films modified GCE were well displayed in Fig. 3a. As clearly, the reduction peak current corresponding to the reductive process of nitro groups on the PNP molecule at bare GCE surface is relatively lower (Curve I). After the ERGO films modified, curves II, a significant electrocatalytical response of the reduction of PNP with a large current on the modified electrode can be gained. Similar behaviors have also been reported previously, the reduction peaks can be ascribed to the reduction of electroactive group of nitro of PNP molecule due to the irreversible four-electron reduction process from 4-NP to 4-hydroxylaminophenol (4-HAP) [18, 37-39]. Obviously, reduction peak currents of PNP on the ERGO/GCE are much higher than that on the bare GCE, which strongly supporting that ERGO modified GCE can effectively catalyze the electrochemical reduction of PNP. It can be attributed to the good electrical conductivity of ERGO films on the ERGO sensing substrate, resulting in adsorbing more target molecules and thereby improving the electrochemical response of modified electrode toward the targets. In fact, most of electrochemical sensors towards PNP were fabricated based on various modifiers with functional and useful sensing materials [18, 22, 40-42], through which the modified electrode surface usually exhibits good catalytical performance toward the electrochemical reduction of PNP molecule. As a direct electrochemical determination method, those modified electrodes have been intensively applied in the past years.

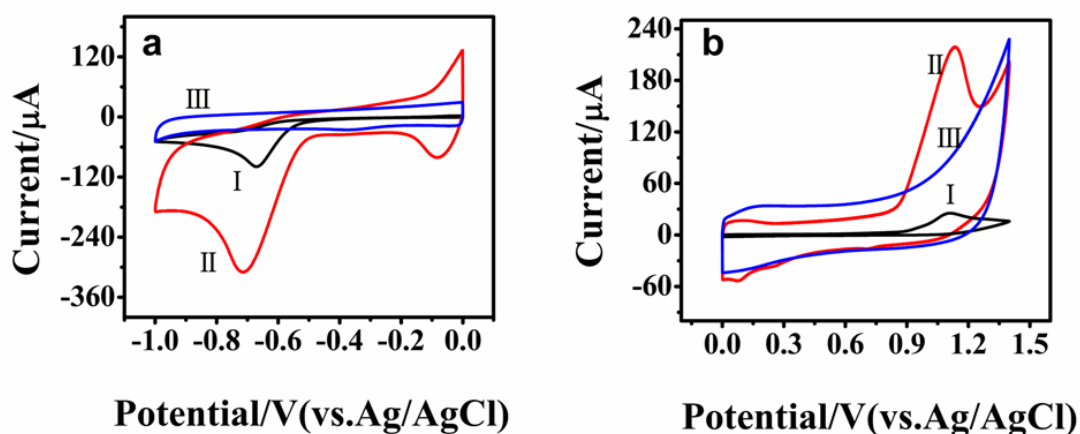


Figure 3. (a) Cyclic voltammograms (reduction process) of 1.0 mM p-nitrophenol in 0.2 M PBS (pH=7.0) at bare (I) and electrochemical reduced graphene oxide films modified glassy carbon electrode (II); Curve III is cyclic voltammograms of electrochemical reduced graphene oxide films modified glassy carbon electrode in the blank solution. (b) Cyclic voltammograms (oxidation process) of 1.0 mM p-nitrophenol in 0.2 M PBS (pH=7.0) at bare (I) and electrochemical reduced graphene oxide films modified glassy carbon electrode (II); Curve III is cyclic voltammograms of electrochemical reduced graphene oxide films modified glassy carbon electrode in the blank solution.

However, another electroactive group, phenol group may be oxidized at more positive potential, which is usually neglected and also may be employed to determine the PNP in the samples. Up to now, there are almost no such reports on detecting PNP using electrochemical oxidation process as a determination signal response. To clarify this issue, the electrochemical oxidation behaviours of 1.0 mM PNP in 0.2 M PBS (pH=7) on bare and ERGO films modified electrodes were also investigated and presented in Fig. 3b. As clearly, a lower current of phenol group oxidation on PNP molecule at bare GCE is well presented (curve I). Different with it, a large current signal occurs on the ERGO/GCE (curve II) with remarkably enhancement (approximately nine times as much as GCE), indicating that the ERGO/GCE exhibits higher sensitivity toward electrochemical oxidation of phenol group oxidation on PNP molecule. The results demonstrate that the electrochemical oxidation currents of PNP at ERGO modified electrode surface may be used as sensing signal to electrochemically detecting PNP. Moreover, the oxidation potential of PNP on bare and ERGO films modified GCE could be recognized accurately around 1.12 V, which is in good agreement with the former reports [43-45]. According to these literatures, the oxidation peak of PNP presented in this case can be ascribed to the oxidation process of phenol groups on PNP molecules, which occurs and give a radical species at high positive potentials [45]. As well known, once p-nitrophenoxy radical was produced, it would be further oxidized and transformed into p-nitrophenoxy cation at a given positive potential on the electrode surface and, resulting in the formation of polymers through the coupling reaction of p-nitrophenoxy radical and p-nitrophenoxy cation, and therefore producing an obvious electrode fouling [43, 46-48]. Based on this, we can conclude that the electrochemical response based on the

