RSC Advances

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/advances

Selective electrochemical determination of trace level copper using salicylaldehyde azine/MWCNTs/Nafion modified pyrolytic graphite electrode by anodic stripping voltammetric method

Yuan Liao [a,b], Qian Li [a], Ying Yue [a], Shijun Shao [a,*]

[a] *Key Laboratory of Chemistry of Northwestern Plant Resources of CAS and Key Laboratory for Natural Medicine of Gansu Province, Lanzhou institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China.*

[b] *University of Chinese Academy of Sciences, Beijing 100039, P. R. China.*

* Corresponding author: Shijun Shao

Tel: +86-931-4968209

Fax: +86-931-8277088

E-mail: sjshao@licp.cas.cn

Abstract:

A novel Cu^{2+} electrochemical sensor based on salicylaldehyde azine/MWCNTs/Nafion-modified pyrolytic graphite electrode was prepared for anodic stripping analysis of Cu^{2+}. Salicylaldehyde azine was synthesized and then used for the selective determination of heavy metal pollutant Cu^{2+} due to its azine structure, which served selective complexing ability toward Cu^{2+}. The use of MWCNTs with their strong adsorption ability could greatly enhance the sensitivity. Nafion, proton-exchange polymer, was used as the conductive matrix in which salicylaldehyde azine and MWCNTs could be strongly fixed to the substrate electrode surface. The as-prepared electrochemical sensor showed remarkably enhanced selectivity and sensitivity towards Cu^{2+}. The response current of the sensor was linear with Cu^{2+} concentration ranging from 5 to 300 nM under 15 min accumulation at open-circuit potential, with a very low detection limitation about 1 nM. The hybrid functionalized electrode also exhibited good selectivity to avoid the interference of other heavy metal ions like Cd^{2+}, Pb^{2+} and Hg^{2+} in their mixture solution together with Cu^{2+}. Real application towards environmental sample analysis confirmed that the modified electrode could be applied for the selective determination of trace level of Cu^{2+} in Yellow River.

Keywords: Salicylaldehyde azine; Carbon nanotubes; Differential pulse anodic stripping voltammograms; Highly selective determination of Cu^{2+}.

1. Introduction

The contamination of natural water by heavy metals is a serious problem in biosystem since the heavy metals can cause many disorders in the plant and animal kingdoms and tend to accumulate through the food chains.[1,2] Copper ion (Cu^{2+}) is an essential heavy metal in human body and plays an important role in various physiologic processes.[3] Excess intake of copper from the polluted water and copper-rich food frequently occurs in recent years.[4] Some serious diseases, such as anemia, Menkes disease and Wilson disease, are associated with the abnormal level of copper in human body.[5,6] The copper-containing waste water which was indiscriminately pumped into ricer during industrial production is still a serious global problem. Thus, monitoring of Cu^{2+} in the environment sample has become essential.

There are various techniques which have been used for determination of copper, such as fluorescence,[7] atomic absorption spectroscopy,[8,9] and inductively coupled plasma-optical emission spectroscopy.[10] In comparison with other methods, electrochemical method has more attractive features including simple, robustness and inexpensive. In the past, mercury based electrodes, chemically modified electrode based on gold coated diamond [12-14] and boron-doped diamond electrodes[15] have been used for the trace heavy metals detection. Whereas, the traditional methods also have some disadvantages like the toxicity, low chemical stability, inconvenience and new electrode materials for trace heavy metals detection are highly sought.[16]

Recently, the use of chemically modified electrodes (CME) wan very common for the determination of several metallic species and the employment of this method could not only enhance selectivity for the analyte but also improve the detection limits.[17-19] The choice of modifier could confer special characteristic to the electrode surface. The electrodes modified with synthesis receptors have been used for the heavy metal detection, where the receptors extracted particular metal ions by complexation in the analysis.[20-22] In the literatures, various receptors such as crown ether,[23] iminodiacetic acid,[24] di-(2-imino-cyclopentylidine mercaptomethyl) disulfide,[25] 2,2-biquinoline-Nafion,[26] and 1,2-bismethyl (2-aminocyclopentene-carbodithioate) ethane[27] have been used for the determination metal ions by using the CME. Though these receptors were known to exhibit higher selectivity, their exploitation in electroanalysis areas were very limited owing to their non-conductive property.

