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Porous Copper-Modified Graphite Pencil Electrode for the Amperometric Detection of 4-Nitrophenol

Abdel-Nasser Kawde*[a, b] and Md. Abdul Aziz[a, c]

Abstract: To overcome the well-known carbon electrodes surface fouling of phenols, we report on a simple and rapid method for the preparation of a disposable porous Cu-modified graphite pencil electrode (Cu-GPE) for sensing 4-nitrophenol (4-NP). The bare- and Cu-modified graphite pencil electrodes were characterized by cyclic voltammetry and SEM. The two electrodes displayed distinct electrocatalytic activities in response to the electrochemical redox reaction of 4-NP. A difference of three orders of magnitude is obtained on the amperometric detection limits of 1.9 µM on porous Cu-modified vs. 1.0 mM on bare-graphite pencil electrode at 3σ. The Cu-GPEs are fabricated utilizing a simple single method, and at an extremely low cost with high stability, selectivity and sensitivity, offering a promising tool for sensing 4-NP.

Keywords: Porous copper • Graphite pencil electrode • Electrodeposition • 4-Nitophenol • Amperometric sensor

1 Introduction

Phenolic compounds are produced in natural ways, used for various purposes, and existed randomly in our environment. For instance, nitrophenols (NPs) are frequently used to synthesis paracetamol, the most popular and safe analgesic and antipyretic drug [1]. Moreover, they are widely used to synthesize other drugs, explosives, insecticides, dyes and for making corrosion inhibitors of woods and rubber chemicals [2–4]. As a result, NPs distribute haphazardly in the environment especially in water and consider toxic to living organisms [2–5]. Besides, they are listed among hazardous wastes and priority toxic pollutants by United State Environmental Protection Agency [6,7]. Among the mononitrophenols, 4-nitrophenol (4-NP) is the most toxic compound [3,8,9]. Hence, measurement of 4-NP is very important.

Several analytical methods have been developed for the measurement of 4-NP such as UV-visible spectrophotometry [10], spectrofluorimetry [11], high performance liquid chromatography [12,13], and flow injection analysis [14]. However, most of these methods require pretreatment; involve separation, extraction and adsorption [15], which is time consuming, and increase the overall analysis cost. As a result, those methods are not suitable to monitor the 4-NP routinely in the field. Compared to other methods, electrochemical determination of the present analyte is favorable due to its simplicity, portability, fast responses, good sensitivity and high selectivity. However, the electrode should be modified with electrocatalyst or electron mediator to detect the 4-NP as most of the conventional electrode shows sluggish electrocatlytic properties for electrochemical redox reaction of the 4-NP. Several modified electrodes showed improved electrocatalytic properties toward 4-NP such as salicylaldehyde-functionalized chitosan-modified carbon black paste electrode [15], crown ether/silver nanoparticle (NP)-modified carbon paste electrode [16], apatite-modified carbon paste electrode [17], β-cyclodextrin functionalized mesoporous silica-modified carbon paste electrode [18], graphene-Au composite-modified glassy carbon electrode (GCE) [19], graphene oxide modified-GCE [20], poly(safranine) modified-GCE [21], ZnO NP- and carbon nanotubes doped chitosan film-modified indium tin oxide electrode [22], hybrid inorganic-organic coatings-modified platinum electrodes [23], screen printed electrodes bulk-modified with bismuth precursors [24], and β-cyclodextrin functionalized graphene/Ag nanocomposite-modified GCE [25]. However, all of these modified electrodes are cost ineffective as their preparations require expensive chemicals including substrate electrodes, and multi steps. Besides, the bare graphite pencil electrode (GPE) is inexpensive, available with a stable renewable surface. It shows poorly electrocatalytic properties toward many electroactive molecules [26–30]. Thus, to fabricate sensitively electrochemical sensors, the modification of the GPE with an inexpensive electrocatalyst in a fast single step method is required to obtain a high electrocatalytic

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[a] A.-N. Kawde,# M. A. Aziz
Chemistry Department, King Fahd University of Petroleum and Minerals
Dhahran, 31261, Kingdom of Saudi Arabia
tel: +966138602145; fax: +966138604277
*e-mail: akawde@kfupm.edu.sa

[b] A.-N. Kawde#
Chemistry Department, Faculty of Science,
Assiut University
Assiut 71516, Egypt

[c] M. A. Aziz
Center of Research Excellence in
Nanotechnology, King Fahd University of
Petroleum and Minerals
Dhahran 31261, Saudi Arabia

[#] Both authors contributed equally to this work property. Nanostructure forms of gold, silver and copper (Cu) have been applied as electrocatalysts for their good electrocatalytic properties [31–33]. Among those, Cu is the most inexpensive electrocatalyst. On the other hand, an electrochemical method is a single step, fast, and simple method to deposit Cu with various size, shape and porosity on electrode surfaces [33,34]. Therefore, electrochemical preparation of porous Cu on the pencil electrode is quite meaningful in electroanalysis.