electrochemical oxidation of PNP at the as-prepared ERGO films modified GCE may be not suitable for the determination of PNP.

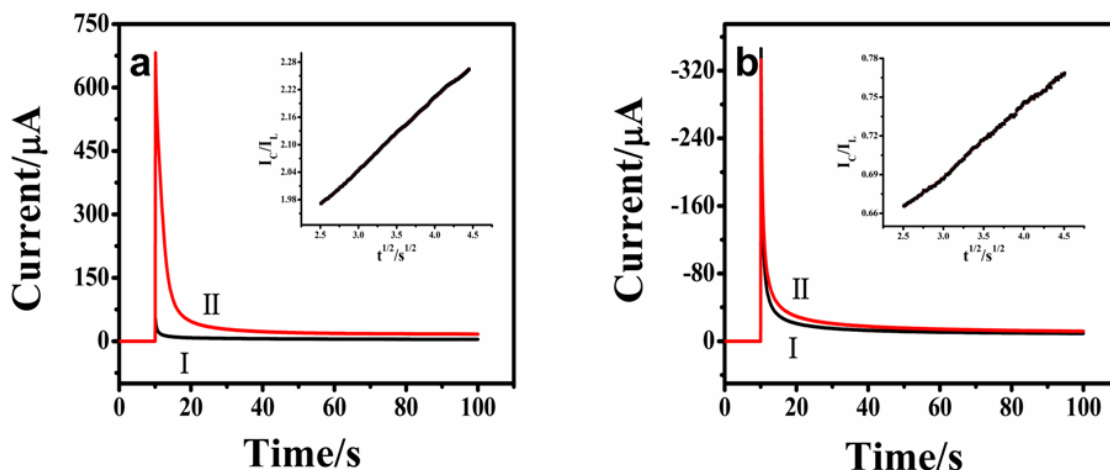


Figure 4. Amperometric response (oxidation process) (a) and (reduction process) (b) of without (curve I) and with (curve II) 1.0 mM p-nitrophenol in 0.2 M PBS (pH=7.0) at electrochemical reduced graphene oxide films modified glassy carbon electrode.

To further confirm it, some necessary evidences on kinetics parameters and detection limit of as-prepared modified electrode towards the target of PNP were investigated. As well known, chronoamperometry is an effective tool and can be employed to measure the kinetics of the electroactive target such as the apparent rate constant (κ) and so on. In this work, chronoamperometry performances of PNP at bare and ERGO films modified GCE were performed by using a double potential step method, respectively. Specifically, for the reduction and oxidation process, the electrode potential firstly was held at 0.0 V for 10 s and then forced it to a appropriate electrochemical reaction potential, i.e., -0.73 V and 1.14 V, respectively (for bare and ERGO modified GCE). As clearly in Fig. 4, both response currents for the reduction and oxidation process of PNP decrease with the time increases at a given potential and, finally a stabilized response currents occur. According to the formula (Formula 1) [49], the apparent rate constant (κ) associated with the PNP reduction and oxidation reaction could be easily determined via plotting values of I_c/I_1 vs $t^{1/2}$.

$$\frac{I_c}{I_1} = \gamma^{\frac{1}{2}} \pi^{\frac{1}{2}} = \pi^{\frac{1}{2}} (kC_0 t)^{\frac{1}{2}} \quad (\gamma = kC_0 t) \quad (1)$$

Where I_c/I_1 is the ratio of the faradaic current collected after and before PNP addition. C_0 is PNP concentration in the bulk solution in M, k and t is the rate constant in $M^{-1}s^{-1}$ and the time elapsed, respectively. For this purpose, the calculated apparent rate constants (k) associated with PNP oxidation and reduction reaction at the proposed ERGO films modified electrode is 0.89 and 6.79 $M^{-1}s^{-1}$, respectively. Obviously, at the ERGO films modified GC electrode, the apparent rate constants k of PNP gained from the reduction reaction was significantly enlarged and was about 8 times than that of the oxidation reaction. These results strongly demonstrate that ERGO films exhibit a significant and different electrocatalytic capability toward various electroactive groups of PNP.

