Electrochemical Detection of 4-Nitrophenol on a Nanoporous Gold Electrode Prepared by One-Step Anode Potential Step Method

Dongsheng Lai[1], Lin Chen[1], Yuqing Liu[1] and Wei Huang[1*]

[1]*Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), National and Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, Key Laboratory of the Assembly and Application of Organic Functional Molecules of Hunan Province, Hunan Normal University, Changsha, 410081, China.*

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

The wastewater containing nitrophenol compounds is discharged into the water and soil environment, causing severe environmental pollution problems. In this paper, a one-step anodic potential step method involving Au(I) disproportionation was used to prepare nanoporous gold (D-NPG) electrodes for the electrochemical detection of 4-nitrophenol (4-NP) by differential pulse voltammetry (DPV). The D-NPG electrode has a high current response to the oxidation peak of 4-hydroxylaminophenol, a product of 4-NP electroreduction. This peak is used in the 4-NP detection. Under the optimized conditions, the resulting detection range is wide (0.01~20 µM) and the detection limit is low (3.5 nM), and its anti-interference ability is good. It can be used for the electrochemical detection of 4-NP in real water samples.

_____

*Corresponding author: E-mail: 17407389@qq.com;

1. INTRODUCTION

Nitrophenol and its derivatives are important organic raw materials for industrial production, which are widely involved in the process of industrial synthesis of pesticides, dyes, paints and medicines. Wastewater containing nitrophenol compounds can cause severe environmental pollution problems [1]. Among them, 4-NP is more toxic and has been included in the priority control pollutant list of the US Environmental Protection Agency [2]. Therefore, it is important for the development of effective methods to detection 4-nitrophenol in the water environment.

Several methods have been employed to detect nitrophenols, such as high performance liquid chromatography [3], spectrophotometry [4], fluorescence [5], enzyme-linked immunosor-bent assay [6], capillary electrophoresis [7] and electrochemical method [8-9]. Among them, electrochemical method is widely used in the detection of environmental pollutants due to their advantages of simplicity, rapidity, low cost, and in-situ detection. In this method, electrode materials commonly used are graphene [10], carbon nanotubes [11], metal oxides [12], metal nanomaterials [13] and so on. For example, Balasubramanian et al. synthesized a new type of $CoMnO_3$ nanosheet by oxalic acid-assisted co-precipitation technology and used it as an electrocatalyst for the highly sensitive detection of 4-NP [14]. The detection method has excellent performance with high sensitivity of 2.458 µA µM^{-1} cm^{-2}, low detection limit of 10 nM and good reproducibility. Ndlovu et al. prepared the composite material of poly(propyleneimine) dendrimer and gold nanoparticle on graphite electrode (PPI-AuNP/EC) by electrodeposition method and used it for the electrochemical detection of 2-NP [15]. The detection has a wide detection range (0.31~50 µM) and a low detection limit (33 nM). Nanoporous gold (NPG) have excellent properties such as large specific surface area, high catalytic activity, and good electrical conductivity, and have been used in electrochemical detection [13,16].

In previous work, a one-step anode potential step method involving Au(I) disproportionation was used to prepare nanoporous gold (D-NPG) electrodes within 5 minutes [16]. As far as we known, there is no detection of 4-NP on the D-NPG. In the present work, the electrochemical redox behavior of 4-NP on D-NPG was discussed at first. Then, the influence of 4-NP

accumulation conditions (potential and time) on 4-NP response were examined. Finally, the D-NPG was used for the differential pulse voltammetry (DPV) detection of 4-NP with high sensitivity, low detection limit and good anti-interference ability.

2. METHODOLOGY

2.1 Reagents

Sulfuric acid, potassium chloride, sodium hydroxide, disodium hydrogen phosphate, sodium dihydrogen phosphate, phosphoric acid and 4-nitrophenol were of analytical grade and were used as received. All solutions were prepared with Millipore ultrapure water.

2.2 Apparatus

The electrochemical experiment was performed on a CHI660C or CHI660E electrochemical workstation (Chenhua Instruments, Shanghai, China) with a three-electrode configuration. A pure gold electrode (purity > 99.99%, 2 mm in diameter), saturated mercurous sulfate electrode (SMSE) and platinum foil were used as the working, reference and counter electrodes, respectively. A PHS-3C pH meter (Shanghai Lida Instrument Co., Ltd.) was used to adjust the pH of the solution. The surface morphology of nanoporous gold was observed by Quanta FEG 250 scanning electron microscope (SEM).