As a continuation of our effort [35] to overcome the phenol fouling of the carbon electrode surfaces, here, we explore the application of the Cu-modified GPE (Cu-GPE) as an efficient transducer for the detection of 4-NP. For obtaining the optimum conditions of the electroanalysis of 4-NP, the effect of Cu(II) ions concentration, deposition potential and time on the preparation of Cu-GPE were investigated. Moreover, the morphology and electrochemical properties of Cu-GPE toward 4-NP were characterized in details.

2 Experimental

2.1 Reagents

Copper sulfate ($CuSO_4$) anhydrous was purchased from BDH Chemicals Ltd (Poole, England). 4-Nitophenol (4-NP), 4-aminophenol, 3,4-dichlorophenol, phenol and sodium acetate buffer (3.0 M, pH 5.2) were supplied by Sigma-Aldrich (St. Louis, MO, USA). The 0.1 M sodium acetate buffer (pH 4.8) was prepared by diluting the 3.0 M acetate buffer. Hi-polymer graphite pencil HB black leads were obtained from Pentel Co. LTD. (Japan). All leads had a total length of 60 mm and a diameter of 0.5 mm, and were used as received. All solutions were prepared with deionized water of resistivity of 18.6 $M\Omega\,cm^{-1}$, which was obtained directly from PURELAB Ultra Laboratory Water Purification System, Veolia Water Technologies (UK).

2.2 Apparatus and Procedures

A Jedo mechanical pencil (Korea) was used as a holder for both bare and Cu-modified graphite pencil leads. Electrical contact with the lead was achieved by soldering copper wire to the metallic part that holds the lead in place inside the pencil. The pencil was fixed vertically with 15 mm of the pencil lead extruded outside, and 10 mm of the lead immersed in the solution. Such length corresponds to a geometric electrode area of 15.90 mm^2. Details of the pencil electrode were described earlier [36]. CHI 660C (CH Instruments, Inc., 3700 Tennison Hill Drive, Austin, TX 78738-5012, USA) was used for the entire electrochemical work. The electrochemical cell contained a bare- or Cu-modified GPE as a working electrode, a Pt wire counter electrode and an Ag/AgCl (Sat. KCl) reference electrode. All electrodeposition works from electroplating solution, and electrooxidation of 4-NP in acetate buffer were carried out without argon purging. Besides, all the experiments related to electrochemical reduction of 4-NP in acetate buffer were performed after purging argon for 30 min. The FE-SEM images were recorded using TESCAN LYRA3 (Libušinatř. 1, 62300 Brno-Kohoutovice, Czech Republic) at Center of Research Excellence in Nanotechnology, King Fahd University of Petroleum and Minerals, Kingdom of Saudi Arabia.

2.3 Preparation of Cu-Modified GPE

10 mm of the extruded bare GPE from pencil, an Ag/AgCl reference and a Pt counter electrodes were immersed into a cell contains different concentrations of $CuSO_4$ in acetate buffer solution (0.1 M, pH 4.8) without Argon purging. Different potentials for different times were applied to deposit copper on the GPE surface. Next, gentle dipping twice into deionized water washed the prepared Cu-modified electrodes. The entire electrochemical measurements were performed right after the preparation of the modified electrodes.

3 Results and Discussion

3.1 Electrochemical Characterization of Bare- and Cu-Modified GPEs

4-NP (Inset of Figure 1B) has a nitro ($-NO_2$) group at the opposite position of a hydroxyl (–OH) group on the benzene ring. As a result, there are two electrochemical possibilities to detect 4-NP by measuring either the oxidation of the –OH group or the reduction of the $-NO_2$ group at the GPE surfaces. Initially, we tried to detect the 4-NP by oxidizing the –OH group using bare- (Figure 1A) and Cu-modified GPEs (data not shown). Figure 1A shows the cyclic voltammograms (CVs) in the absence (a) and presence (b) of 1 mM 4-NP in acetate buffer solution (0.1 M, pH 4.8) at bare-GPE. As shown in Figure 1A, it is clear that 4-NP can be oxidized at the bare-GPE, yet at a potential of +1.07 V, which is high enough to oxidize potential interferents as well. Besides, the oxidation signal of the phenolic group decreases significantly from first to second cycle and then slowly with consecutive cycles until no oxidation signals appear in the 12th cycle of the conducted CV experiment (Figure 1A and its inset). The decrease in the obtained signal is attributed to the deposition of oxidative products (dimer or polymer) at the carbon electrode surfaces which hinders any further oxidation of 4-NP [37]. Such behavior is quite similar to the oxidation of phenols at various electrode surfaces [35,38,39]. Also, due to a huge oxidation current of Cu, no good oxidation signals of 4-NP was obtained at the Cu-GPEs surfaces (data not shown).

