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Electrocatalytic reduction and detection of 4-nitrophenol in water at free-standing Cu nanowire electrode

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ABSTRACT

This work reports a study on the electrocatalytic reduction and detection of 4-nitrophenol (4-NP) in water at a free-standing Cu nanowire (CuNW) electrode. The electrochemical impedance spectra measurement demonstrates that, compared with a CuNW-modified glassy carbon electrode (GCE), the free-standing CuNW electrode has a much lower electron transfer resistance, as well as a much higher electrochemical active surface area as suggested by the double layer capacitance ratio between two electrodes. A comparative study of the electroreduction of 4-NP at different Cu electrodes by cyclic voltammetry (CV) reveals that no reduction peak appears at a Cu wire electrode with low active surface area but fast charge transfer while a broad peak is observed at the CuNW-modified GCE with slow charge transfer but relatively high active surface area compared to the Cu wire electrode. Benefitting from the combination of fast electron transfer and high active surface area, however, the 4-NP reduction peak at the free-standing CuNW electrode is narrow and positively shifted with its current being more than 30 times higher than that at CuNW-modified GCE. These features allow an investigation of this free-standing electrode as a 4-NP sensor via a simple electrochemical technique (namely CV), revealing a much better performance than the reported porous Cu-modified graphite pencil electrode, namely a linear range of 4 to 2200 mM, a sensitivity of 4.831 mA×mM^{-1}, and a detection limit of 1.0 mM at a signal-to-noise ratio of 3.

Keywords: *Cu nanowires; Electrochemical sensor; Free-standing electrode; 4-Nitrophenol*

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1. INTRODUCTION

4-Nitrophenol (4-NP) is widely used as raw material or intermediate to produce pharmaceuticals, pesticides, and dyes. The extensive use of 4-NP, however, has resulted in an increasing discharge of 4-NP-bearing wastewater and aroused an environmental concern due to its high resistance to biological degradation and strong toxic effect on humans, animals, and plants[1-4]. 4-NP can, for example, irreversibly damage the liver and kidneys of humans and animals [4]. In view of its water-soluble nature and strong toxicity even at low concentrations, monitoring the concentration of 4-NP in water is of great importance.

The concentration of 4-NP can be determined by a number of analytical methods, such as spectroscopy [5], chromatography [6], fluorescence [7], and electrochemical techniques [8-10]. The electrochemical approach based on the reduction of 4-NP at the cathode has drawn great attention due its simplicity, low cost and quick response [8-17]. Since the performance of 4-NP electrochemical sensor depends on the cathode used, the choice of a suitable electrode material is of great importance. Noble metals, e.g. Au and Ag, are commonly used as the electrocatalysts for sensing 4-NP because of their excellent electrocatalytic activity for reduction of 4-NP [9-12], and various Au or Ag-based composites have recently been developed for detection of 4-NP, including Au-graphene [13], Au-reduced graphene oxide (RGO) [14], Ag-multilayer carbon nanotube (MCNT) [15], and Ag-RGO [16]. On the contrary, despite that Cu has been found to be a good catalyst for reduction of 4-NP in the presence of $NaBH_4$ [18], this non-noble metal was seldom used as the 4-NP electrochemical sensor in the past probably due to the fact that the performance of the reported Cu-based 4-NP sensors, e.g. porous Cu-modified graphite pencil electrode (GPE) [17], are generally not comparable to those of the commonly used Au and Ag based sensors.