2.3 Preparation of D-NPG

In this experiment, the one-step anode potential step method reported by our research group was used to prepare nanoporous gold film [16]. First, the gold electrode is polished by 2000 grit carbimet paper and cleaned in Millipore water under ultrasonic waves. Secondly, the smooth Au electrode was electrochemically cleaned by cyclic voltammetry (CV) in a 1 M H_2SO_4 solution. Then, the as-cleaned smooth gold electrode was run by a linear voltammetry scan (10 mV/s) between -0.2 and 1.1 V in a 1 M KCl solution to determine the preparation potential of D-NPG. Finally, a constant anodic potential (0.91 V) near Au passivation was selected to prepare the D-NPG with a short time of 300 s.

During the preparation at 0.91 V, a monovalent gold species (Au(I)), which is unstable and can spontaneously disproportionate to produce zero-valent gold atoms, the latter aggregate and deposit on the gold surface to form a nanoporous

gold film (D-NPG) [16]. Since the preparation potential is close to the passivation zone, the porous surface can be stabilized under the protection of the thin layer of gold oxide.

The as-prepared D-NPG was scanned by CV (-0.7 ~ 1.1 V, 100 mV s^{-1}) in a 1 M H_2SO_4 solution until the CV curve was stable. The D-NPG roughness was calculated to be 254 based on the reduction peak of gold oxide monolayer in CV curve [16].

2.4 Electrochemical Determination of 4-NP

The nitrophenol detection on D-NPG electrode was tested by differential pulse voltammetry (DPV) in a 0.5 M H_2SO_4 solution. Before the DPV test, the D-NPG electrode was applied by a constant potential (-0.38 V for 30 min typically) in the H_2SO_4 solution containing 4-NP for the accumulation of 4-NP. Finally, a forward potential scan from -0.05 to 0.3 V was performed to get an anodic DPV curve.

3. RESULTS AND DISCUSSION

3.1 Morphology Characterization of D-NPG

The SEM image of D-NPG shows a typical nanoporous gold surface (Fig. 1), which is composed of massive aggregated gold nanoparticles. During preparation, the newborn gold atoms/clusters from Au(I) disproportionation are highly unstable and easy to aggregate in the absence of protective agent [16]. A Such a nanoporous structure owns many active sites and nanochannels, which are beneficial to the transfer, surface adsorption and reaction of 4-NP.