Next, we examined the reduction of 4-NP at bare- (Figure 1B) and Cu-modified GPE (Figure 1C). Figure 1B shows the cyclic voltammograms (CVs) of the bare GPE in absence (a) and presence (b) of 1.0 mM 4-NP in an acetate buffer solution (0.1 M, pH 4.8). The CV data are

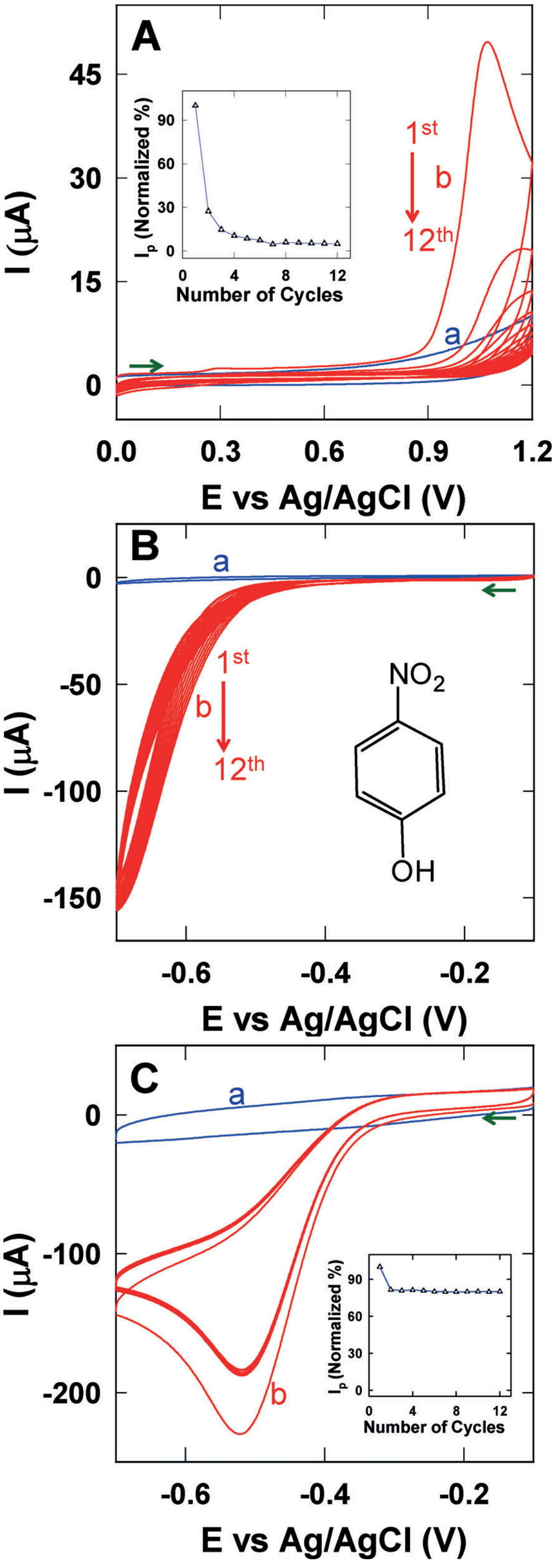

Fig. 1. CVs in an acetate buffer solution (0.1 M, pH 4.8) in absence (a) and presence (b) of 1 mM 4-NP obtained at the bare- (A and B) and Cu-modified GPEs prepared by 60 s electrodeposition of 0.1 M $CuSO_4$ at −1.0 V (C). Insets of A and C are the corresponding plots of normalized peak current % of 4-NP related to 1st cycle vs. number of cycles at bare- (A) and Cu-modified GPE (C). Scan rate: 100 mV/s.

shown in Figure 1B, curves a and b confirmed that 4-NP is reduced at the bare GPE, yet at a relatively high negative potential and with no well-defined peaks obtained within the entire potential window. For an ideal 4-NP sensor, the obtained reduction potential should be shifted towards more anodic potential values. With a contrast to the oxidation current, the reduction current of 4-NP did not change significantly with increasing the number of cycles (from 2nd to 12th cycles) during the entire CV experiment. To reduce the 4-NP at a lower potential with a stable electrochemical signal, the GPE was modified with Cu from a solution of 0.1 M $CuSO_4$ in 0.1 M acetate buffer solution (0.1 M; pH 4.8) by electrodeposition at −1.0 V for 60 s. The CVs were recorded in acetate buffer solution (0.1 M, pH 4.8) in the absence (Figure 1C, curve a) and presence (Figure 1C, curve b) of 1 mM 4-NP at Cu-GPE. The CVs shown in Figure 1C (curves a and b) confirmed that 4-NP is reduced at the Cu-GPE surface with a peak potential of −0.52 V, which is more anodic than that obtained on bare GPE surfaces. Besides the obtained electroreduction current of 4-NP at Cu-GPE (Figure 1C, curve b) is significantly higher than that of bare GPE (Figure 1B, curve b). The reduction of 4-NP at the Cu-GPE could be attributed to the excellent electrocatalytic properties of Cu. According to literature [40,41], the reduction mechanism of 4-NP occurring at the Cu-modified electrodes is most probably as follow.

