Talanta 94 (2012) 178–183

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A highly sensitive electrochemical assay for silver ion detection based on un-labeled C-rich ssDNA probe and controlled assembly of MWCNTs

Genping Yan, Yonghong Wang, Xiaoxiao He*, Kemin Wang*, Jing Su, Zhifeng Chen, Zhihe Qing

State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Biology, College of Chemistry & Chemical Engineering, Hunan University, Key Laboratory for Bio-Nanotechnology and Molecule Engineering of Hunan Province, Changsha 410082, PR China

ARTICLE INFO

Article history:
Received 14 December 2011
Received in revised form 2 March 2012
Accepted 4 March 2012
Available online 10 March 2012

Keywords:
Silver ion
MWCNTs
C-rich ssDNA
MHA/SAM
Electrochemical assay

ABSTRACT

We report here a highly sensitive electrochemical sensing platform for Ag^+ detection based on Ag^+-induced conformational change of cytosine-rich single stranded DNA C-rich ssDNA probe and the controlled assembly of MWCNTs. In the protocol, the gold electrode was first modified with a dense 16-mercaptohexadecanoic acid self-assembled monolayer (MHA/SAM). The hydrophobic MHA/SAM isolated the electrode from the electroactive indicator in the aqueous solution, which resulted in the electronic transmission blocking. It was eT OFF state. In the presence of Ag^+, C–Ag^+–C coordination induced the conformational change of C-rich ssDNA probe from random-coil structure to fold into a hairpin structure, which cannot wrap on the surface of the MWCNTs. Then the "naked" MWCNTs can be assembled on the MHA/SAM gold electrode, mediating the electron transfer between the electrode and the electroactive indicator. It generated measurable electrochemical signals (eT ON). The resulting change in electron transfer efficiency was readily measured by differential pulse voltammetry at target Ag^+ concentrations as low as 1.3 nM. The linear response range for Ag^+ detection was from 10 to 500 nM. This method dose not need of electroactive molecules labeling on the C-rich ssDNA probe. Moreover, it has good selectivity to other environmentally relevant metal ions. Therefore, the developed electrochemical assay is an ideal method for Ag^+ detection with some advantages including sensitivity, selectivity, simplicity, low-cost, and no requirement for probe label preparation. We expect that this strategy could be a generalized platform for DNA-based sensing.

1. Introduction

Silver, as one of indispensible high toxic heavy metals, has been used extensively in photography, batteries and semiconductor industry [1,2]. Thousands of tons of silver and its compounds are released into the environment from industrial wastes and emissions annually [2,3]. Silver ions (Ag^+), as one of the important existence type of silver, could produce dose-dependent cytopathogenic effects on many kinds of cell types, including human gingival fibroblasts, keratinocytes, human tissue mast cells and endothelial cells, and so on, because it could bind with various metabolites and inactivate sulfhydrylenzymes [4–6]. In addition, owing to strong oxidation, Ag^+ can easily enter into the human body, leading to internal organ edema, and even to death. Thus, it is of great importance to develop sensitive and selective methods for detection of trace amounts of Ag^+ in environmental and food related samples.

Traditional methods, such as atomic absorption spectroscopy [7,8], and inductively coupled plasma-mass spectroscopy (ICP-MS) [9,10], as well as ion-selective electrodes (ISEs) [11] had been used to detect trace levels of Ag^+ in aqueous media. Most of them were somewhat sophisticated, expensive and time consuming. Recently, a number of highly sensitive and selective methodologies for the determination of Ag^+ have been developed, based on chromophores [12], semiconductor nanocrystals [13], gold nanoparticles [14], carbon based materials [15,16], oligonucleotides [17], DNAzymes [18]. Among these methodologies, DNA–metal base pairs as the sensing elements currently attract considerable attention for sensitive and specific detection of Ag^+. Since Ono et al. found Ag^+ can selectively coordinate cytosine (C) bases to form stable C–Ag^+–C complex [19], many novel colorimetric biosensors [20,21] as well as fluorescent biosensors [22,23] have been developed to detect Ag^+ in aqueous media by taking advantage of specific C–Ag^+–C interaction and signal amplification of nanomaterials. Although these methods have their own advantages, in practical detection, they still have some limitations and disadvantages, such as high background signal, relatively low sensitivity, high cost in synthesis of dye labeled DNA sequence and so on. Electrochemical assays demonstrate its superiority in sensitivity, simple instrumentation and easy

* Corresponding authors. Tel.: +86 731 88821566; fax: +86 731 88821566.
E-mail addresses: xiaoxiaohe@hnu.edu.cn (X. He), kmwang@hnu.edu.cn (K. Wang).

0039-9140/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2012.03.014

miniaturization, which is very important in practical application. But until now, few electrochemical assays for Ag^+ detection using the specific interaction of Ag^+ with C–C mismatches and signal amplification of nanomaterials have been developed.