3.2 CV Behavior of 4-NP on D-NPG Electrode

Fig. 2A shows the CV behaviors of 4-NP on D-NPG in H_2SO_4 solution. There is no obvious characteristic peak of 4-NP in the CV from the blank solution (the black dotted line). When 4-NP was added, a reduction peak (R) appears around -0.38 V during the first negative potential scan. It is assigned to the irreversible four-electron reduction of 4-NP to 4-hydroxylaminophenol (4-HAP) (reaction 1 of Fig. 2B) [17-18]. During the positive scan, an oxidation peak (O1) appeared at about 0.1 V. Its reduction peak (R1) appeared at about 0.1 V on the second negative scan. The pair of redox peaks O1/R1 is corresponding to the two-electron reversible process between 4-HAP and 4-nitrosophenol (4-NSP) (reaction 2 of Fig. 2B) [17-18]. With continuous scanning, the current of peak R decreases, which may be due to that the competitive adsorption of reaction intermediates inhibits the 4-NP adsorption on the D-NPG electrode surface [19]. At the same time, the O1/R1 redox increase due to the accumulation of 4-HAP on the surface. Besides, after scanning several cycles of CV, a pair of small redox peaks (O2/R2) [20] appeared at around -0.3 V. They may be related to intermolecular or intramolecular reactions (for example, polymerization).
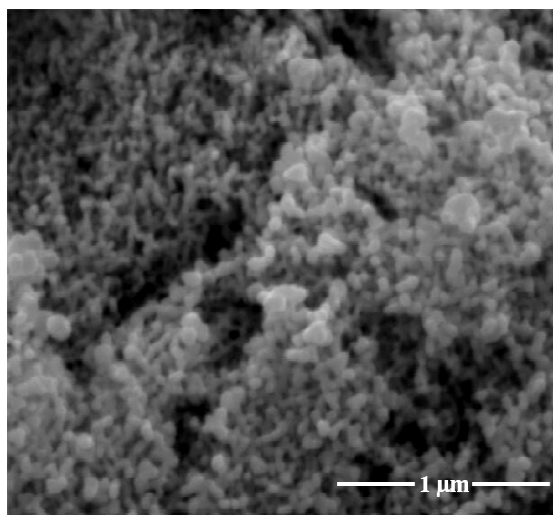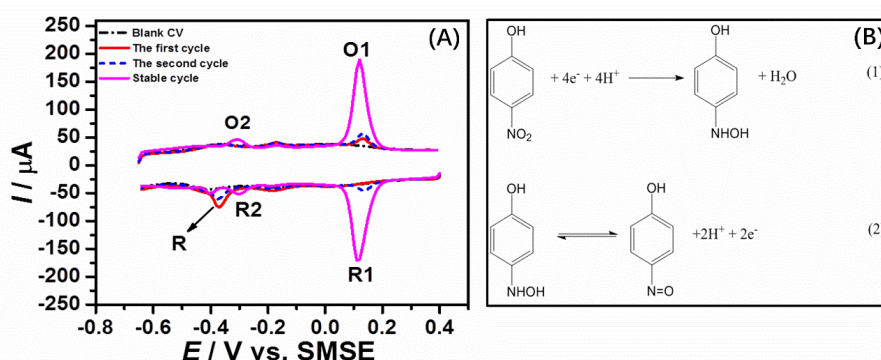

Fig. 1. SEM of D-NPG

Fig. 2. (A) CV behavior of D-NPG electrode in 0.5 M H_2SO_4 + 100 µM 4-NP solution and (B) 4-NP reaction mechanism
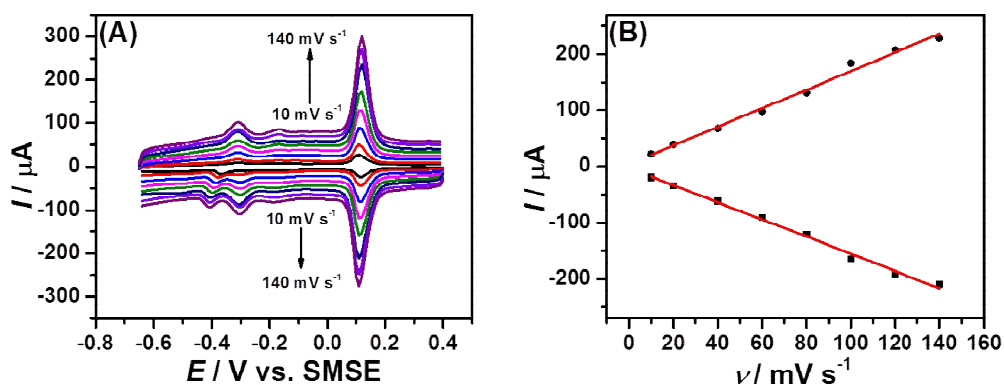

Fig. 3. (A) CVs of D-NPG electrode in 0.5 M H_2SO_4 + 100 µM 4-NP solution under different scan rates, and (B) The linear relationship between the current of the redox peak (O1/R1) and the scan rate v

Fig. 3A shows the influence of the scan rate on the CVs of 4-NP on the D-NPG electrode. The O1/R1 peak currents (I_{O1} and I_{R1}) increase linearly with the scan rate (v), which are expressed as I_{O1} = 1.65935v + 4.05516 (R^2 = 0.991) and I_{R1} = -1.53177v - 2.33787 (R^2 = 0.994) (Fig. 3B), indicating that the O1/R1 redox processes are controlled by surface step [18].