Therefore, it is necessary to improve the matrix conductivity when receptor is employed in the electrochemical sensor. Nanoscaled materials, such as metal nanoparticles, carbon materials, and mesoporous silica, exhibit unique chemical, physical and electronic properties and thus have been applied to fabricate novel modified electrode for heavy metal ions sensing.[28-35]

Herein we report a new method for the synthesis, characterization, and metal recognition properties of salicylaldehyde azine (SA) (2,2'-(1*E*,1'*E*)–hydrazine-1,2-diylidenebis(methan-1-yl-1-ylidene) diphenol). In this work, a receptor SA has been combine with MWCNTs as a novel modifier for selective determination heavy metal copper using differential pulse anodic stripping voltammetry. The selective complexing ability of SA and the electrical conductivity of MWCNTs synergistically improved the electrochemical performance towards Cu^{2+} sensing. Nafion, a sulfonated cation-exchange polymer, supplied the good stability of the functionalized hybrid electrode. It has been confirmed that such a fabricated SA/MWCNTs/Nafion hybrid modified PGE could remarkably enhance the sensitivity and selectivity for stripping measurement of Cu^{2+}.

2. Experimental

2.1 Apparatus and chemicals

The electrochemical measurements were carried out on a CHI660C electrochemical workstation (CHI Instrument, Shanghai, China). All measurements were performed in a conventional three-electrode cell, consisting of an unmodified PGE (Tianjin Aidahengsheng Technology Co., China) or the modified PGE, a saturated calomel electrode (SCE) and a platinum wire were used as working electrode, reference electrode, and counter electrode, respectively. The morphology of the SA/MWCNTs/nafion/PGE was determined with a JEOL 2010 TEM (JEOL, Japan) equipped with a LaB6 filament at 200kv. UV-vis spectra were recorded on a Perkin Elmer Lambda 35 UV-vis Spectrophotometer with quartz cuvette (pathlength = 1 cm).

All reagents were of analytical grade and used as received. 0.1 M phosphate buffer solution (PBS) at pH 7.0 was prepared from NaH_2PO_4 and Na_2HPO_4 and the pH value was adjusted with 1 M H_2SO_4 or NaOH solution. Nafion was obtained from Aldrich. The stock solutions of Cu^{2+}, Cd^{2+}, Pb^{2+} and Hg^{2+} were prepared from their nitrate salts in deionised water. Multi-wall carbon nanotubes were synthesized according to the literature.[36]

2.2 Synthesis of SA

1.22 g salicylaldehyde was dissolved in 50 mL ethanol and 0.25 mL of hydrazine hydrate (99%) was added at room temperature. The reaction mixture was allowed to stir at room temperature overnight. After completion of reaction the obtained yellow precipitate was filtered and washed several times with cold ethanol with a yield 85%. EI-MS: (M+H) 241.2. ^1H NMR (400Hz, DMSO-d6), δ: 11.122 (s, 2H), 8.999 (s, 2H), 7.676-7.699 (m, 2H), 7.372-7.414 (m, 2H), 6.943-6.982 (m, 4H).

2.3 Preparation of the electrode

The modified electrodes were prepared by casting method. Prior to the surface coating, the pyrolytic graphite electrode (PGE) was carefully polished with 1.0, 0.3, and 0.05 μm alumina powders in series, and then treated with 50% nitric acid, ethanol and water in ultrasonic bath, respectively. Original 5% w/w Nafion solution was diluted to 0.5% w/w solution with *N,N*-dimethylformamide (DMF). Then 1 mg of MWCNTs and 1 mg of SA were added into above solution and sonicated for 20-30 min to form a homogeneous suspension. Finally, 5 μL SA-MWCNTs-Nafion suspension was casted on the pretreated PGE surface and dried under an infrared lamp. For comparison, Nafion/PGE, SA/Nafion/PGE, MWCNTs/Nafion/PGE and SA/MWCNTs/Nafion/PGE were prepared in the similar method.

2.4 Electrochemical measurements

0.1 M PBS at pH 7.0 was used as the supporting electrolyte. The SA/MWCNTs/Nafion/PGE at open-circuit potential was immersed into a buffer solution containing Cu^{2+} or other ions for 15 min without applying any potential and stirring during the accumulation period. As comparison to the open-circuit accumulation, the electrocaccumulation was performed by applying the potential at -1.2 V for 15 min in a solution containing Cu^{2+} or other ions. Subsequently, the electrode was rinsed thoroughly with deionized water and transferred to the fresh supporting electrolyte, which had been deoxygenated by nitrogen bubbling for 30 min, while a potential of -0.6 V was applied to the electrode for about 30 s to reduce Cu^{2+}. Using differential pulse anodic stripping voltammetry, quantitative determinations of Cu^{2+} was performed at an optimized condition: amplitude of 0.05; pulse width of 0.05 s; sampling width of 0.0167 s; pulse period of 0.2 s; quiet time of 2 s. After each measurement, the modified electrode was regenerated by applying 0.3 V for 200 s in fresh supporting electrolyte to remove the previous residual copper from the electrode surface.