In this article, we report a study on the electrocatalytic reduction and detection of 4-NP in water at a free-standing Cu nanowire (CuNW) electrode, with a CuNW-modified glassy carbon electrode (GCE) being investigated for comparison. Interest in this work is based on the following considerations. (i) Since the free-standing CuNW electrode, fabricated by thermal annealing of CuNWs, owns a high active surface area [19] and thus has the advantage over the modified electrodes which often have a low active surface area. As a result, despite the fact that the noble metals Au and Ag are generally more active than Cu in the electroreduction of 4-NP, the free-standing CuNW electrode might exhibit a performance that can be comparable to those of Au and Ag based sensors because these Au and Ag based sensors are normally based on the modified electrode structure. (ii) Different from the modified electrodes with electrocatalysts decorated on a conductive substrate, in the free-standing CuNW electrode CuNWs serve as both conductive substrate and electrocatalyst. A fast charge transfer is therefore assumed at the free-standing electrode due to the absence of both the substrate-electrocatalyst interface and the polymer binder, but no work provides evidence for this speculation. (iii) Although the free-standing electrode has above-mentioned advantages over the modified electrodes, how these advantages affects the electroreduction of 4-NP is unknown. Therefore, the present work focuses on the difference in electron transfer between free-standing CuNW electrode and CuNW-modified electrode, the effect of both electron transfer resistance and active surface area on the electroreduction of 4-NP at the electrodes, and the performance of the free-standing CuNW electrode as a 4-NP sensor.

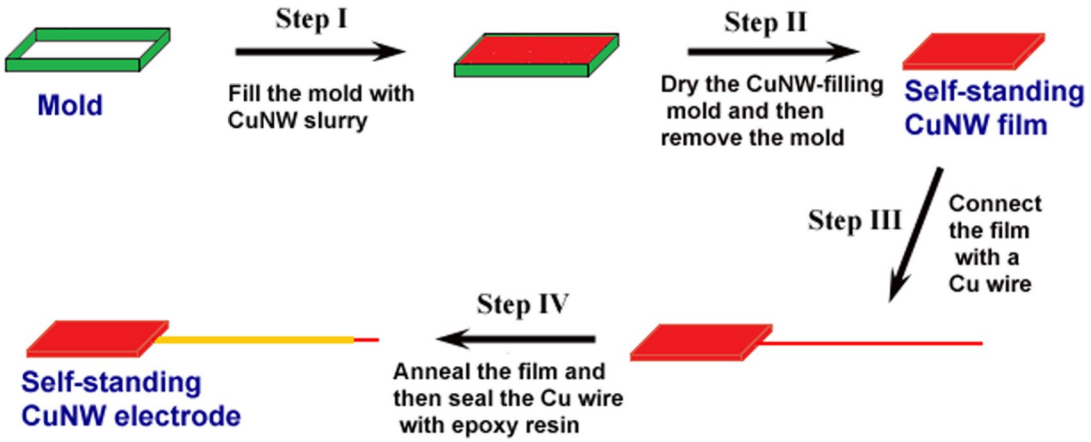

Fig. 1. Schematic illustration for preparation of free-standing CuNW electrode.

2. EXPERIMENTAL

All chemicals were of analytical grade and used as received without further purification. Double-distilled water was used for preparing all solutions. CuNWs used in the experiments were synthesized via a cheap and environmentally friendly method developed by our group [21].

To prepare the free-standing CuNW electrode (see Fig. 1), a mould used for controlling the size of the electrode was first filled with CuNW slurry obtained by dispersing CuNW into ethanol. After dried in N_2 atmosphere at 70ºC, the obtained CuNW film was connected with a Cu wire and then annealed under Ar atmosphere at 600ºC for 30 min. Finally, the Cu wire was sealed with epoxy resin to obtain a free-standing CuNW electrode with a size of about 0.5′0.6′0.05 cm^3. For comparison, a CuNW-modified glassy carbon electrode (GCE) was also prepared according to the following procedure. A bare GCE with a diameter of 3 mm was polished with 1mm and 0.05mm alumina slurries, and then successively sonicated in acetone, ethanol, and deionised water followed by drying at room temperature. 15 mg of CuNWs was dispersed into 1 mL of water, and then 90 mL of chitosan solution (1 wt.%, pH=5) was added into the dispersion and ultrasonicated. Finally, 20 mL of the resulting dispersion was drop-cast onto the GCE and air-dried at room temperature.