3.3 Influence of Accumulation Conditions on DPV Response

Differential pulse voltammetry (DPV) is a commonly used electrochemical measurement technique that can be used to detect trace amounts of inorganic and organic substances. Prior to DPV test, the electrode surface needs to accumulate substance under certain condition to obtain high DPV response. As shown in Fig. 4A, when the accumulation potential moves negatively to -0.38 V, the DPV current of oxidation peak O1 reaches the highest value. As shown in Fig. 4B, the O1 peak current increases continuously with the increase of the accumulation time. It reaches a high level at the time of 30 min finally, indicating that the electrochemical adsorption equilibrium has been reached. Therefore, the accumulation potential of -0.38 V and the accumulation time of 30 min is the optimal condition for DPV detection of 4-NP.

3.4 DPV Detection of 4-NP

Fig. 5A shows the DPV response of different concentrations of 4-NP on the D-NPG electrode under the optimal detection conditions. As shown in Fig. 5B-a, the peak current increases linearly with the increase of the 4-NP concentration. The linear concentration range is 0.01-20 µM, and the linear equation is I = 40.95949 c – 14.32156 (R^2 = 0.991). The detection limit is calculated to be 3.5 nM (3σ/slope) [18-19]. Comparing the detection performance of the D-NPG electrode with the work reported in other literatures (Table

15

1), it is found that the D-NPG electrode have lower detection limit and wider detection range.

Moreover, short accumulation time results in obvious low detection sensitivity. When the accumulation last for only 4 min (curve b), the response of the D-NPG electrode to 4-NP weakens. Note that the slope of linear curve a is 3.28 times that of curve b. The fact indicates that it takes enough time to adsorb 4-NP on the inner and outer surfaces of the nanoporous gold film. At the same time, the slope on the D-NPG electrode was compared with that on the smooth gold electrode. It can be seen from Fig. 5B that under the same accumulation condition (curve a and c), the slope of linear curve on the D-NPG electrode (40.95949, curve a) is 3077 times that of the smooth gold electrode (~0.01331, curve c), indicating very high sensitivity for the detection of 4-NP on the D-NPG surface.

3.5 Effect of Interferents

In order to evaluate whether the D-NPG electrode has anti-interference performance, we carried out the effect of some interferents on the detection of 1 µM 4-NP. From Table 2, 100 fold of inorganic ions, 50 fold of 3-NP and 100 fold of 2-NP had no obvious interference (the deviation is less than 5%), indicating that the D-NPG electrode has good anti-interference ability.

In addition, the storage stability of the D-NPG electrode was also investigated. The electrode is stored at low temperature for 4 weeks. In the first week, the 4-NP current response has decayed obviously due to the aggregation of high active and unstable Au clusters/nanoparticles. Afterwards, little change on the DPV response happens in the next three weeks, indicating the surface is stable.
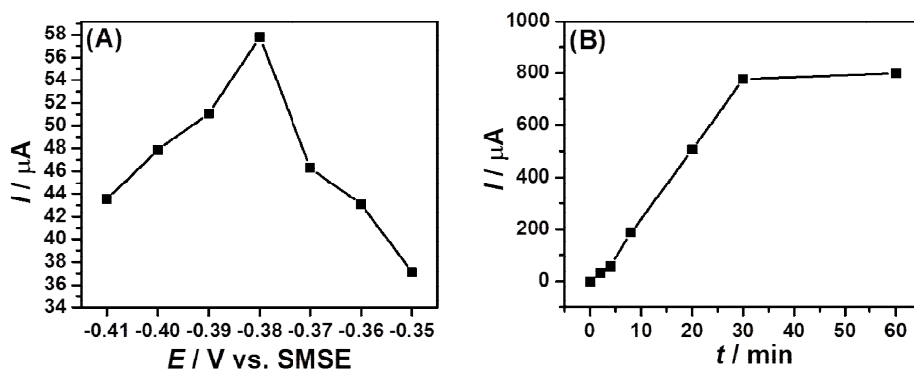

Fig. 4. The influence of accumulation (A) potential and (B) time on peak current of O1 at fixed (A) time of 4 min and (B) potential of -0.38 V