3. Results and discussion

3.1 The selective binding properties of SA towards metal ions

Based on the outstanding ability to selectively coordinate with metal ions, the bisazine-type receptors have been used as ionophore molecules for ion-selective electrodes and other applications.[37-40] In this work, salicylaldehyde azine (SA) was synthesized by an easy and effective method (Supporting information, Fig. S1). The metal ions binding properties of receptor SA have been firstly studied by using UV-vis spectroscopic techniques. SA itself displayed two strong absorption bands at 290 and 350 nm in CH_3CN/H_2O (1:1, v/v) mixture at neutral pH 7 buffered with HEPES-NaOH. In the presence of various cations such as Fe^{3+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Ag^{+}, Mg^{2+}, Hg^{2+}, Fe^{2+}, Na^{+}, K^{+} and Ca^{2+} (all as their nitrate salts), only Cu^{2+} remarkably changed the absorption spectrum of SA, whereas the other cations tested induced negligible responses (Supporting information, Fig. S2). Upon addition of Cu^{2+} (0~20 equiv) to a solution of SA (2.0×10^{-5} M), as shown in Fig. 1, the absorption band of SA at 290 nm gradually decreased along with a slight blue shift, and the absorption band at 350 nm gradually disappeared while a new red-shift absorption band centered at 405 nm appeared, which was responsible for the mixed solution color change from colorless to yellow-green (Inset of Fig. 1). During the titration of Cu^{2+} with the solution of SA, a clear isosbestic point at 380 nm was observed, indicating the existence of coordination equilibrium between the several structures. The ESI-MS analysis of the interaction system of SA with Cu^{2+} exhibited one main peaks at m/z = 304.00, assigned to $SA{\cdot}Cu^{2+}$ complex (m/z calc = 304.02).

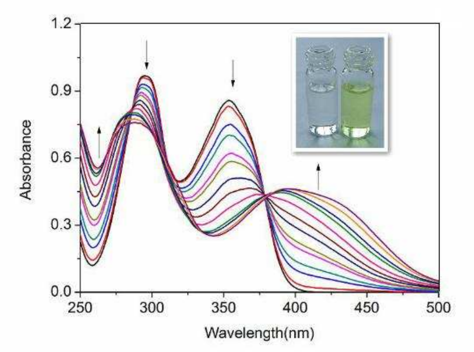


Fig. 1. Absorption spectra of SA (2.0×10^{-5} M) in CH_3CN-H_2O (1:1, v/v) buffer solution upon addition of Cu^{2+} (0~20 equiv); Inset: The color change of the mixed solution of SA (2×10^{-5} M) upon addition of 1 equiv of Cu^{2+} in CH_3CN-H_2O (1:1, v/v) buffer solution.

The above results indicated the highly selective metal ions binding properties of SA, which can be used as a colorimetric probe for selective detection of Cu^{2+} in aqueous buffer media. Based on the selective complexing ability of SA towards Cu^{2+}, the SA-modified pyrolytic graphite electrodes were further constructed for the electrochemical determination of Cu^{2+}.

3.2 Characterization of SA/MWCNTs/Nafion composite film

Fig. 2 showed the scanning electron microscopic (SEM) images of MWCNTs/Nafion and SA/MWCNTs/Nafion composite film coated on a PGE. It could be observed that MWCNTs/ Nafion composite film was homogeneously casted on the electrode surface (Fig. 2a). This surface morphology gave an accessible large surface area. When SA was introduced into the MWCNTs/ Nafion composite, the homogeneously distribution of MWCNTs on the electrode surface was not affected (Fig. 2b). However, the profile of MWCNTs became rough and conductivity decreased because SA and MWCNTs were miscible throughout the matrix. This result was similar with the former report.[23] Furthermore, MWCNTs formed the network on the electrode and could be more effective for electron transfer, increasing the sensitivity of the sensors.