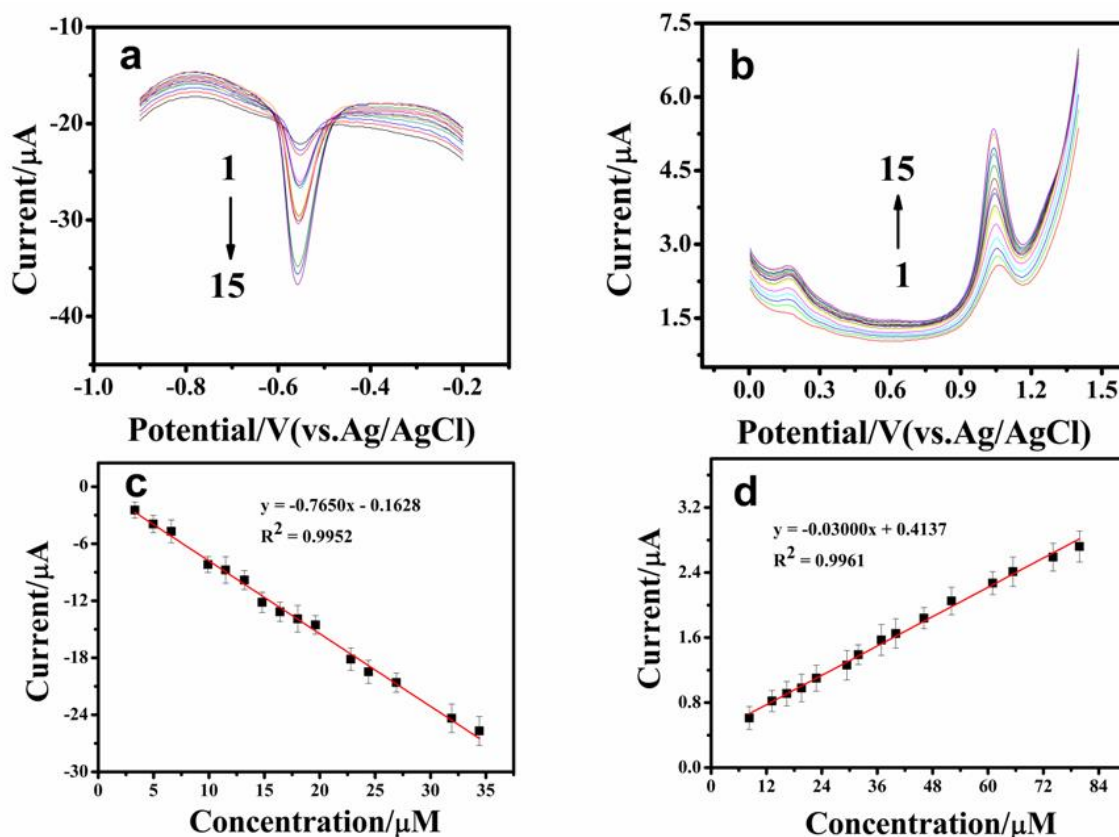


Figure 5. (a) Differential pulse voltammograms of PNP at electrochemical reduced graphene oxide films modified glassy carbon electrode (reduction process) with different concentrations of (1-15): 3.3, 5.0, 6.6, 9.9, 11.5, 13.2, 14.8, 16.4, 18.0, 19.6, 22.8, 24.4, 26.9, 31.9, 34.4 $\mu\text{M L}^{-1}$ in 0.2 M PBS (pH=7.0) and the corresponding calibration curve (c) and (b) differential pulse voltammograms of oxidation process with PNP concentrations of (1-15): 8.3, 13.2, 16.4, 19.6, 22.8, 29.4, 31.9, 36.9, 40.0, 46.1, 52.1, 61.0, 65.4, 74.1, 79.8 $\mu\text{M L}^{-1}$ in 0.2 M PBS (pH=7.0) and the corresponding calibration curve (d).