The surface morphology of the samples was examined by scanning electron microscope (SEM, Hitachi S-4700) operating at 15 kV. Electrochemical measurements were performed at room temperature with a CHI660E workstation (CHI Instruments). The setup was a conventional three-electrode cell with a platinum wire as counter electrode and a saturated calomel electrode (SCE) as reference electrode. Unless otherwise stated, all measurements were conducted in 0.15 M acetate buffer solution with a pH value of 5. Before measurement, N_2 purging was performed to remove the oxygen from the electrolyte solution.

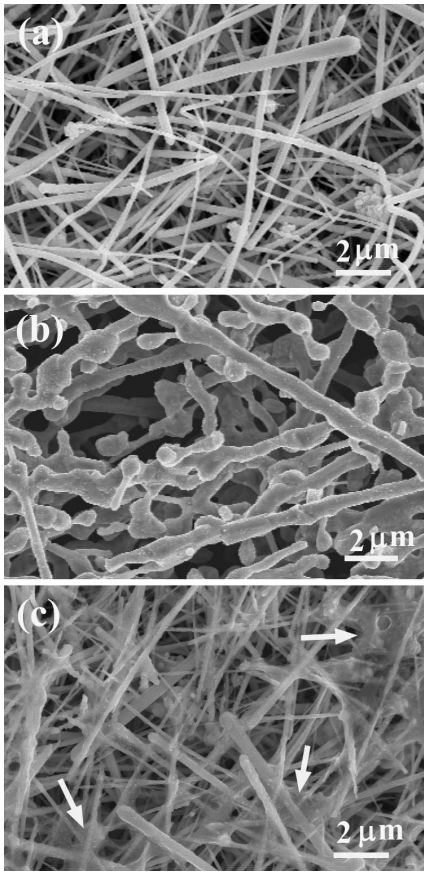

Fig. 2. SEM images of (a) CuNW film before annealing, (b) CuNW film after annealing, and (c) the binder-containing CuNW film in CuNW-modified GCE with binder materials being indicated by arrows

3. RESULTS AND DISCUSSION

3.1. Characterization of CuNW-based electrodes

Our previous study has revealed that the annealing of CuNW film at 600°C can achieve a free-standing CuNW electrode of good physical stability [19]. Although a modification on the preparation of CuNW film is made in this work, the morphologies of the unannealed film (Fig. 2a) and annealed film (namely free-standing CuNW electrode, Fig. 2b) are similar to those obtained in our previous work [19]. It is obvious that the free-standing CuNW electrode owns a porous network structure resulting from the melting of CuNWs, as is evident from the change in nanowire size and shape after annealing. Benefitting from its porous network structure, the as-formed CuNW electrode can offer an electrochemical active surface area 200 times higher than that of a Cu wire electrode with a similar geometrical surface area [19]. In the case of CuNW-modified GCE, however, despite no change in nanowire size and shape, the polymer binder can be observed on the surface of some CuNWs (Fig. 2c). Undoubtedly, the use of polymer binder in preparation of CuNW-modified GCE will not only block the catalytic active

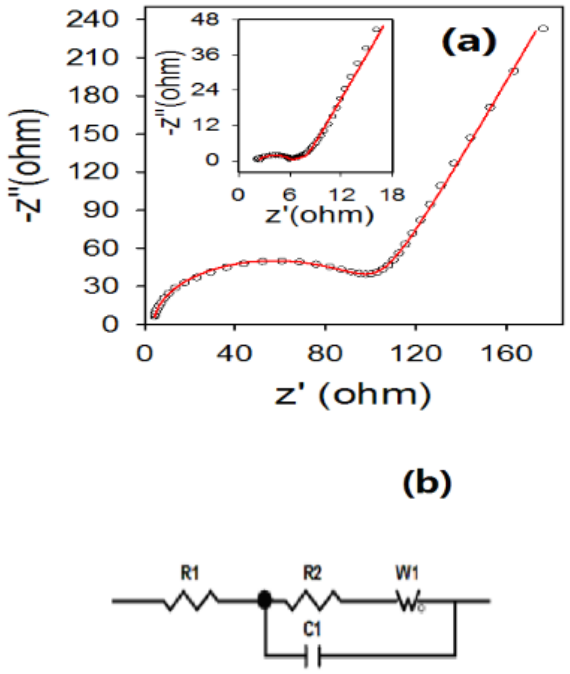

Fig. 3. (a) Electrochemical impedance spectra (open circles) of CuNW-modified GCE recorded in 0.1 M KCl solution containing 0.01 mM [Fe(CN)6]3-/4-. Inset is the impedance spectra of free-standing CuNW electrode. The red curves were the fitting curves based on the Randles equivalent circuit (b).

sites but also increase the electron transfer resistance.