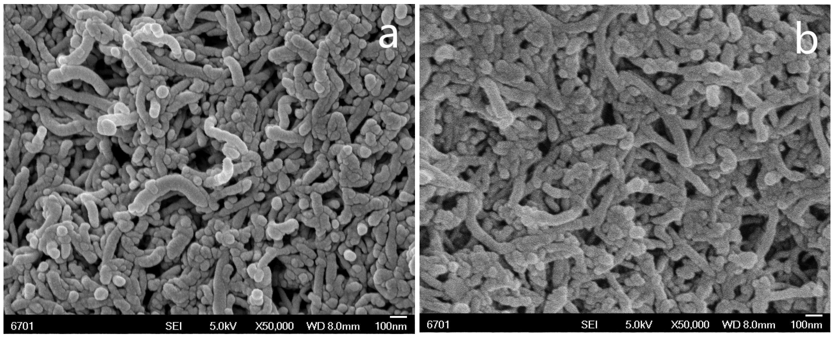
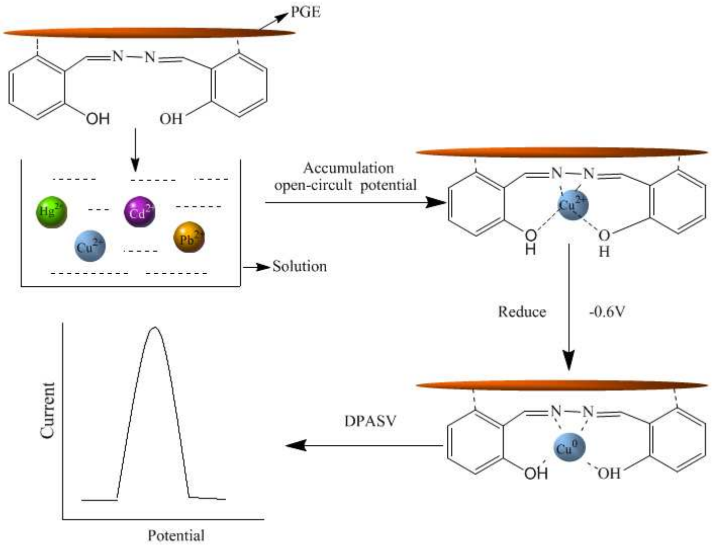


Fig. 2. SEM images of the electrode surface prepared at different modifier: (a) Nafion/MWCNTs/PGE and (b) SA/MWCNTs/Nafion/PGE

3.3 Electrochemical behavior of Cu^{2+} at SA/MWCNTs/Nafion/PGE

The combination of accumulation and reduction prior to the actual stripping detection process can enhance both the sensitivity and the selectivity of analysis of metal ions.[41] For this work, the structural features of SA facilitated the formation of SA•Cu^{2+} complex in the course of open-circuit accumulation. The complex Cu^{2+} could be further reduced to Cu^0, which deposited on the modified electrode, under cathodic potentiostatic conditions for a define time period. Finally, the deposited Cu^0 was stripped off the electrode and the stripping current could be measured. The diagrammed illustration was depicted in Scheme 1.



Scheme 1. Schematic illustration of Cu^{2+} detection using SA/MWCNTs/Nafion modifier.

The typical cyclic voltammetric behaviour of SA/MWCNTs/Nafion/PGE in 0.1M PBS was shown in Fig. 3. Compared with the cyclic voltammogram of the electrode in pure PBS (dotted line), a well-defined anodic voltammetric peaks at -0.1V attributed to oxidation of metallic copper can be obtained after accumulation of Cu^{2+} (solid line) .

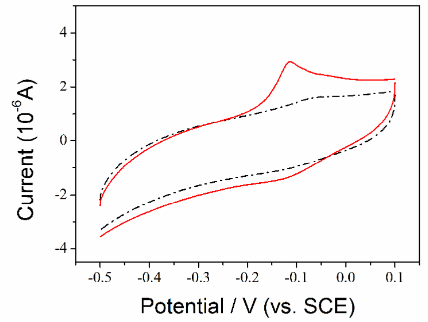


Fig. 3. Cyclic voltammograms of the SA/MWCNTs/Nafion/PGE in 0.1 M pH 7.0 PBS with (solid line) and without (dotted line) open-circuit 15 min accumulation. Accumulation solution: PBS containing 5.0 μM Cu^{2+}. Scan rate: 100 mV/s. Reduction potential -0.6 V for 120s.

To clarify the function of each component in the electrode coating matix, further investigation using differential pulse anodic stripping voltammetry was carried out under the same experimental conditions. Fig. 4 depicted the DPASV performance of 5.0 μM Cu^{2+} in 0.1 M PBS (pH 7.0) at various modified PGEs. No peaks were observed in bare and Nafion film modified electrode after accumulation at open-circuit potential for 15 min (Fig. 4a and 4b). The weak stripping peak was observed at SA/Nafion/PGE (Fig. 4c) due to the formation of SA•Cu^{2+} complex on modified electrode surface. Compared with SA/Nafion/PGE, larger stripping peak at -0.17 V was observed for MWCNTs/Nafion/PGE (Fig. 4d), indicating that MWCNTs with large surface area could provide multiadsorbing sites and increase the stripping currents. Further, the highest peak at -0.15 V was found for SA/MWCNTs/Nafion/PGE under the same conditions (Fig. 4e), and the current response observed at SA/MWCNTs/Nafion/PGE was improved by nearly 2-fold higher than that at MWCNTs/Nafion/PGE. The most probable reason was that MWCNTs could improve the accumulation capacity of the modified electrode, and SA was capable of forming a strong complex with Cu^{2+}. The combination MWCNTs with SA on Nafion/PGE could synergistically enhance accumulation of Cu^{2+} from the sample solution to the modified electrode surface and result in the significant increase of the stripping peak current.

