

Electrochemical solid-phase nanoextraction of copper(II) on a magnesium oxinate-modified carbon paste electrode by cyclic voltammetry

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Received: 17 September 2009 / Revised: 16 November 2009 / Accepted: 8 December 2009 / Published online: 23 January 2010
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Abstract Solid-phase nanoextraction is a sample preparation technique, which combines nanotechnology with analytical chemistry, and brings analytical chemistry to a higher level, particularly for complex system analysis. This paper describes a typical example of electrochemical solid-phase nanoextraction and electrochemical detection. Trace amounts of copper (5.0×10^{-13} mol/L) were extracted by electrochemical solid-phase nanoextraction on to the magnesium oxinate nanoparticle-modified carbon paste electrode surface in a pH 7.2 phosphate buffer system at -0.50 V for 100 s. The extraction is achieved by the cation exchange between copper(II) in the aqueous solution and magnesium(II) from the magnesium oxinate nanoparticles on the electrode surface. The extracted copper shows an irreversible anodic peak at about 0.2 V (vs. saturated calomel electrode). The peak current is proportional to the scan rate, which shows this to be a surface-controlled process. The oxidation peak current is proportional to the logarithm of the copper concentration in the range $5.0 \times 10^{-13} \sim 5.0 \times 10^{-7}$ M with a slope of 2.215. This powerful method uses the carbon paste electrode to combine extraction with electrochemical analysis.

Keywords Electrochemical solid-phase nanoextraction · Copper cation(II) · Cyclic voltammetry · Nanocolloidal of magnesium oxinate · Nanoparticle-modified carbon paste electrode

Introduction

Solid-phase microextraction (SPME) was developed by Pawliszyn and coworkers as a solvent-free green sample preparation method [1–3] and has been widely used in many areas [4–6]. If the adsorbent consists of nanoparticles, the method is called solid-phase nanoextraction (SPNE) [7, 8]. The SPNE method retains all the advantages of SPME and has some new characteristics, such as a larger specific adsorption area, multiple active sites for recognitions of the analyte(s), controllable surface states, and modificative solid nanoparticle surface. The combination of electrochemistry with SPNE is a new technique for sample preparation called electrochemical solid-phase nanoextraction (ESPNE). In ESPNE, electrochemistry offers a way to control the redox states of extractants and analytes, and the nonuniformed electric field on nanoparticle-modified electrode surface offers a dielectric force for the separations. Some examples have shown the possibility for integration of analysis with separation [9–12].

Chemical-modified electrodes have attracted many people's attention for its variety functions in electrochemistry [13, 14] and electroanalysis especially the preconcentration of analytes from matrix solutions [15, 16]. The carbon paste electrode (CPE), composed of a flexible mixture of solid and liquid phase, offers a renewable electrode surface for the solid and liquid extractants and is very suitable for ESPNE [17].

Copper is a very important heavy element in everyday life and in biological systems [18]; there are more than 30 enzymes that include copper. For this reason, the development of effective separation and preconcentration methods for the trace analysis of copper in the environment and in clinical situations is a very interesting topic [19]. In the present paper, a magnesium oxinate (Mg-Ox) nanoparticle

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colloidal solution was used to modify graphite powder and to prepare a Mg-Ox nanoparticle-modified carbon paste electrode. Mg-Ox as the solid phase extractor extracts trace copper from aqueous solution by an exchange reaction between magnesium(II) and copper(II) and forms a copper oxinate (Cu-Ox) compound. The kinetics of the ESPNE process was studied by cyclic voltammetry, and some interesting results were obtained.

Experimental

Instrument and reagents

Electrochemical experiments were carried out on a CHI electrochemical system (CHI Co., USA) with three electrodes, a piece of platinum wire as the auxiliary electrode, a home-made magnesium oxinate-modified carbon paste electrode (Mg-Ox-CPE) as the working electrode, and a KCl-saturated calomel electrode (SCE, model 232) as the reference electrode. All the potentials reported here were with respect to this reference electrode. All reagents used were analytically pure. Oxine (purchased from the Shanghai Chemical Co.) was dissolved in methanol (1.0 g/mL) before use. Copper nitrate was used to prepare a 1.0 mM standard copper solution. Magnesium nitrate was made into a 0.010 M stock solution for the preparation of the magnesium oxinate colloidal solution. Absolute methanol was used as the solvent for oxine. Potassium chloride was made into a 1.0-M stock solution as the electrolyte. Sodium hydroxide, disodium phosphate, citric acid, and sodium borate were used in the pH buffer systems. All the solutions were prepared with ultrapure milliQ water (18.2 M Ω , from Milli-Q A-10). All electrolyte solutions were deaerated with high-pure nitrogen gas for 20 min prior to the electrochemical experiments in order to remove oxygen.