It is clear that the calculated apparent rate constants (k) of PNP reduction at ERGO films modified electrode is much higher than the oxidation ones. To evaluate it, differential pulse voltammeters of PNP with different concentrations collected on the basis of reduction and oxidation process were recorded and presented in Fig. 5. As clearly (Fig. 5a and c), the peak currents of the PNP reduction at the ERGO films increase linearly with the increase of PNP concentration over a range of 3.3 to 34.4 $\mu\text{M L}^{-1}$ with a correlation coefficient of 0.9952. Similarly, for the oxidation reaction of PNP (Fig. 5b and d), the obtained peak currents are also linearly related with the PNP concentration over a range of 8.3 to 79.8 $\mu\text{M L}^{-1}$ with a correlation coefficient of 0.9961 as well as with a detection limit of 0.55 and 2.13 $\mu\text{M L}^{-1}$ for the reduction and oxidation reaction ($3\sigma/b$), respectively. Here, σ and b is the standard deviation of the blank (measured 20 times) and the slope of the calibration curve, respectively. Furthermore, by comparing to reported electrochemical sensing platforms (Table 1), the sensitivity of ERGO films modified GCE toward PNP electrochemical reduction is higher and exhibits more opportunities for the construction of simple, fast, and sensitive detecting method toward PNP

than the electrochemical oxidation. In addition, the potential utility on the specific response of the developed ERGO modified electrode toward PNP determination based on the current signals offered by the reduction process associated with nitro group on PNP molecule was verified by using standard addition method. As clearly in Table 2, the results strongly demonstrate that the proposed electrochemical sensor exhibits a good feasibility and applicability for PNP determination as well as with satisfying recoveries. All these results demonstrate that the electroactive nitro group on the PNP molecule is more appropriate than the phenol group for the construction of sensitive electrochemical sensor due to the lower detection limit found in this work as well as the serious electrode fouling induced by the formation of polymers involved with the phenol group of PNP molecule.

Table 1 Comparison of various electrochemical sensors for p-nitrophenol determination

The employed modified electrodes	Low detection limited (μM)		Linear range(μM)	References
	Based on oxidation process	Based on reduction process		
Poly p-aminobenzene sulfonic acid		0.3	3~700	9
β -cyclodextrin functionalized Au@graphene nanohybrids		0.0038	0.01~200	10
β -cyclodextrin functionalized mesoporous silica	0.01		0.2~1.4	13
CeO ₂ -ZnO nanoellipsoids		1.163	0.1~1.0	14
Apatite		0.008	0.2~100	17
Graphite Nanoflake	0.7		1~6000	18
polyelectrolyte-functionalized graphene		0.02	0.06~110.0	19
polycarbazole/N-doped graphene		0.062	80~200.0	20
graphene oxide		0.02	0.1~120.0	23
nitrogen-doped reduced graphene oxide		0.007	0.02~0.50	24
polyfurfural films		0.04	0.75~100.0	30
ordered mesoporous carbon		0.1	2~90.0	39
Mg(Ni)FeO	0.2		2.0~200	41
Electrochemical reduced graphene oxide	2.13	0.55	3.3~34.4 (For reduction Process) 8.3~79.8 (For oxidation Process)	This work

Table 2 Determination of p-nitrophenol in different water samples by using standard addition

Samples	Added (μM)	Found (μM)	Recovery (%)	RSD (% _{n=5})
Yellow river	1.2	1.240	103.3	2.43
Tap-water	0.8	0.795	99.4	2.32
Waste water	1.6	1.673	104.5	2.17

Table 3 Statistical parameters of p-nitrophenol determination at ERGO modified electrode based on different electroactive groups

Detecting process	Apparent rate constant($\kappa/M^{-1}s^{-1}$)	Linear range (μM)	Detection Limit (μM)
Reduction process	6.79	3.3~34.4	0.55
Oxidation process	0.89	8.3~79.8	2.13

4. CONCLUSIONS

In summary, we have successfully demonstrated a simple yet effective comparative study on the electrochemical determination of p-nitrophenol based on the different response signals by reduction and oxidation process of nitro group and phenol group on PNP molecule, in which electrochemical reduction graphene oxide films modified surface on a glass carbon electrode were proposed as sensing substrate. The electrochemical behaviours of p-nitrophenol at electrochemical reduction graphene oxide modified surface were offered by using cyclic voltammograms, differential pulse voltammetry and chronoamperometry. As a result, a significant differences of electrocatalytic activity and electrochemically detecting sensitivity toward PNP on the basis of the reduction and oxidation process of nitro and phenol group were point out (Table 3), where the experimental results demonstrate that the electrochemical response based on the electrochemical reduction process possesses higher apparent rate constant (κ) and lower detection limit than the oxidation reaction. This study not only provides novel evidences on the superiority of electrochemical determination toward PNP through electrochemical reduction of nitro group than another electroactive group of phenol species on the target molecule, but also opens a new avenue to utilizing electrochemical reduction graphene oxide for the electrochemical investigation of objective molecules with dual and multiple electroactive groups.

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