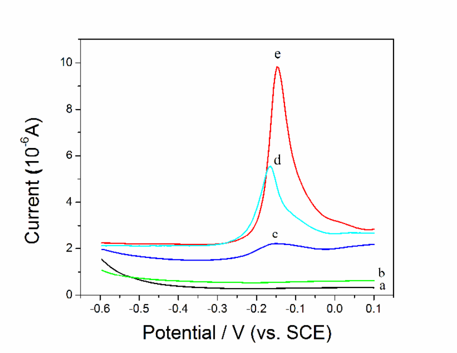


Fig. 4. Differential pulse anodic stripping voltammetry of 5.0 μM Cu^{2+} in 0.1 M PBS pH 7.0 : (a) bare PGE electrode; (b) Nafion/PGE; (c) SA/Nafion/PGE; (d) MWCNTs/Nafion/PGE; (e) SA/MWCHTs/Nafion/PGE. Amplitude of 0.05 V; pulse width of 0.05 s; pulse period of 0.2 s; quiet time of 2 s.

3.4 Optimization of experimental parameters

Fig. 5a showed the effect of pH of the supporting electrolyte on the Cu^{2+} differential pulse anodic stripping peak current at SA/MWCNTs/Nafion/PGE. The peak current increased notably with the pH from 6.0 to 7.0, and then decreased from 7.0 to 8.0, which were due to SA instability at low pH value and the precipitation of Cu^{2+} at high pH value. Therefore, pH 7.0 was selected for subsequent measurements. Furthermore, the effect of accumulation time on peak current was illustrated in Fig. 5b. The peak current increased rapidly with increasing accumulation time from 5 min to 15 min. Further increasing the accumulation time, there was gradual increases in current response. The similar process was observed in the influence of reduction time on peak current (Fig. 5c). The current response increased sharply with increasing reduction time from 30 s to 120 s, and then increased slightly from 120 s to 300 s. Based on sensitivity and short analysis of time, 15 min accumulation time and 120 s reduction time were chosen in the subsequent experiments. Finally the effect of reduction potential was investigated in the potential range of -0.8 V to -0.4 V, as depicted in Fig. 5d. The peak current increased with the reduction potential from -0.8 V to -0.6 V, and decreased from -0.6 V to -0.4 V, which might be attributed to substantial hydrogen evolution at the modified PGE surface. Hence, a potential of –0.6 V was chosen for the further experiments.

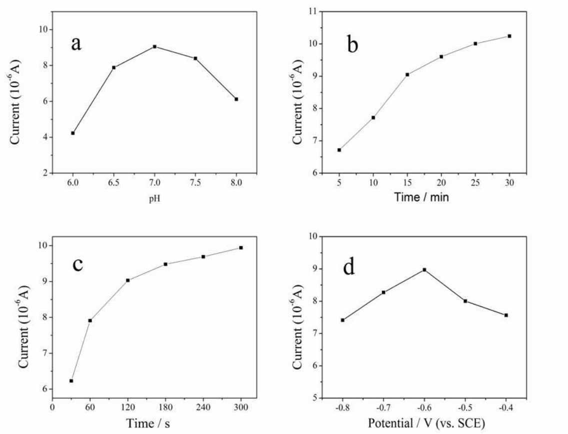


Fig. 5. Differential pulse anodic stripping voltammetry of 5.0 μM Cu^{2+} in 0.1 M PBS pH 7.0 : (a) effect of pH; (b) effect of accumulation time; (c) effect of reduction time; (d) effect of reduction potential. Amplitude of 0.05 V; pulse width of 0.05 s; pulse period of 0.2 s; quiet time of 2 s.

3.5 Determination of Cu^{2+} at SA/MWCNTs/Nafion/PGE

Fig. 6 showed the DPASV of varying concentration of Cu^{2+} in 0.1 M PBS at SA/MWCNTs/Nafion/PGE with an open-circuit accumulation 15 min. The stripping peak current increased linearly with Cu^{2+} concentration ranging from 5.0 nM to 300 nM. The correlation coefficient was found to be 0.997 and the calculated limit of detection for 15 min of open-circuit accumulation was 1.0 nM. The performance characteristics of the proposed electrode for Cu^{2+} electroanalysis was comparable or superior to some reported chemical modified electrodes, as summarized in Table 1. The relative standard deviation of 10 determinations for 40 nM is 0.91%, indicating the good reproducibility of the modified electrode. The current response at SA/MWCNTs/Nafion/PGE had no significant change after its preparation for three weeks under ambient circumstances, showing high stability of SA/MWCNTs/Nafion/PGE.