The preparation of the Mg-Ox-CPE working electrode

The basic electrode was prepared as follows. Graphite powder (no. 200, spectrometrically pure), epoxy resin, and polyamide resin were mixed into a paste with a weight ratio of 8:3:2, tightly pressed into a clean glass tube (inner diameter is about 4 mm) with a copper wire at the other end as an electrode lead, and solidified in air for 72 h. After the solidification, the upper end of the electrode was scraped out to produce an \sim 1 mm cavity to give a room for the carbon paste. This solid graphite-epoxy composite electrode (GECE) with a small cavity was used as the basic electrode for the Mg-Ox-CPE.

An oxine methanol solution (20.0 mL) was mixed with 3.5 mL of 0.010 M Mg(NO₃)₂ solution and 1.5 g graphite powder stirred with a glass bar and heated to 100°C to

evaporate the methanol. The result was the magnesium oxinate-modified graphite powder. The modified graphite powder was then mixed with clinical fossillin in the weight ratio 1:1 to give a uniform paste. The paste was used to fill the cavity of the prepared basic GECE, polished on a glassine paper, and used as the working electrode.

Results and discussion

The electrochemical behavior of copper on the Mg-Ox-CPE

In the 0.5 M KCl electrolyte solution (pH 7.2), the Mg-Ox-modified CPE showed no electrochemical redox peaks in the potential range -0.5 – 0.5 V (curve 1 in Fig. 1a).

But when the solution included 0.5 mM copper(II), the electrode showed two pairs of quasi-reversible redox peaks, as shown in curve 2 in Fig. 1a. The anodic peaks were located at 0.17 and 0.324 V, and the cathodic peaks were

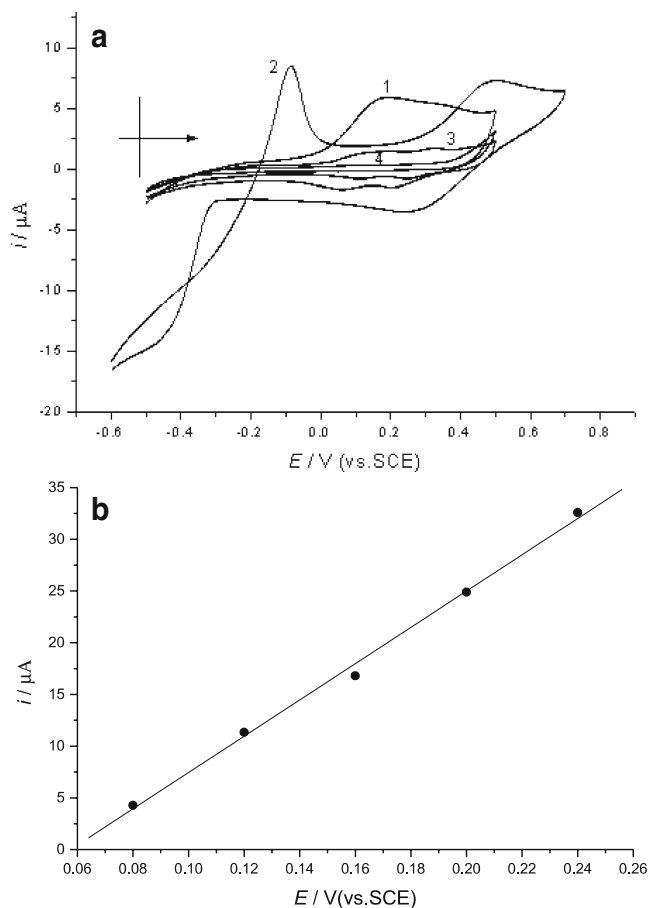
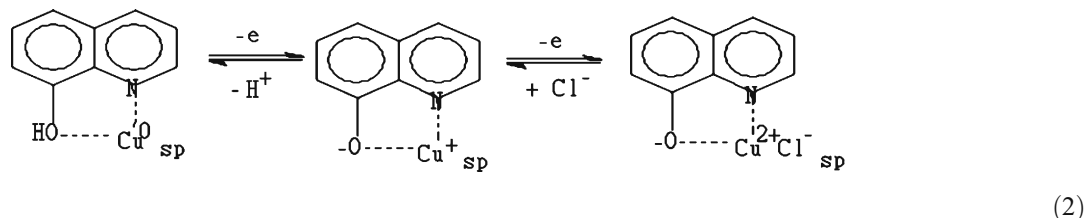
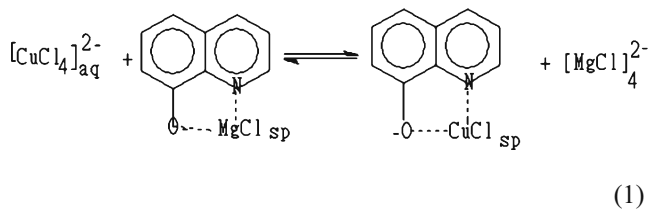