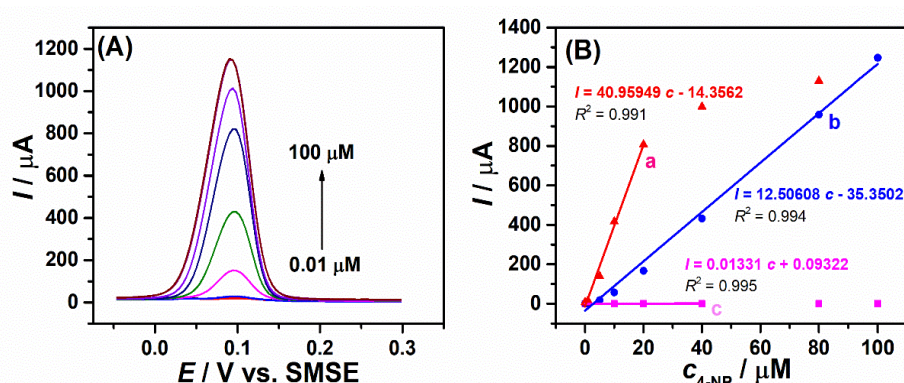**Fig. 5. (A) DPV curve of D-NPG electrode in 0.5 M H₂SO₄ solution containing different concentrations of 4-NP (accumulation time of 30min), and (B) dependence of the DPV peak current on 4-NP concentration at (a) smooth gold and (b, c) D-NPG electrode. Accumulation time: a and c are 30 min, and b is 4 min**

16

Table 1. Performance comparison of electrochemical detection of 4-NP on gold nanomaterials

Electrode material	Method	Linear range (µM)	Detection limit (nM)	Ref.
AuNPs/RGO[a]/GCE	DPV	0.05–2.0, 4.0-100	10	[21]
	SWV	0.05–2.0	20	
CuNPs/4,4'-bpy/Au[b]	CA	1–500	0.34	[22]
lamellar ridge-Au[c]	DPV	0.025-1, 1-300	20	[23]
AuNP-SPC[d]	*i-t*	0.1-315	98	[24]
Au@MWCNTs[e]	DPV	0.01-50, 80-500	—	[25]
Au–ZnO–SiO$_2$[f]/GCE	DPV	0.01–1.2	2.8	[26]
		0.05–3.5	13.7	
β-CD-Au@CGS[g]/GCE	DPV	0.01-200	3.8	[27]
ERG-AuNP[h]/GCE	LSV	0.036-90	10	[28]
Au-Cu(1:3)[i]/GCE	SWV	0.1-15	80	[29]
DVD@NP.Au/Hg[j]	SWV	5-250	1000	[30]
D-NPG	DPV	0.01-20	3.5	This work

a: Au nanoparticles/reduce grapheme oxide film; b:copper metal nanoparticles/4,4'-bipyridine modified gold electrode; c: lamellar-ridge architectured gold; d: Au nanoparticles electrodeposited screen printing carbon electrodes; e: gold nanoparticles decorated multi-walled carbon nanotubes; f: ZnO and gold nanoparticles dispersed into a silica matrix; g: β-CD-gold nanoparticles were anchored onto carboxylic graphene nanosheets (CGS); h: graphene–gold nanocomposite film; i: gold-copper alloy nanoparticles; j: gold digital versatile disc platform modified with nano-porous mercury/gold (Hg/Au) amalgam

Table 2. The influence of different interfering ions on the detection of 1 µM 4-NP

Interferent	Concentration (µM)	Deviation (%)
Al^{3+}	100	2.69
Cl$^-$	100	-2.92
Co^{2+}	100	-3.41
Cu^{2+}	100	-4.78
K$^+$	100	-3.68
Ni^{2+}	100	1.41
NO$_3^-$	100	3.53
Zn^{2+}	100	0.85
2-NP	100	-3.26
3-NP	50	3.33

Table 3. Determination results of 4-NP in water samples (*n* = 3)

Sample		Added (µM)	Found (µM)	RSD (%)
		4-NP	4-NP	4-NP
Lake water	0	Not detected	-	-
	5	5.34	1.08	106.8
	10	9.84	2.83	98.4
Tap water	0	Not detected	-	-
	5	4.78	4.36	95.6
	10	10.09	1.07	100.9

The D-NPG electrode was used to detect 4-NP in real tap water and lake water. No 4-NP signal can be detected in actual water samples. The possible reason is that the water sample does not contain 4-NP or the concentration is lower than the detection limit of the electrode. So, we use the standard addition method for determination. It can be concluded from Table 3 that the recovery of 4-NP is between 95.6% and 106.8%, which shows that the D-NPG electrode can be applied to detect the 4-NP in actual water samples.