To compare the electron transfer resistance between free-standing CuNW electrode and CuNW-modified GCE, the electrochemical impedance spectra (EIS) of two electrodes were recorded. In EIS, a linear portion at low frequencies is associated with a diffusion limited electrochemical process and a semicircle portion at high frequencies is related to an electron transfer limited process with the semicircle diameter being equal to the electron transfer resistance. Fig. 3(a) presents the impedance spectra obtained in the form of Nyquist plots, which were fitted based on the Randles equivalent circuit as shown in Fig. 3(b). This equivalent circuit consists of the ohmic resistance of the electrolyte solution (R1), the charge transfer resistance (R2), the Warburg impedance (W1) and the double layer capacitance (Cl). The obtained value of R2 for the free-standing CuNW electrode is about 3.5 W whereas R2 is about 90.7 W for the CuNW-modified GCE, indicating that the electron transfer at the free-standing CuNW electrode is much faster than that at CuNW-modified GCE. The very low electron transfer resistance observed in free-standing CuNW electrode can be attributed to the fact that CuNWs serve as both conductive substrate and electrocatalyst and thus can overcome the drawbacks resulting from the use of polymer binder and the presence of substrate-electrocatalyst interface. In addition, the double layer capacitance ratio between free-standing CuNW electrode and CuNW-modified GCE obtained by this fitting is about 24.3. This implies that the electrochemical active surface area of the free-standing CuNW electrode should be much higher than that of the CuNW-modified GCE.

3.2. Electrocatalytic reduction of 4-NP at different Cu electrodes

To clarify the effect of both charge transfer and active surface area on the reduction of 4-NP, three types of Cu electrodes, namely polished Cu wire electrode with fast charge transfer but low active surface area,