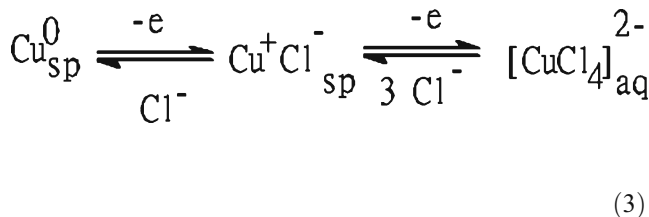
Fig. 1 **a** The cyclic voltammograms of copper on different electrodes. 1 The modified CPE in background electrolyte, 2 the modified CPE in the copper solution extracted for 5 s, 3 the bare CPE in copper solution, 4 the modified CPE in copper solution extracted for 50 s. Scan rate 100 mV/s. 0.50 M KCl electrolyte solution (pH 8.0). **b** The relationship between the oxidation peak current and scan rate

located at 0.202 and 0.062 V, with peak–peak potential differences of about 110 mV. The electrochemical reactions can be described as



Here, aq stands for the aqueous solution, and SP stands for the solid phase, that means that the reaction occurs at electrode surface and not in the solution.

On the bare CPE (electrode composed of modified graphite powder and clinical fossillin), copper(II) gave a capacitance–voltage curve without redox peaks as shown in curve 3 in Fig. 1a. The anodic peaks were located at –0.086 and 0.492 V, and the cathodic peaks were located at 0.253 and –0.488 V. The electrochemical reactions can be described as



Compared with the bare CPE, the copper(II) on the Mg-Ox-CPE shows a better electrochemical reversibility.

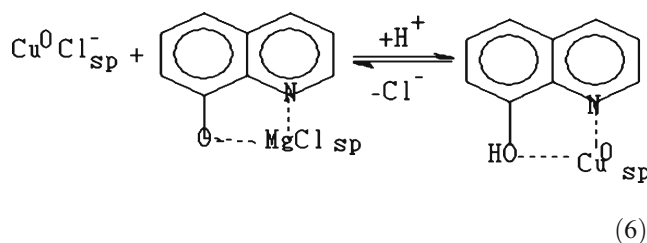
According to the peak potential description [20],

$$E_p = E^{0'} - RT/aF \left[0.780 + \ln(D_0^{1/2}/k_0) + \ln(aFv/RT) \right]^{1/2} \quad (4)$$

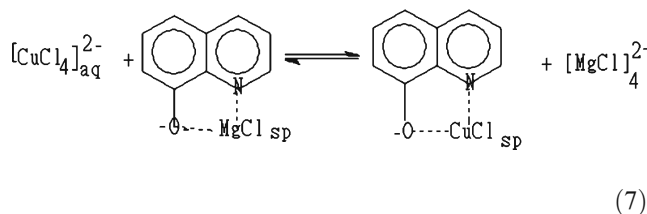
Under the same experimental conditions, for the given reactants and products, the interaction thermodynamic constant of copper atoms with oxinate can be calculated from the first anodic peak potential difference between bare

CPE and modified CPE, 0.256 V, giving 2.14×10^4 corresponding to the following expression and reaction:

$$\begin{aligned} \Delta G^0 &= -nF(E_{\text{modified}}^{0'} - E_{\text{bared}}^{0'}) = -nF \Delta E^{0'} \\ &= -RT \ln(K) \end{aligned} \quad (5)$$