$$HO-C_6H_4-NO_2 \xrightarrow{4e^-} HO-C_6H_4NHOH \xrightarrow{2e^-} HO-C_6H_4NH_2$$

The Cu-GPE showed a significant overvoltage decrease on the reduction of 4-NP compared to that of bare GPE. Therefore, electrodeposited Cu is suitable as a mediator to shuttle electrons between 4-NP and GPE, and facilitates the electrochemical generation following the electron exchange with 4-NP. The inset of Figure 1C is the plot of normalized reduction peak height of 1 mM 4-NP at the Cu-modified GPE vs. number of cycles in the conducted CV experiment. This plot gives a hint on the stability of the fabricated sensor, and confirms that the reduction current is decreased a little from the 1st to the 2nd cycles and remains constant from the 2nd to the 12th cycles i.e. the Cu-modified GPE is quite stable to reduce 4-NP.

3.2 Parameters Optimization for Preparation of Cu-Modified GPE

To obtain best conditions for 4-NP reduction, we optimized the fabrication conditions of the CuGPE. Firstly, we varied the concentration of $CuSO_4$ from 0.1 M to 0.5 M at constant applied potential (−1.0 V) and time (60 s). The CVs of the modified electrode in acetate buffer (0.1 M, pH 4.8) containing 1 mM 4-NP shows the reduction peak height increases with increasing the concentration of $CuSO_4$ up to 0.3 M (Figure 2A). Further increases in the concentration of $CuSO_4$ (Figure 2A) decreases the reduction peak height of 4-NP i.e. 0.3 M is the optimum concentration for $CuSO_4$ to prepare CuGPE.

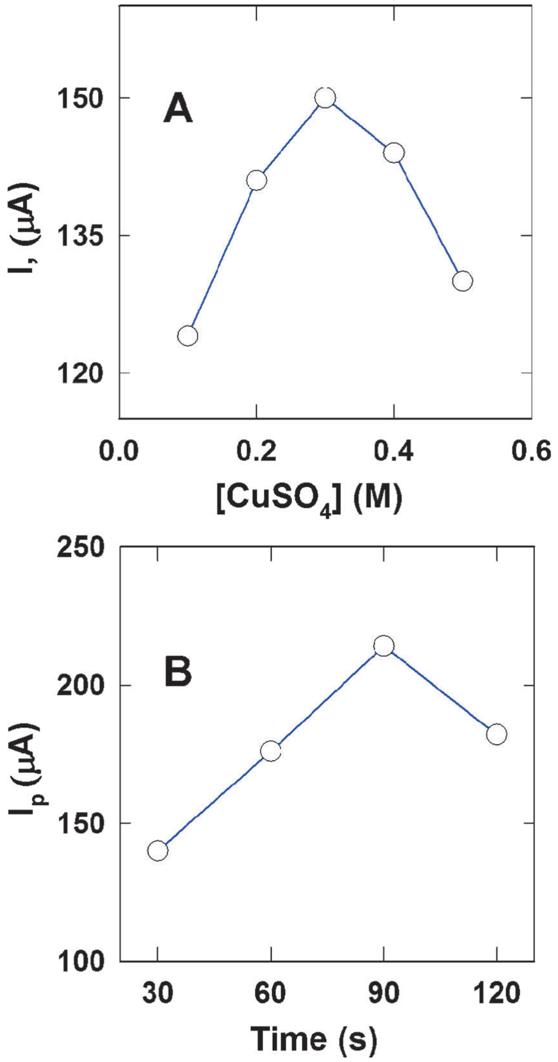

Fig. 2. Corresponding plots of 1 mM 4-NP in acetate buffer solution (0.1 M, pH 4.8) using CV cathodic peak current for various Cu-modified-GPE fabricated of different concentrations of $CuSO_4$ at −1.0 V for 60 s (A), and of different copper electrodeposition times at −1.2 V for 0.3 M $CuSO_4$ solution (B).