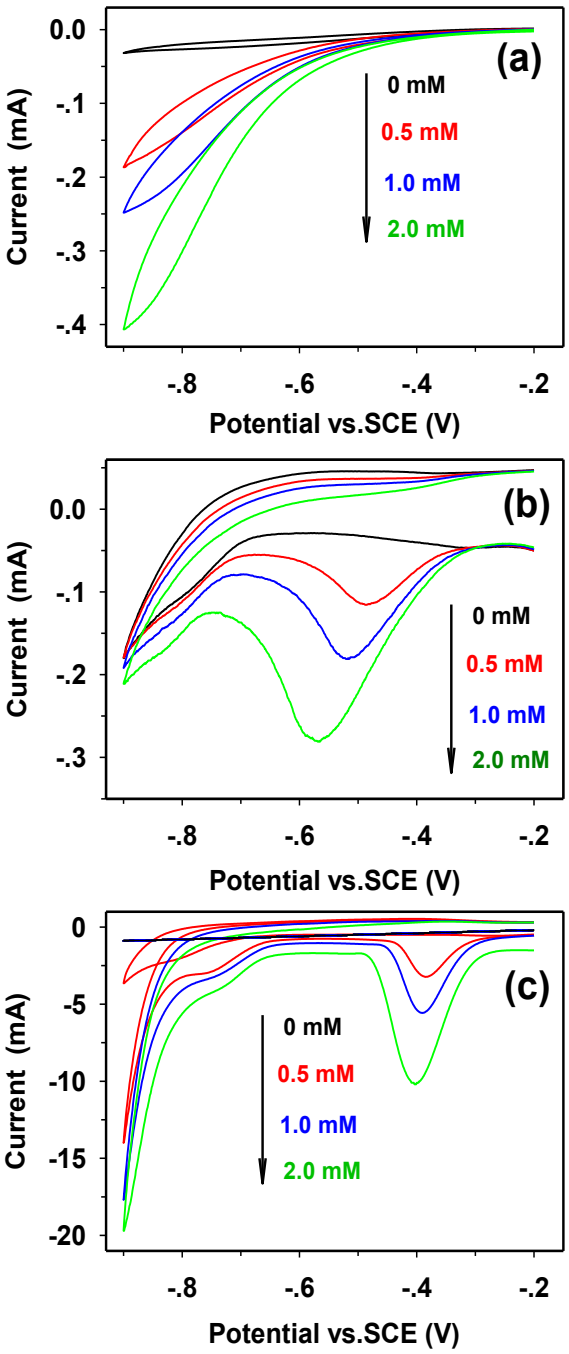

Fig. 4. CV curves recorded at different electrodes in an acetate buffer solution in the absence or presence of 4-NP (pH=5): (a) Cu wire electrode of 1.5 mm in diameter and 1.0 cm in length, (b) CuNW-modified GCE, and (c) free-standing CuNW electrode. The scan rate is 50 mV s−1.

CuNW-modified electrode with slow charge transfer but relatively high active surface area compared to the Cu wire electrode, and free-standing CuNW electrode with fast charge transfer and high active surface area, were studied by cyclic voltammetry (CV). At the Cu wire electrode, no well-defined peak associated with the reduction of 4-NP appears in the potential window of -0.2 to -0.8V (vs. SCE), irrespective of the concentration of 4-NP used (Fig. 4a). At the CuNW-modified GCE (Fig. 4b), however, we can observe a well-defined peak with its peak current being increasing with increasing the 4-NP concentration,

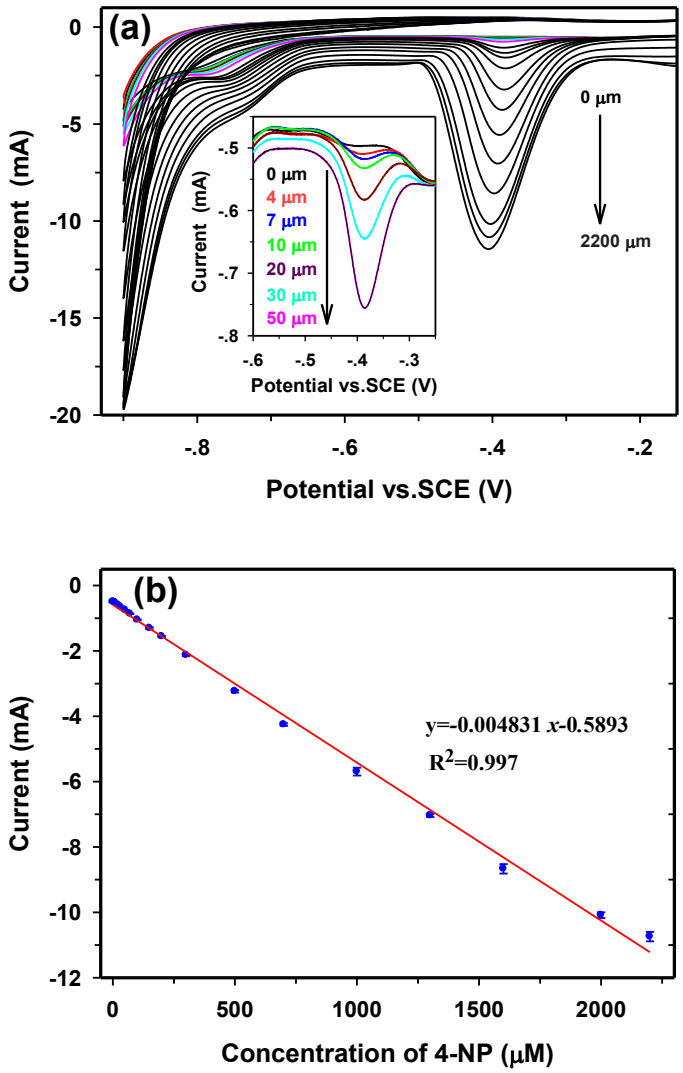

Fig. 5. (a) CV curves recorded at free-standing CuNW electrode with a scan rate of 50 mV s−1 in an acetate buffer solution containing different concentrations of 4-NP (pH=5) with the inset being an enlarged version at low 4-NP concentration and (b) plot of peak current against 4-NP concentration with the straight line being its linear fitting. The error bars indicate the standard deviation of triplicate determinations for each concentration of analyte.