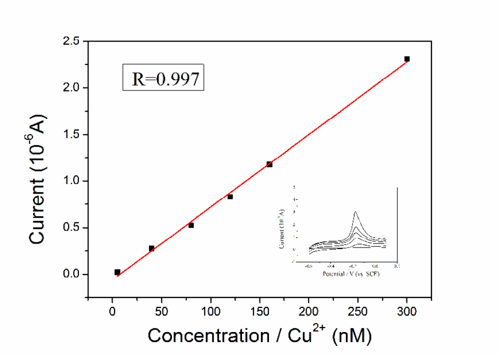


Fig. 6. Differential pulse anodic stripping voltammetry of 5.0-300 nM Cu^{2+} in 0.1 M PBS pH 7.0 at SA/MWCNTs/Nafion/PGE. Amplitude of 0.05 V; pulse width of 0.05 s; pulse period of 0.2 s; quiet time of 2 s.

Table 1. Comparison of various modified electrodes for the detection of Cu^{2+}.

Modifier	Method	Linear range (M)	Limit of detection (M)	Reference
2-aminothiazole	DPASV	7.5×10^{-8}-2.5×10^{-6}	3.1×10^{-8}	42
Natural zeolite	DPASV	5.0×10^{-8}-5.0×10^{-6}	1.5×10^{-8}	43
PCHA	DPASV	1.0×10^{-8}-1.0×10^{-6}	5.0×10^{-10}	44
Mercury film	DPASV	1.0×10^{-5}-5.0×10^{-9}	1.0×10^{-9}	45
Calix[4]arene	DPASV	5.0×10^{-8}-1.6×10^{-6}	1.1×10^{-8}	46
Salicylidine-functionalized polysiloxane	Potentiometry	2.3×10^{-7}-1.0×10^{-3}	2.7×10^{-8}	47
BHAB	Potentiometry	5.0×10^{-8}-1.0×10^{-2}	3.0×10^{-8}	48
SA/MWCNTs/Nafion	DPASV	5.0×10^{-9}-3.0×10^{-7}	1.0×10^{-9}	this work

3.6 Interference

The stripping analysis of Cu^{2+} can be affected by interferences in the presence of other heavy metal ions such as Cd^{2+}, Pb^{2+} and Hg^{2+}, which generated large errors in stripping analysis, especially in the presence of higher concentration (>0.1μM).[41] In this work, Cd^{2+}, Pb^{2+} and Hg^{2+} were selected to evaluate the anti-interference of the modified electrode. Fig. 7 showed the differential pulse stripping voltammograms obtained at the SA/MWCNTs/Nafion/PGE using electroaccumulation and open-circuit accumulation for Cu^{2+} in the presence of 10-fold excess of Cd^{2+}, Pb^{2+}, Hg^{2+}, respectively. Four peak were observed at the potential of -0.82, -0.61, -0.16, 0.72 V by using 15 min electroaccumulation in the mixture solution, which were assigned to the stripping peak of Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}, respectively. This showed that the interfering metal ions were electrodeposited together with the target ion at the modified electrode during the electroaccumulation procedure, which resulted in a poor selectivity. This phenomenon was similar with the former report.[41] Compared to the electroaccumulation, only one stripping peak of Cu^{2+} was obtained at -0.16 V by using 15 min open-circuit accumulation. This might be attributed to SA with an outstanding ability to selectively coordinate with Cu^{2+}. These results showed that the modified electrode exhibited high selectivity and sensitivity for Cu^{2+} over other interference or competing metal ions by open-circuit accumulation procedure. The current peak of Cu^{2+} observed at the SA/MWCNTs/Nafion/PGE by open-circuit accumulation was less than the same electrode by electrodeposition, which might be due to less Cu^{2+} adsorption on electrode surface during the open-circuit accumulation.

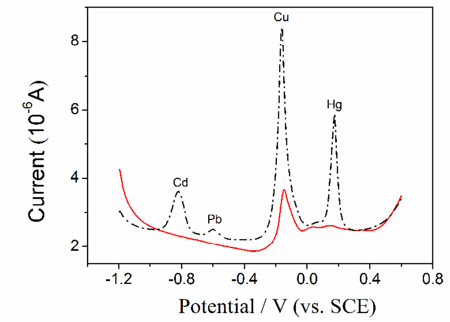


Fig. 7. Differential pulse anodic stripping voltammetry obtained at SA/MWCNTs/Nafion/PGE in 0.1 M PBS pH 7.0 containing 0.5 μM Cu^{2+} + 5.0 μM Pb^{2+} + 5.0 μM Hg^{2+} + 5.0 μM Cd^{2+}. Solid line: open-circuit 15 min accumulation. Dotted line: electroaccumulation at -1.2 V for 15 min. Amplitude of 0.05 V; pulse width of 0.05 s; pulse period of 0.2 s; quiet time of 2 s.