Such decrease could be attributed to the expected increase on the size of the deposited Cu particles on the GPE surface. Secondly, we varied the electrodeposition potential from −0.8 V to −2.0 V at a constant concentration $CuSO_4$ (0.3 M) and electrodeposition time (60 s). The reason of using −0.8 V for the electrodeposition of 4-NP is to assure a complete reduction of Cu^{2+} to Cu^0 as the CV data of Cu^{2+} in acetate buffer (0.1 M, pH 4.8) shows the reduction of Cu^{2+} to Cu^{1+} at −0.28 V, and the reduction of generated Cu^{1+} to Cu^0 at −0.55 V (data not shown). The plot of reduction peak height vs. electrodeposition potential of Cu (data not shown) indicates the peak height of the 4-NP reduction increases with increasing of the electrodeposition potential during the preparation of the Cu-GPE. However, the Cu-GPEs prepared at more cathodic potentials than −1.2 V were relatively unstable. As a result, −1.2 V was chosen for further experiment to prepare the Cu-GPE. Lastly, we varied the Cu deposition time from 30 to 120 s at a constant electrodeposition potential (−1.2 V) and concentration of 0.3 M $CuSO_4$ solution. The plot (Figure 2 B) of the reduction peak height of 4NP vs. electrodeposition time shows that the reduction peak height increases with the increase of the electrodeposition time until 90 s and decreases with all further increases in the deposition time. However, 60 s deposition time was selected as an optimum electrodeposition time due to the instability of the fabricated Cu-GPEs at 90 s. Hence, it is concluded that the optimum concentration of $CuSO_4$, electrodeposition potential and time are 0.3 M, −1.2 V and 60 s, respectively to prepare the Cu-GPE.

3.3 Morphology of the Cu-Modified GPE

The Cu-modified GPE, prepared at optimum conditions, was subjected to record FE-SEM images. The lower and upper parts of the image (Figure 3 A) present the bare- and Cu-modified GPE, respectively for the same graphite lead. This image indicates that Cu was deposited on GPE at optimum conditions. Figure 3 B and C are the magnified view of the upper part and lower part of Figure 3 A

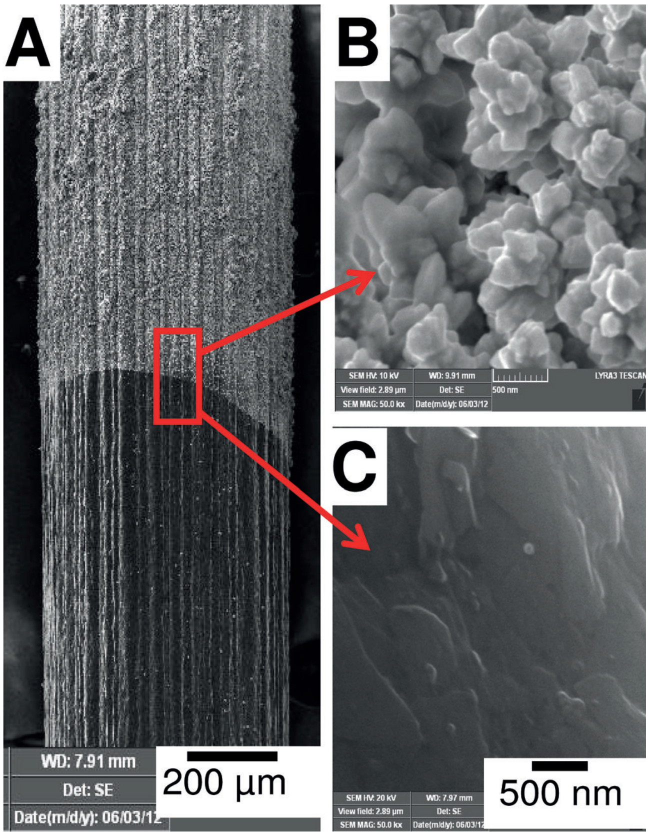

Fig. 3. (A) FE-SEM images of copper-modified- (upper part) and bare-GPE (lower part). Cu-modified GPE was prepared by electrodeposition for 60 s from 0.3 M $CuSO_4$ at −1.2 V. (B) and (C) are the magnified view of the copper-modified- and bare-GPE, respectively.

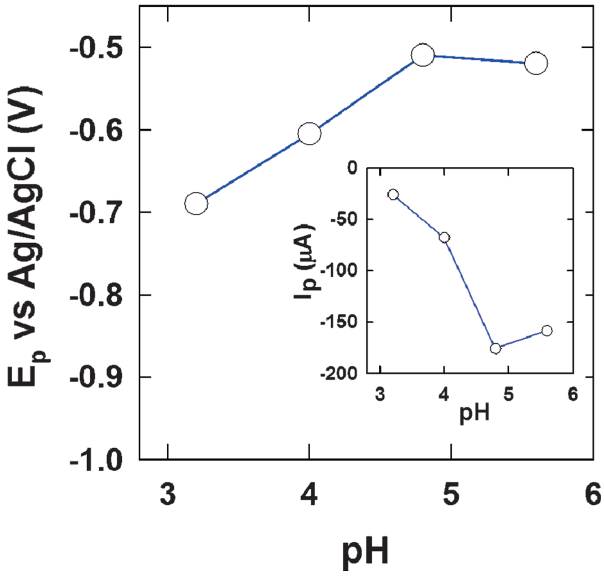

Fig. 4. Corresponding plots of 1 mM 4-NP in 0.1 M acetate buffer solution of different pH using CV cathodic peak potential or peak current (Inset) for Cu-modified-GPE fabricated of 0.3 M $CuSO_4$ at −1.2 V for 60 s.