4. CONCLUSIONS

In this work, an anodic potential step method was used to prepare nanoporous gold film (D-NPG) for the electrochemical detection of 4-NP. Experiment results show that the D-NPG electrode has a high detection performance to

the 4-NP with a wide detection range (0.01-20 µM), low detection limit (3.5 nM), good anti-interference ability, and can be used for the electrochemical detection of 4-NP in real water samples. Further work can be carried out on some nanoporous non-noble metal materials.

ACKNOWLEDGEMENTS

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Buikema AL, McGimres MJ, Cairns J. Phenolics in aquatic ecosystems: A selected review of recent literature. Marine Environ. Res. 1979;2:87–181.
2. US Environmental Protection Agency. Fed. Regist. 1987;52:25942-25953.
3. Belloli R, Barletta B, Bolzacchini E, Meinardi S, Orlandi M, Rindone B. Determination of toxic nitrophenols in the atmosphere by high-performance liquid chromatography. J. Chromatogr. A. 1999;846:277-281.
4. Kusakabe S, Ohara M. Multiple-wavelength data treatment of ultraviolet-visible spectra for 1:1 electron donor-acceptor adducts of p-nitrophenol in heptane. Anal. Chim. Acta. 1991;242:57-64.
5. Nistor C, Oubiña A, Marco MP, Barceló D, Emnéus J. Competitive flow immunoassay with fluorescence detection for determination of 4-nitrophenol. Anal. Chim. Acta. 2001;426:185-195.
6. Tingry S, Innocent C, Touil S, Deratani A, Seta P. Carbon paste biosensor for phenol detection of impregnated tissue: modification of selectivity by using β-cyclodextrin-containing PVA membrane. Mat. Sci. Eng. C: Mater. 2006;26:222-226.
7. Tsukagoshi K, Kameda T, Yamamoto M, Nakajima R. Separation and determination of phenolic compounds by capillary electrophoresis with chemiluminescence detection. J. Chromatogr. A. 2002;978:213-220.
8. Sangili A, Annalakshmi M, Chen SM, Balasubramanian P, Sundrarajan M. Synthesis of silver nanoparticles decorated on core-shell structured tannic acid coated iron oxide nanospheres for excellent electrochemical detection and efficient catalytic reduction of hazardous 4-nitrophenol. Compos. Part B: Eng. 2019;162:33-42.
9. Wang M, Liu Y, Yang L, Tian K, He L, Zhang Z, Jia Q, Song Y, Fang S. Bimetallic metal-organic framework derived FeO_x/TiO_2 embedded in mesoporous carbon nanocomposite for the sensitive electrochemical detection of 4-nitrophenol. Sensor. Actuat. B: Chem. 2019;281:1063-1072.
10. Wiench P, Grzyb B, González Z, Menéndez R, Handke B, Gryglewicz G. pH robust electrochemical detection of 4-nitrophenol on a reduced graphene oxide modified glassy carbon electrode. J. Electroanal. Chem. 2017;787:80-87.
11. Nehru R, Chen TW, Chen SM, Tseng TW, Liu X. 4-Nitrophenol detection in water sample using linear sweep voltammetry with f-multi walled carbon nanotubes modified electrode. Int. J. Electrochem. Sci. 2018;13:7778-7788.
12. Veeramani V, Sivakumar M, Chen SM, Madhu R, Dai ZC, Miyamoto N. A facile electrochemical synthesis strategy for Cu_2O (cubes, sheets and flowers) microstructured materials for sensitive detection of 4-nitrophenol. Anal. Methods. 2016;8:5906-5910.
13. Kim J, Han S, Kim Y. Effect of a roughness factor on electrochemical reduction of 4-nitrophenol using porous gold. Korean J. Chem. Eng. 2017;34:2498-2501.
14. Balasubramanian P, Balamurugan T, Chen SM, Chen TW. Simplistic synthesis of ultrafine $CoMnO_3$ nanosheets: As an excellent electrocatalyst for highly sensitive detection of toxic 4-nitrophenol in environmental water samples. J. Hazard. Mater. 2019;361:123-133.
15. Ndlovu T, Arotiba OA, Sampath S, Rui WK, Mamba BB. Poly (propyleneimine) dendrimer-gold nanoparticle modified exfoliated graphite electrode for the

electrochemical detection of o-nitrophenol. J. Appl. Electrochem. 2011;41:1389-1396.