3.7 Application to real sample analysis

In order to test its accuracy in practical analysis, SA/MWCNTs/Nafion/PGE was used for the determination of Cu^{2+} in the Yellow River. Yellow River samples were filtered through a standard 0.45 μm filter and analyzed using the standard addition method. The results were shown in Table 2.

Thus the SA/MWCNTs/Nafion/PGE had a great potential for real sample analysis with a high accuracy and good reliability.

Table 2. Recovery study of Cu^{2+} in yellow river.

Added (Cu^{2+} nM)	Found (nM)	Recovery (%)
40	41.7 ± 1.7	104
60	59.3 ± 2.1	98.8
80	81.0 ± 1.4	101

4. Conclusion

In this work, a novel chemically modified pyrolytic graphite electrode for selective determination of Cu^{2+} has been developed. Due to the combination of the selective complexing ability of SA with Cu^{2+} and the good conductivity of MWCNTs, SA/MWCNTs/Nafion/PGE has shown remarkably enhanced sensitivity and selectivity for Cu^{2+} determination in the presence of other metal ions. The as-fabricated electrochemical sensor was successfully applied in determining Cu^{2+} in real water samples with satisfactory result. In addition, the present results suggested that such a designing scheme could provide an excellent platform for electroanalysis and had potential for fabrication of chemical sensors for heavy metals.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (20972170 and 21275150) and the Funds for Distinguished Young Scientists of Gansu (1210RJDA013).

Reference

1 C. Tu, Y. Shao, N. Gan, D. Xu and Z. J. Guo, *Inorg. Chem.*, 2004, **43**, 4761–4766.

2 E. L. S. Wong, E. Chow and J. J. Gooding, *Electrochem. Commun.*, 2007, **9**, 845–849.

3 Y. J. Zheng, Q. Huo, P. Kele, F. M. Andreopoulos, S. M. Pham and R. M. Leblanc, *Org. Lett.*, 2001, **21**, 3277–3280.

4 S. A. Reddy, K. J. Reddy, S. L. Narayan and A. V. Reddy, *Food Chemistry.*, 2008, **109**, 654–659.

5 C. Vulpe, B. Levinson, S. Whitney, S. Packman and J. Gitschier, *Nat Genet.*, 1993, **1**, 7–13.

6 L. Zeng, E. W. Miller, A. Pralle, E. Y. Isacoff and C. J. Chang, *J. Am. Chem. Soc*, 2006, **128**, 10–11.

7 M.T. Fernandez-Arguelles, W. J. Jin, J. M. Costa-Fernandez, R. Pereiro and A. Sanz-Medel, *Anal. Chim. Acta.*, 2005, **549**, 20-25.

8 M. Yuce, H. Nazir and G. Donmez, *Bioelectrochem*, 2010, **79**, 66-70.

9 B. Rezaei, E. Sadeghi and S. Meghdadi, *J. Hazard. Mater.*, 2009, **168**, 787-792.

10 M. Bingöl, G. Yentür, B. Erand, A. B. Öktem, *Czech Journal of Food Sciences.*, 2010, **28**, 213–216.

11 C. A. Sahin and I. Tokgoz, *Anal. Chim. Acta.*, 2010, **667**, 83-87.

12 A. Economou and P. R. Fielden, *Analyst*, 2003, **128**, 205–212.

13 O. A. Farghaly and M. A. Ghandour, *Environ Res.*, 2005, **97**, 229–235.

14 Y. Song and G. M. Swain, *Anal. Chim. Acta.*, 2007, **593**, 7–12.

15 O. El Tall, N. Jaffrezic-Renault, M. Sigaud and O. Vittori, *Electroanalysis*, 2007, **19**, 1152–1159.

16 I. Svancara, C. Prior, S. B. Hocever and J. Wang, *Electroanalysis*, 2010, **22**, 1405–1420.

17 M. R. Ganjali, N.Motakef-Kazami, F. Faridbod, S. Khoee, P. Norouzi, *Journal of Hazardous Materials,* 2010, **173**, 415-419.

18 B. C. Janegitz, L. H. Marcolino-Junior, S. P. Campana-Filho, R. C. Faria, O. Fatibello-Filho, *Sensors and Actuators B: Chemical*, 2009, **142**, 260-266.

19 P. R. Oliveira, A. A. Tanaka, N. R. Stradiotto, M. F. Bergamini, *Current Analytical Chemistry*, 2012, **8**, 520-527.

20 D. W. M. Arrigan, *Analyst*, 1994, **119**, 1953-1966.

21 K. Kalcher, J. M. Kau.mann, J. Wang, I. Svancara, K. Vytras, C. Neuhold and Z. Yang, *Electroanalysis*, 1995, **7**, 5-22.