indicating that this peak is related to the reduction of 4-NP. These observations hint that although the electron transfer is fast at the Cu wire electrode, its low active surface area leads to a very low 4-NP consumption rate and is thus responsible for the lack of reduction peak in the CV scan. As shown in Fig. 4c, a well-shaped peak associated with the reduction of 4-NP can be also observed at the free-standing CuNW electrode. However, a close examination of the reduction peaks observed at two types of CuNW electrodes reveals several significant differences. (i) The reduction peaks at the CuNW-modified GCE, especially in the case of high 4-NP concentrations, are broad and asymmetrical, which is similar to that observed at a porous Cu-modified GPE. [17] By comparison, the reduction peaks at the free-standing CuNW electrode look more narrow and symmetrical, regardless of whether the concentration of 4-NP is high or low. (ii) In comparison with that at the CuNW-modified GCE, the peak potential at the free-standing CuNW electrode is positively shifted, hinting that the reduction of 4-NP at this electrode is easier. (iii) For a given 4-NP concentration, the peak current at the free-standing CuNW electrode is more than 30 times higher than that at the CuNW-modified GCE. The differences observed should be related to the fact that compared with the CuNW-modified GCE, the free-standing CuNW electrode not only has a much lower electron transfer resistance but also possesses a higher active surface area originating from its porous network structure. These observations also suggest that the free-standing CuNW electrode owns a much higher catalytic activity for electroreduction of 4-NP in comparison with the CuNW-modified GCE.

Besides the reduction peak in the potential window of -0.2 to -0.6V, which is commonly attributed to the reduction of $–NO_2$ to -NHOH, a shoulder peak in the potential range of -0.6 to -0.8V can be also observed at the free-standing CuNW electrode. This peak should be related to the reduction of -NHOH to $–NH_2$. However, no oxidation peak is visible in the reverse scan, implying that the reduction of 4-NP at the free-standing CuNW electrode is an irreversible process.

To understand the detailed reduction mechanism observed in the potential window of -0.2 to -0.6V, the number of electrons transferred in the rate-determining step (n_α) is evaluated. The value of n_α is obtained by Eq. (1)

$$\alpha \cdot n_\alpha = 47.7/(E_P - E_{P/2}) \quad (1)$$

where a, E_p and $E_{p/2}$ are, respectively, the charge transfer coefficient, *peak potential* and half-height *potential* [22]. Since the charge transfer coefficient a is generally assumed to be 0.5 in a totally irreversible electrode process [22], n_α is calculated to be about 2 by using E_p = 390 mV and $E_{p/2}$ = 341 mV in the case of 1mM 4-NP present in the solution. The result suggests that the rate-determining step is a two-electron step, and thus the possible reduction mechanism in the potential window of -0.2 to -0.6V at free-standing CuNW electrode is proposed as follows.

$$R\text{-}NO + 2e + 2H^+ \rightarrow R\text{-}NHOH \text{ (fast)}$$
$$R\text{-}NO_2 + 2e + 2H^+ \rightarrow R\text{-}NH + H_2O \text{ (slow, rate-determining step)}$$