i.e. Cu-modified GPE, and bare GPE, respectively. By comparing Figure 3B and C, it is clear that Cu was deposited on pencil at optimum deposition conditions as random submicroparticles (white) with high porosity. This Cu-modified GPE, which was prepared at optimum condition, is denoted as pCu-GPE in rest parts of the manuscript.

3.4 Effect of pH Toward Reduction of 4-NP at Bare-, and pCu-GPE

The reduction process of the selected nitrophenol was evaluated at different pH values of the acetate buffer solution at both bare and modified graphite surfaces by recording the CV of 1 mM 4-NP (data are not shown). Only at the modified graphite electrode surface, a relatively well-defined peak for the reduction of 4-NP is obtained. Figure 4 shows the reduction behavior of 4-NP at pCu-GPE in acetate buffer solution with pH values 3.2, 4.0, 4.8 and 5.6 in term of both potential and current. Thus pH of 4.8 was selected to carry on the present study. Meanwhile no defined peaks were obtained for the reduction of 4-NP at the bare graphite electrode surface at any of the various studied pHs.

3.5 Amperometric Determination of 4-NP

The 4-NP concentration-dependent signal and detection limits at the bare- and the pCu-GPE were measured using the amperometric method. Figure 5 shows typically amperometric responses of (a) bare GPE and (b) pCu-GPE and at −0.5 V upon successive additions of 50 µM 4-NP. The pCu-GPE (Figure 5b) yielded a well-defined and sensitive signal for each addition of 4-NP, whereas the bare GPE gave a relatively poor signal (Figure 5a). The concentration-dependent signal was linear over the entire 4-NP concentration range tested at the pCu-GPE (R^2=0.9997) or the bare GPE (R^2=0.9985), after subtracting the mean of the corresponding zero 4-NP response. The corresponding linear regression equations of bare and pCu-GPE are i (µA)=0.3312−0.0011 C (µmol/L) and i (µA)=−1.9651−0.1969 C (µmol/L), respectively. The detection limits of 4-NP at the applied potential of −0.5 V for the pCu-GPE and bare GPE were 1.9 µM and 1.0 mM, respectively. The sensor described here is compared with a variety of other 4-NP sensors in Table 1, for a variety of electrochemical detection methods, sensing materials (transducers), sensing media, analytical ranges, square of the correlation coefficients, and detection limits. Table 1 shows that the performance of the sensor

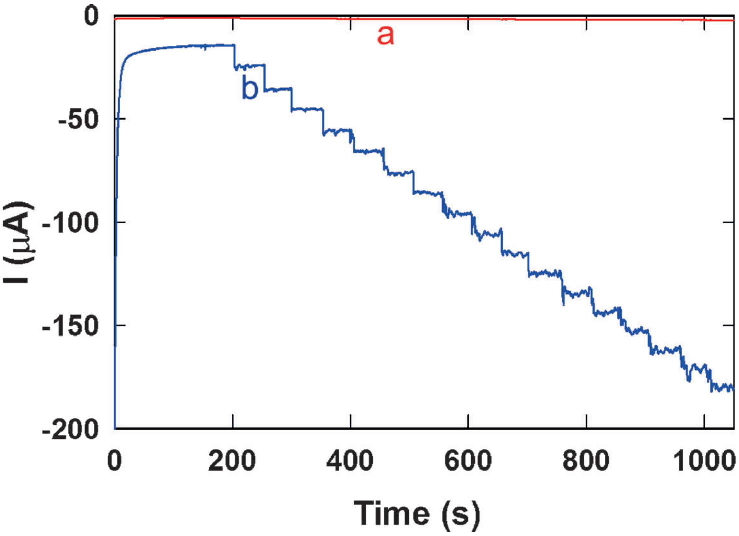

Fig. 5. Amperograms of (a) bare- and Cu-modified-GPE in 10 mL acetate buffer solution (0.1 M, pH 4.8) at −0.50 V of the successive additions of 50 µM of 4-NP.

Table 1. A comparison of the fabricated sensor with other reported modified electrode-based sensors for 4-NP detection.