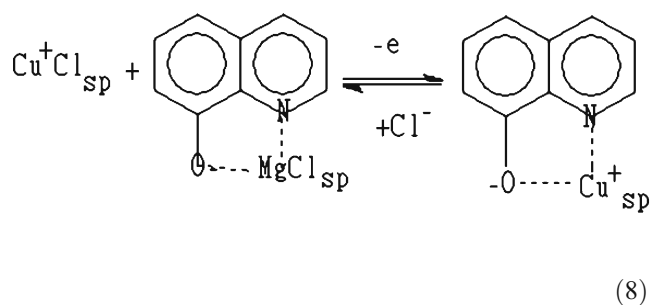


The interaction thermodynamic constant of copper(II) with oxinate can be calculated from the first reduction peak potential difference, 0.051 V, giving 7.29 corresponding to the reaction,



From the second cathodic peak potentials of copper on bared CPE and on modified CPE in KCl electrode solution,

the reaction constant of 1.98×10^9 was obtained for the following reaction:



From the calculations, it can be seen that the oxinate interacts strongly with copper atom and cuprous ion, which offer more possibility for the extraction of copper atom and cuprous ion. With the increase of extraction time, the amount of copper accumulated on the electrode surface increases, and the first oxidation peak shifts to the positive direction and combines with the second one to form one broad peak, as shown in curve 4 in Fig. 1a for the 50-s extraction time. The plot of oxidation peak current at 0.17 V against scan rate in the range 0.08–0.25 V/s is a straight line (Fig. 1b) with a regression equation of $i = -10.092 + 175.45 v$, ($R=0.998$, standard deviation (SD)=0.814). This peak current–scan rate relationship indicates that electrochemical reaction is the surface-controlled process, that means that the reactant is adsorbed on the electrode surface, and the reaction just occur at the electrode surface as an important evidence for the solid-phase nanoextraction [15].

The effects of potential

In a 0.5 M KCl electrolyte solution at pH7.2 including 5.0×10^{-11} mol/L Cu(II), extraction potential was set in the range from -0.40 to -0.90 V for 100 s, and then, the cyclic voltammetric experiments were performed at a scan rate of 100 mV/s. Plotting the oxidation peak current against extraction potential gives a straight line with the regression equation $i = -15.914 + 38.16 E$, ($R=0.9989$, SD=0.3326) in the potential range $-0.50 \sim -0.90$ V, as shown in Fig. 2.

This result indicates that the amount of extracted copper is directly proportional to the applied potential with a slope of 38.15, which is corresponding to Faradian efficiency of electrochemical process. The extraction process is mainly controlled by an electrochemical process, e.g., the copper(II) is first reduced to cuprous ions, further reduced to copper atoms, and deposited on the electrode surface and strongly interacts with oxinate. This is another evidence of the significant advantage of ESPNE over the SPNE. Among the heavy

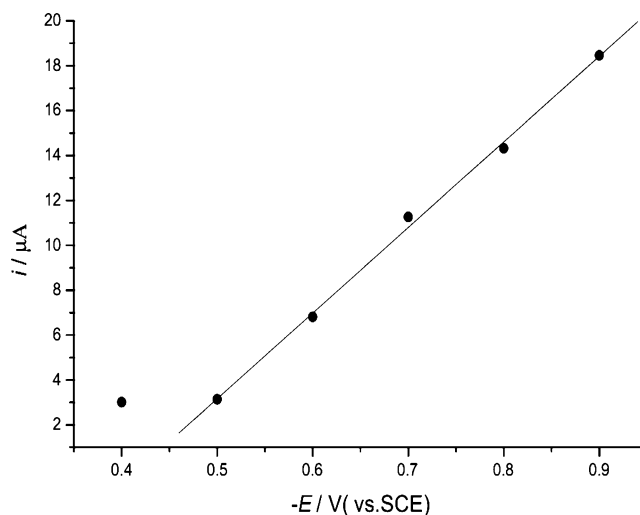


Fig. 2 The relationship between the oxidation peak current and extraction potential in 0.50 M KCl electrolyte solution at pH7.2 including 5.0×10^{-11} M Cu(II). The extraction time is 100 s; the scan rate is 100 mV/s