16. Xia Y, Huang W, Zheng J, Niu Z, Li Z. Nonenzymatic amperometric response of glucose on a nanoporous gold film electrode fabricated by a rapid and simple electrochemical method. Biosens. Bioelectron. 2011;26:3555-3561.

17. Wang P, Xiao J, Liao A, Li P, Guo M, Xia Y, Li Z, Jiang X, Huang W. Electrochemical determination of 4-nitrophenol using uniform nanoparticle film electrode of glass carbon fabricated facilely by square wave potential pulses. Electrochim. Acta. 2015;176:448-455.

18. Wang P, Xiao J, Guo M, Xia Y, Li Z, Jiang X, Huang W. Voltammetric determination of 4-nitrophenol at graphite nanoflakes modified glassy carbon electrode. J. Electrochem. Soc. 2015;162:H72-H78.

19. Liu Z, Du J, Qiu C, Huang L, Ma H, Shen D, Ding Y. Electrochemical sensor for detection of p-nitrophenol based on nanoporous gold. Electrochem. Commun. 2009;11:1365-1368.

20. Liu Z, Zhang H, Ma H, Hou S. Selective determination of p-nitrophenol based on its unique voltammetric behavior on nanoporous gold. Electroanalysis. 2011;23:2851-2861.

21. Tang Y, Huang R, Liu C, Yang S, Lu Z, Luo S. Electrochemical detection of 4-nitrophenol based on a glassy carbon electrode modified with a reduced graphene oxide/Au nanoparticle composite. Anal. Methods. 2013;5:5508-5514.

22. Barman K, Changmai B, Jasimuddin S. Electrochemical detection of para-nitrophenol using copper metal nanoparticles modified gold electrode. Electroanalysis. 2017;29:2780-2787.

23. Guo X, Zhou H, Fan T, Zhang D. Electrochemical detection of p- nitrophenol on surface imprinted gold with lamellar-ridge architecture. Sensor. Actuat. B: Chem. 2015;220:33-39.

24. Tang YY, Chen PY. Nanoparticle-electrodeposited electrodes used for p-nitrophenol detection in acidic media: effect of electrodeposition parameters on particle density, size distribution, and electrode performance. J. Chin. Chem. Soc. 2011;58:723-731.

25. Al-Kahtani AA, Almuqati T, Alhokbany N, Ahamad T, Naushad M, Alshehri SM. A clean approach for the reduction of hazardous 4-nitrophenol using gold nanoparticles decorated multiwalled carbon nanotubes. J. Clean. Prod. 2018;191:429-435.

26. Ghazizadeh AJ, Afkhami A, Bagheri H. Voltammetric determination of 4-nitrophenol using a glassy carbon electrode modified with a gold-ZnO-SiO$_2$ nanostructure. Microchim. Acta. 2018;185, 296.

27. Yang L, Zhao H, Li Y, Li CP. Electrochemical simultaneous determination of hydroquinone and p-nitrophenol based on host–guest molecular recognition capability of dual β-cyclodextrin functionalized Au@graphene nanohybrids. Sensor. Actuat. B: Chem. 2015;207:1-8.

28. Jiao XX, Luo HQ, Li NB. Fabrication of graphene-gold nanocomposites by electrochemical co-reduction and their electrocatalytic activity toward 4-nitrophenol oxidation. J. Electroanal. Chem. 2013;691:83-89.

29. Shah A, Akhtar M, Aftab S, Shah AH, Kraatz HB. Gold copper alloy nanoparticles (Au-Cu NPs) modified electrode as an enhanced electrochemical sensing platform for the detection of persistent toxic organic pollutants. Electrochim. Acta. 2017;241:281-290.

30. Afzali F, Zavar MHA, Rounaghi G, Ashraf N. Gold digital versatile disc platform modified with nano-porous mercury/gold amalgam as a solid-state disposable electrochemical sensor for detection of para-nitrophenol. Electrochim. Acta. 2016;209:654-660.

Peer-review history:
The peer review history for this paper can be accessed here:
http://www.sdiarticle4.com/review-history/69373