3.3. Electrochemical detection of 4-NP

Based on the above results, the performance of the free-standing CuNW electrode as a 4-NP sensor was also examined by a simple electrochemical technique (namely CV) and the reduction peak associated with the reduction of $–NO_2$ to -NHOH was chosen as the indicator for detection of 4-NP (Fig. 5a). It is obvious that this sensor can response well to 4-NP, either at low concentrations (e.g. several mM) or high concentrations (e.g. above 1 mM). The peak current is linearly related to 4-NP concentration in the range of 4 to 2200 μM with a regression equation of $I(mA) = 4.831' 10^{-3} C(\mu M) - 0.5893$ and a correlation coefficient R^2 of 0.997 (Fig. 5b). A sensitivity of 4.831 $mA \times mM^{-1}$ is obtained from the slope of the linear regression line. The limit of detection (LOD) of this sensor is obtained by LOD =3s/s, where s and s are, respectively, the standard deviation of the blank signal and the sensitivity of the sensor. The value of LOD is calculated to be about 1.0 mM. The linear range, sensitivity and LOD of our sensor were compared with the Cu-based sensors and some Ag or Au-based sensors reported in the literature (Table 1). It is clear that our sensor not only possesses a lower detection limit but also has a much broader linear range and higher sensitivity than the Cu-based sensor reported by Kawde *et al* [17]. Moreover, in comparison with most of Ag or Au-based sensors, our Cu-based sensor also owns its advantages: a higher sensitivity and a broader linear range up to 2200 μM, with its detection limit being comparable to some Ag or Au-based sensors, e.g. Au/GCE [10], Ag-MCNT/GCE [15], Au amalgam/Au disc [9], Ag amalgam electrode [8], and Au-graphene/GCE [13].

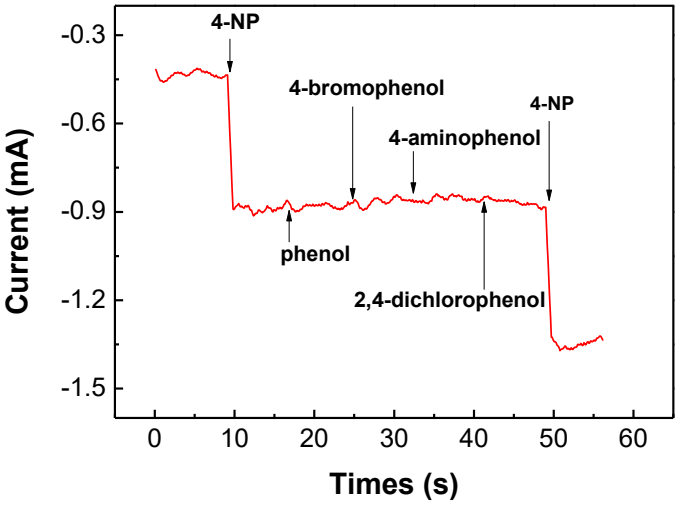

Fig. 6. Amperometric responses of free-standing CuNW electrode to successive additions of 4-NP (0.8 mM), phenol (8 mM), 4-bromophenol (8 mM), 4-aminophenol (8 mM), 2,4-dichlorophenol (8 mM) and 4-NP(0.8 mM) in an acetate buffer solution (pH=5). The applied potential was -0.4 V.

To understand the anti-interference ability of our new Cu-based 4-NP sensor, the interference from several substances which were selected as the interfering materials in the detection of 4-NP at the Cu-modified GPE [17], namely phenol, 4-aminophenol, 4-bromophenol, and 2,4-dichlorophenol was investigated. The method of amperometry was used to study the response of the free-standing CuNW electrode to these chemicals, in which phenol, 4-aminophenol, 4-bromophenol, and 2,4-dichlorophenol at a level of 8 mM was successively injected before measuring the current response to 0.8 mM 4-NP. As illustrated in Fig. 6, it is clear that the amperometric response of our free-standing CuNW electrode to 0.8 mM 4-NP is not affected by the addition of 8 mM phenol, 4-aminophenol, 4-bromophenol, or 2,4-dichlorophenol, indicating a good anti-interference ability of our sensor.