Sensing method	Transducer	Sensing media	Analytical range (µM)	R^2	Detection limit (µM)	Ref.
Amperometry	pCu-GPE	0.1 M Acetate buffer (pH 4.8)	50–850	0.9997	1.91	This work
Amperometry	Graphene-Au composite on GPE	0.1 M H_2SO_4	0.47–10750	0.9943	0.47	[19]
Square wave voltammetry	Inorganic-organic coatings on Pt electrode	0.1 M PB (pH 6.0)	30–90	0.9954	8.23	[23]
Differential pulse voltammetry	Graphene-SPE	0.02 M H_2SO_4	10–620	0.9837	0.60	[37]
Semiderivative voltammetry	AuNP-GCE	0.1 M PB (pH 6.0)	10–1000	–	8.00	[42]

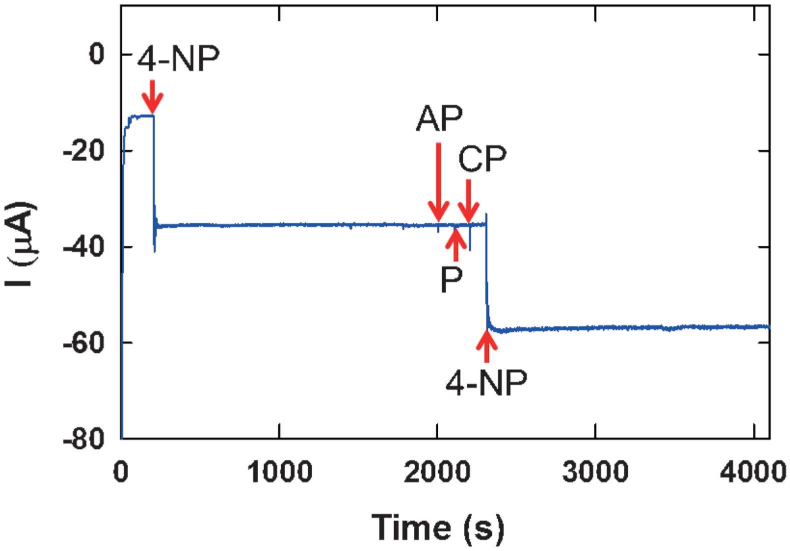

Fig. 6. Amperometric responses of Cu-modified-GPE to successive additions of 4-NP, 4-aminophenol, phenol, 3,4-dichlorophenol and 4-NP. Other preparation and working conditions were as described in Figures 3 and 5.

developed here was comparable to the performances of other existing 4-NP sensors.

3.6 Stability and Selectivity

Figure 6 presents the amperometric response to successive additions of 4-NP, 4-aminophenol (AP), phenol (P), 3,4-dichlorophenol (CP) and again 4-NP at −0.5 V for a given pCu-GPE surface. A well-defined 4-NP response was observed upon addition of 100 µM 4-NP. The response remained stable during a prolonged 30.0 min experiment. Afterward, subsequent injections of 50 µM of 4-AP, 50 µM of P and 50 µM of CP did not produce any additional signals or even alter the obtained current response. A further addition of 100 µM 4-NP produces a well-defined and reproducible response, that is still stable during a prolonged 30.0 min experiment. Such experiment reflects the good sensing sensitivity, selectivity and stability of 4-NP at the fabricated pCu-GPE.

4 Conclusions

We successfully fabricated a novel, extremely low-cost, disposable, and easily fabricated 4-NP sensor based on the electrodeposited porous Cu on GPE. The highly reproducible fabrication sensor exhibits a remarkable electrocatalytic activity towards 4-NP reduction at low detection limit, greater analytical selectivity, sensitivity, and stability. The performance of the novel pCu-GPE proved to be excellent, and found to be suitable for the analytical determination of various 4-NP concentrations.

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References

[1] M. J. Vaidya, S. M. Kulkarni, R. V. Chaudhari, *Organ. Proc. Res. Develop.* **2003**, *7*, 202.

[2] E. A. Hutton, B. Ogorevc, M. R. Smyth, *Electroanalysis* **2004**, *16*, 1616 and cited references therein.

[3] M. R. H. Poden, S. K. Bhattacharya, M. Qu, *Water Res.* **1995**, *29*, 391.

[4] Agency for Toxic Substances and Disease Registry (ATSDR), *Toxicological Profile for Nitrophenols* **1992**, 1.

[5] G. Schuurmann, R. K. Somashekar, U. Kristen, *Environ. Toxicol. Chem.* **1996**, *15*, 1702.

[6] US Environmental Protection Agency Fed. Regist. **1989**, *52*, 131.

[7] L. H. Keith, W. A. Telliard, *Environ. Sci. Technol.* **1979**, *13*, 416.

[8] US Environmental Protection Agency, *Ambient Water Quality Criteria for Nitrophenols*, **1980**, c-19.

[9] M. R. Haghighi-Podeh, S. K. Bhattacharya, *Wat. Sci. Tech.* **1996**, *34*, 345.

[10] G. Norwitz, N. Nataro, P. N. Keliher, *Anal. Chem.* **1986**, *58*, 639.