22 P. Ugo and L. M. Moretto, *Electroanalysis*, 1995, **7**, 1105–1113.

23 S. Anandhakumar and J. Mathiyarasu, *Microchim Acta.*, 2013, **180**, 1065-1071.

24 R. Agraz, M. T. Sevilla and L. Hernandez, *Anal. Chim. Acta.*, 1993, **283**, 650–656.

25 M. S. Won, J. H. Park and Y. B. Shim, *Electroanalysis*, 1993, **5**, 421–426.

26 Z. Gao, A. Ivaska and P. Li, *Anal. Sci.*, 1992, **8**, 337–343.

27 A. Safavi, M. Pakniat and N. Maleki, *Anal. Chim. Acta.*, 1996, **335**, 275–282.

28 P. K. Sahoo, B. Panigrahy, S. Sahoo, A. K. Satpati, D. Li, D. Bahadur, *Biosens Bioelectron*, 2013**, 43**,

293-296.

29 R. Z. Ouyang, S. A. Bragg, J. Q. Chambers, Z. L. Xue, *Anal Chim Acta*, 2012**, 722**, 1-7.

30 W. Chemnasiry, F. E. Hernandez, *Sensors and Actuators B: Chemical*, 2012, **173**, 322–328.

31 A. Mohadesi, Z. Motallebi, A. Salmanipour, *Analyst*, 2010, **135**, 1686–1690.

32 J. Chang, G. Zhou, E. R. Christensen, R. Heideman, J. Chen, *Anal.Bioanal. Chem*, 2014, 1–19.

33 A. Afkhami, F. Soltani-Felehgari, T. Madrakian, H.Ghaedi, M. Rezaeivala, *Anal. Chim. Acta*, 2013, **771**, 21–30.

34 D. P. Wang, Y. Tang, W. D. Zhang, *Microchim.Acta*, 2013, **180**, 1303–1308.

35 M. Sadhukhan, S. Barman, *J.Mater.Chem.A*, 2013, **1**, 2752–2756.

36 L. Chen, H. Liu, K. Yang, J. Wang and X. Wang, *Mater. Chem. Phys.*, 2008, **112**, 407–411.

37 M. Suresh, A. K. Mandal, S. Saha, E. Suresh, A. Mandoli, R. D. Liddo, P. P. Parnigotto and A. Das, *Org. Lett.*, 2010, **12**, 5406–5409.

38 Y. Y. Fu, H. X. Li and W. P. Hu, *Eur. J. Org. Chem.*, 2007, **15**, 2459–2463.

39 A. Caballero, R. Martinez, V. Lloveras, I. Ratera, J. Vidal-Gancedo, K. Wurst, A. Tarraga, P. Molina and J. Veciana, *J. Am. Chem. Soc*., 2005, **127**, 15666–15667.

40 R. Martinez, A. Espinosa, A. Tarraga and P. Molina, *Org. Lett.* 2005, **7**, 5869–5872.

41 D. W. Pan, Y. Wang, Z. P. Chen, T. T. Lou and W. Qin, *Anal. Chem.*, 2009, **81**, 5088-5094.

42 R. M. Takeuchi, A. L. Santos, P. M. Padilha and N. R. Stradiotto, *Talanta*, 2007, **71**, 771–777.

43 S. K. Alpat, U. Yuksel and H. Akcay, *Electrochem. Commun.*, 2005, **7**, 130–134.

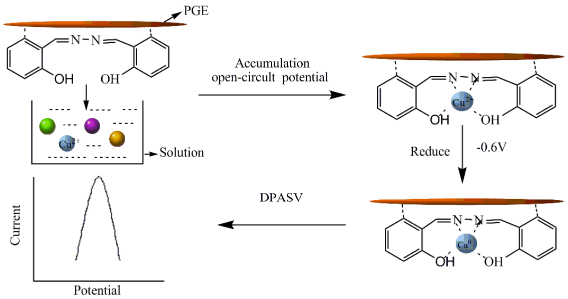
44 H. Alemu and B. S. Chandravanshi, Anal. *Chim. Acta.*, 1998, **368**, 165–173.

45 B. S. Sherigara, Y. Shivaraj, R. J. Mascarenhas and A. K. Satpati, *Electrochim. Acta.,* 2007, **52**, 3137–3142.

46 E. C. Canpolat, E. Sar, N. Y. Coskun and H. Cankurtaran, *Electroanalysis*, 2007, **19**, 1109–1115.

47 H. M. Abu-Shawish, S. M. Saadeh and A. R. Hussien, *Talanta*, 2008, **76**, 941-948.

48 M. B. Gholivand, M. Rahimi-Nasrabadi, M. R. Ganjali and M. Salavati-Niasari, *Talanta*, 2007, **73**, 553–560.



Schematic illustration of Cu^{2+} in solution detection using SA/MWCNTs/Nafion modified PGE.