The stability and inter-electrode reproducibility of our sensor were also studied. When the free-standing CuNW electrode was stored under N_2 atmosphere at room temperature for 20 days, the response to 1 mM 4-NP still retained 93.7% of its original value, implying that the electrode can be used in long-term routine applications. To test the inter-electrode reproducibility, three free-standing CuNW electrodes were prepared, and their response to the reduction of 0.5 mM 4-NP was investigated by CV. The peak current recorded at these independent electrodes shows a relative standard of 4.8%, indicating a good inter-electrode reproducibility.

The practical application of our new 4-NP sensor was tested by measuring the concentration of 4-NP in three samples. Sample 1 was the laboratory wastewater containing 4-NP in unknown quantity, whereas Sample 2 or Sample 3 was prepared by adding a given amount of 4-NP into tap water or river water (before adding4-NP, no 4-NP was detected in both tap water and river water). For comparison, the concentration of 4-NP was also measured by spectrometry (performed on a UV-vis 7600 spectrophotometer). Table 2 shows a comparison between the results measured by two methods, as well as the recovery obtained by our sensor. It is obvious that the 4-NP concentration in each sample obtained by our sensor is close to that by spectrometry, with the relative differences for three samples being 4.8%, 1.5%, and 1.4%, respectively. The recoveries measured for Sample 2 and Sample 3 by our sensor are about 101.3 and 102.3%, respectively. These results suggest that our sensor can be used for detection of 4-NP in water.

4. CONCLUSIONS

We have presented a study on the use of a free-standing CuNW electrode as the electrochemical sensor for detection of 4-NP. This new 4-NP sensor owns a porous network structure with CuNWs being serving as both conductive substrate and electrocatalyst, and thus both the polymer binder and the substrate-electrocatalyst interface are absent. EIS measurement reveals that the free-standing CuNW electrode has a much lower electron transfer resistance and a much higher active surface area in comparison with the CuNW-modified GCE. The fast electron transfer, along with high active surface area, make the free-standing CuNW electrode more catalytically active for electroreduction of 4-NP than the CuNW-modified GCE. An investigation of this free-standing electrode as the 4-NP sensor by a simple electrochemical technique, namely CV, demonstrates that this new Cu-based 4-NP sensor exhibits a much better performance than the reported porous Cu-modified GPE. In addition, compared with most of Ag or Au-based sensors, our Cu-based sensor also owns its advantages: a higher sensitivity and a broader linear range up to 2200 mM, with its detection limit being comparable to some Ag or Au-based sensors.

Table 1. Comparison between the performances of Cu, Ag, and Au-based sensors for 4-NP detection

Electrode materials	Analytical method	Linear ange (μM)	Sensitivity (μA/μM)	Detection limit[a] (μM)	Correlation coefficient R^2	Refs.
Au-graphene/GCE	Amperometry	470-10075	0.0523	0.47	0.9943	13
Au-RGO/GCE	Differential pulse votammetry	4-100 0.05-2	0.11 2.29	¾ 0.01	0.9975 0.9981	14
Au amalgam /Au disc	square wave voltammetry	5-250	0.01	1	0.9975	9
Au/GCE	Semiderivative voltammetry	10-1000	¾	8	¾	10
Ag-MCNT/GCE	LSV	3–120	2.88	1.3	0.9992	15
Ag-RGO/GCE	Amperometry	1-500	0.283	0.114	0.9981	16
Ag/GCE	Differential pulse votammetry	0.1-350	0.2055	0.015	0.9854	12
Ag amalgam electrode	Differential pulse votammetry	10-100	$1.57´10^{-3}$	1.5	0.993	8
Cu/GPE	Amperometry	50-850	0.1969	1.91	0.9997	17
Free-standing CuNW electrode	CV	4-2200	4.831	1.0	0.997	This work

Table 2. 4-NP concentrations of different samples measured by our sensor and by spectrometry

Water samples	Added (mM)	Found by our sensor (mM)	Found by spectrometry (mM)	Relative difference between two methods	Recovery by our sensor (%)
No. 1	¾	45.7	43.5	4.8%	¾
No. 2	440	445.7	439.1	1.5%	101.3
No. 3	35	35.8	35.3	1.4%	102.3

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