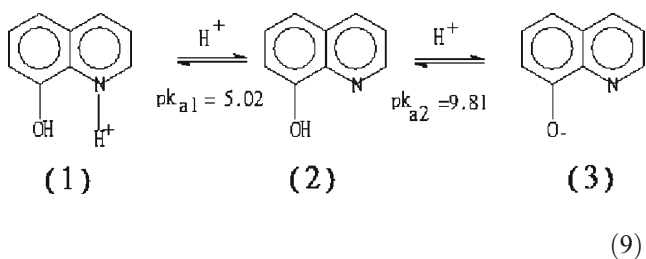
elements, copper is the most reducible element, so in order to increase the selectivity of the ESPNE and avoid interference by other metals, an extraction potential of -0.50 V was chosen as the optimum condition for the measurements.

The effects of solution pH

In the 0.50 mol/L KCl electrolyte solution, including 5.0×10^{-11} mol/L Cu(II), the solution pH was controlled with a suitable pH buffer system in the range pH 2–10, the extraction potential was set to -0.5 V for 100 s, and then, the cyclic voltammetric experiments were performed at a scan rate of 100 mV/s. The oxidation peak current increases with solution pH, reaches a maximum at pH 7.2, and then decreases, as shown in Fig. 3a.

In the pH range 2.0–7.2, the oxidation peak current is proportional to the solution pH with a regression equation of $i_{\text{pa}} = -0.7045 + 0.275 \text{ pH}$ ($R=0.9927$, SD=0.0698). The oxidation peak potential was plotted against solution pH to give a straight line with regression equation, $E_{\text{pa}} = 0.3969 - 0.03688 \text{ pH}$ ($R=0.9904$, SD=0.0123) as shown in Fig. 3b. According to Nernstian equation [15], the slope of 0.03688 indicates that there are two protons taking part in the oxidation reaction. At the experimental pH, the main form of oxine is shown in Scheme (2), but Scheme (3) form is favorable for interactions with copper. During the redox processes (Scheme (1)), there is two proton transferred, as described in Scheme (2). When $\text{pH} > 7.2$, the copper(II) tends to form a $\text{Cu}(\text{OH})_2$ precipitate in aqueous solution, which inhibits

the extraction process, and results in a decrease of the oxidation peak current.



The effect of extraction time

In a KCl electrolyte solution at pH7.2 including 5.0×10^{-11} mol/L Cu(II), the effect of different extraction times at an extraction potential of -0.50 V on the cyclic voltammetric experiments at 100 mV/s scan rate was studied. The oxidation peak currents were plotted against extraction time to give a straight line in the range 20–300 s with a regression equation of $i_{pa} = 0.3887 + 0.069 t$ ($R = 0.9931$, $SD = 0.8466$), as shown in Fig. 4. This result indicates that, by using lower extraction potential, a suitable solution pH and keeping the extraction far away from the saturated stage, a straight line can be obtained, showing that this solid phase nanoextraction is very suitable for trace element extraction and determination.

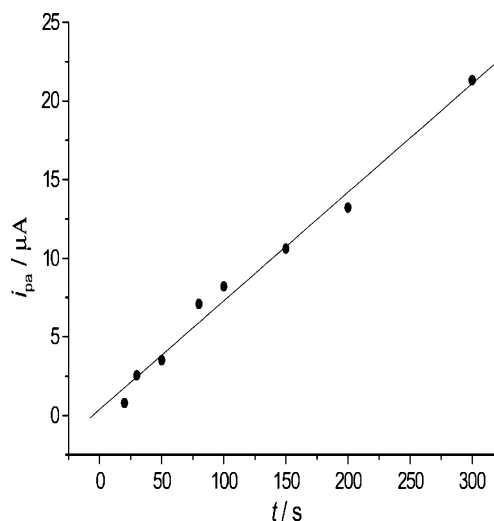


Fig. 4 The relationship between the oxidation peak current and extraction time. The experimental conditions were the same as those in Fig. 3

The effect of concentration of copper(II)

Under the optimum experimental conditions with a KCl electrolyte solution at pH7.2 containing various concentrations of Cu(II), the extraction potential was set at -0.50 V for 100 s, then the cyclic voltammetric experiments were performed at a 100-mV/s scan rate. The oxidation peak current obtained was plotted against the logarithm of the copper concentration, and a straight line was obtained in the concentration range of 5.0×10^{-13} – 5.0×10^{-7} mol/L with a regression equation of $i_{pa} = 9.687 + 2.215 \ln [c, \text{mol/L}]$ ($R = 0.9979$, $SD = 0.5221$), as shown in Fig. 5. The logarithmic relation [21] shows that the first order chemical reaction consisting of the exchange between copper(II) and magnesium(II) is the rate determining step in the extraction, so the ESPNE is favorable for trace element separation and analysis with higher sensitivity, higher selectivity, and over a wide concentration range.