[11] W. Zhiheng, Z. Jihua, L. Jun, Z. Genxi, *Chin. J. Anal. Chem.* **1993**, *21*, 581.

[12] J. J. Scanlon, P. A. Falquer, G. W. Robinson, G. E. O'Brien, P. E. Sturrock, *Anal. Chim. Acta* **1984**, *158*, 169.

[13] R. Belloli, B. Barletta, E. Bolzacchini, S. Meinardi, M. Orlandi, B. Rindone, *J. Chromatogr. A* **1999**, *846*, 277.

[14] M. Manera, M. Miro, J. M. Estela, V. Cerda, M. A. Segundo, J. L. F. C. Lima, **2007**, *600*, 155.

[15] P. Deng, Z. Xu, Y. Feng, J. Li, *Sens. Actuators B* **2012**, *168*, 381and cited references therein.

[16] G. Rounaghi, R. M. Kakhki, H. Azizi-Toupkanloo, *Mater. Sci. Eng. C* **2012**, *32*, 172.

[17] M. A. E. Mhammedi, M. Achak, M. Bakasse, A. Chtaini, *J. Hazardous Mater.* **2009**, *163*, 323.

[18] X. Xu, Z. Liu, X. Zhang, S. Duan, S. Xu, C. Zhou, *Electrochim. Acta* **2011**, *58*, 142.

[19] W. Zhang, J. Chang, J. Chen, F. Xu, F. Wang, K. Jiang, Z. Gao, *Res. Chem. Intermed.* **2012**, *38*, 2443.

[20] J. Li, D. Kuang, Y. Feng, F. Zhang, Z. Xu, M. Liu , *J. Hazardous Mater.* **2012**, *201–202,* 250.

[21] X.-Y. Liu, *Bull. Korean Chem. Soc.* **2010**, *31*, 1182.

[22] Y. Hu, Z. Zhang, H. Zhang, L. Luo, S. Yao, *Thin Solid Films* **2012**, *520*, 5314.

[23] S. Lupu, C. Lete, M. Marin, N. Totir, P. C. Balaure, *Electrochim. Acta* **2009**, *54*, 1932.

[24] N. Lezi, A. Economou, J. Barek, M. Prodromidis, *Electroanalysis* **2014**, *26*, 766.

[25] W. Liu, C. Li, Y. Gu, L. Tang, Z. Zhang, M. Yang, *Electroanalysis* **2013**, *25*, 2367.

[26] K. Asadpour-Zeynali, P. Najafi-Marandi, *Electroanalysis* **2011**, *23*, 2241.

[27] Y. Dilgin, B. Kızılkay, B. Ertek, F. Işık, D. G. Dilgin, *Sens. Actuators B, Chem.* **2012**, *171–172*, 223.

[28] T. Vural, F. Kuralay, C. Bayram, S. Abaci, E. B. Denkbas, *Appl. Surf. Sci.* **2010**, *257*, 622.

[29] M. A. Aziz, A. Kawde, *Microchim. Acta* **2013**, *180*, 837.

[30] M. A. Aziz, A. Kawde, *Talanta* **2013**, *115*, 214.

[31] M. A. Aziz, S. Patra, H. Yang, *Chem. Commun.* **2008**, 4607.

[32] G. Wang, W. Wang, J. Wu, H. Liu, S. Jiao, B. Fang, *Microchim. Acta* **2009**, *164,* 149.

[33] R. Qiu, H. G. Cha, H. B. Noh, Y. B. Shim, X. L. Zhang, R. Qiao, D. Zhang, Y. I. Kim, U. Pal, Y. S. Kang, *J. Phys. Chem. C* **2009**, *113*, 15891.

[34] H.-C. Shin, J. Dong, M. Liu, *Adv. Mater.* **2003**, *15*, 1610.

[35] A. Kawde, M. A. Morsy, N. Odewunmi, W. Mahfouza, *Electroanalysis* **2013**, *25*, 1547.

[36] J. Wang, A. Kawde, *Anal. Chim. Acta* **2001**, *431*, 219.

[37] A. Arvinte, M. Mahosenaho, M. Pinteala, A.-M. Sesay, V. Virtanen, *Microchim. Acta* **2011**, *174*, 337.

[38] N. B. Tahar, R. Abdelhedi, A. Savall, *J. Appl. Electrochem.* **2009**, *39*, 663.

[39] Y. Nakabayashi, M. Wakuda, H. Imai, *Anal. Sci.* **1998**, *14*, 1069.

[40] K. Polat, M. Aksu, A. Pekel , *J. Appl. Electrochem.* **2002**, *32*, 217.

[41] H. Udupa, M. Rao, *Electrochim. Acta* **1967**, *12*, 353.

[42] L. Chu, L. Han, X. Zhang, *J. Appl. Electrochem.* **2011**, *41*, 687.

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