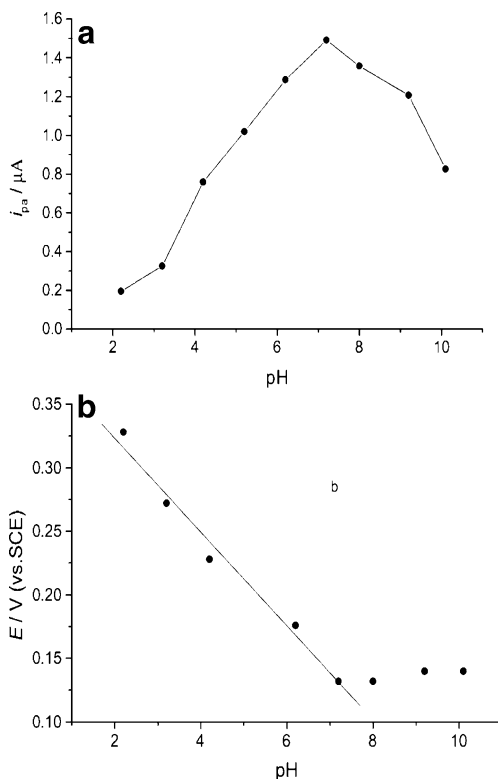


Fig. 3 The relationships of the oxidation peak current (a) and potential (b) with solution pH. The experimental conditions were the same as those in Fig. 2

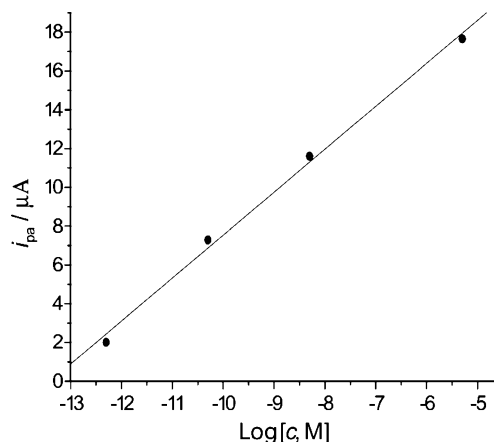


Fig. 5 The relationship between the oxidation peak current and the concentration of copper under optimum conditions

Conclusions

In this paper, the ESPNE behavior of copper ions on a carbon paste electrode modified with magnesium oxinate colloidal nanoparticles has been described. Some important results are obtained as follows:

1. The combination of SPNE with electrochemistry has been successfully developed based on the carbon paste electrode, which is a true integrated technique for separation and analysis.
2. The insulated nanoparticles, such as magnesium oxinate from the colloidal solution, were suitably modified on the CPE of the conducting graphite powder. The nanoparticle-modified CPE are very suitable for ESPNE, which was then used for the direct detection of metal cations or anions due to the exchanges reactions between cations or anions in the nanoparticles.
3. The colloidal solution of magnesium oxinate precipitate systems with the ion exchange mechanism offers a new way for the SPNE.
4. In the ESPNE system, the electrochemical electrode offers an extra strong electric field for separation, extraction, and detection due to the nanoparticles on the surface of carbon paste electrode.
5. Under the optimum experimental conditions, the ESPNE technique can be used for trace level substance preconcentration and detection by means of ion exchange reactions between ions from precipitates modified on electrode surface and ions in aqueous solution. This paper describes a successful example of ESPNE. Further work will be carried out on the practical uses of the method in the detection of copper ions in environmental and biological systems.

Acknowledgments The author would like to acknowledge the financial support of the Chinese National Science Foundation (20875063), Liaoning Education Ministry (2004-c022), National Key Laboratory on Electroanalytical Chemistry (2006-06), and the Science Bureau of the Shenyang government (2007-GX-32).

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