Carbon nanotubes (CNTs) exhibit great chemical stability, large aspect ratio, excellent electrical conductivity, and high electrocatalytic activity [24]. In addition, CNTs can interact with biomolecules through versatile covalent and nocovalent functionalization strategies. These properties make CNTs widely used in biosensors. Among these CNTs based sensors, single-walled carbon nanotubes (SWCNTs) were mostly used [22]. As reported, MWCNTs, which has similar properties, was also confirmed to be a good material in nucleic acid detection. The process of the ssDNA–CNT association undergoes much faster on MWCNTs than that of on SWCNTs. Moreover, MWCNTs can also be well dispersed when wrapped by ssDNA [25–27].

In this paper, we demonstrate the first use of the specific interaction of Ag^+ with C–C mismatches and the controlled assembly of MWCNTs for developing a highly sensitive electrochemical sensing platform to detect Ag^+. In the protocol, one un-labeled C-rich ssDNA probe was employed. The presence of Ag^+ can induce conformational change of cytosine-rich DNA probe from random-coil structure to fold into a hairpin structure, which cannot wrap on the surface of the MWCNTs. Then the "naked" MWCNTs can be assembled onto the 16-mercaptohexadecanoic acid self-assembled monolayer (MHA/SAM) modified gold electrode, resulting in the electron transfer between the electrode and the electroactive indicator (ferrocenecarboxylic acid (FcCOOH)). It generated measurable peak current signals. As the peak current on the gold electrode depended on the assembly of MWCNTs, which was correlative with the concentration of Ag^+, the Ag^+ ions could just be indirectly detected. Here, the effect of Na^+ concentration and incubation time of MWCNTs/Ag^+/C-rich ssDNA mixture with MHA/SAM modified electrode on this assay had been investigated, respectively. Under the optimized conditions, the assay showed good electrochemical response upon the addition of Ag^+ and had good selectivity to other environmentally relevant metal ions.

2. Experimental

2.1. Materials and instruments

Multi-walled carbon nanotubes (MWCNTs) (purity >90%, diameter <10 nm, length 5–15 μm) were purchased from Shenzhen Nanotech Port Company (Shenzhen, China). The cytosine-rich single stranded DNA (C-rich ssDNA) was purchased from Sangon Inc. (Shanghai, China). The sequence of the C-rich ssDNA probe used in this work was as follows: 5′-CTCTCTTCTCTTCATTTTTCAACACAACACAC-3′. 3-(*N*-morpholino)propanesulfonic acid (MOPS), $AgNO_3$ were obtained from Dingguo bio-technology Co. Ltd. (Beijing, China). 90% 16-mercaptohexadecanoic acid (MHA) and ferrocenecarboxylic acid (FcCOOH) were purchased from Sigma Aldrich Chemical Co. All other chemicals were obtained from Reagent & Glass Apparatus Corporation of Changsha and were used without further purification. All solutions were prepared and diluted using ultrapure water (18.2 MΩ cm) from the Millipore Milli-Q system.

Electrochemical measurements were performed at room temperature using a CHI660A electrochemical workstation (Shanghai Chenhua Instrument Corporation, China). A conventional three-electrode cell was employed, which involved a gold working electrode of a diameter of 2 mm, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE).

2.2. Pretreatment of MWCNTs

To lower the background and improve the utilization efficiency of C-rich DNA, the purchased MWCNTs were further purified. Briefly, 5 mL of 10 mM MOPS buffer (pH 7.0) containing 0.5 mg/mL MWCNTs was sonicated (200 W) for 2 h in ice bath using an ultrasonic crasher to obtain a black dispersed suspension. Then the resulting suspension was centrifuged at 1000 rpm for 5 min to remove large MWCNTs. The small piece of MWCNTs supernatant was collected and then for further sensing application. And the final concentration was about 0.1 mg/mL.

2.3. Preparation of MHA/SAM modified gold electrode

The insulated 16-mercaptohexadecanoic acid self-assembled monolayer modified gold electrode can be a good platform for controlled assembly of MWCNTs as signal transduction. It was prepared as follows. The gold electrode (2 mm diameter) was dipped in freshly prepared piranha solution (H_2SO_4/H_2O_2, 7:3 by volume) for 10 min and rinsed with ultrapure water thoroughly. Then the gold electrode was polished carefully with alumina powder of 0.3 μm and 0.05 μm, followed by sequentially sonicated for 5 min each in ultrapure water, ethanol, and ultrapure water. The electrode was then scanned in 0.1 M H_2SO_4 between −0.2 V and 1.55 V at 100 mV/s until a reproducible cyclic voltammogram (CV) was obtained. After being washed with ultrapure water and dried with purified nitrogen. The pretreated electrodes were immersed into an ethanol solution of MHA (20 mM) for 24 h at 25 °C to allow formation of a dense MHA self-assembled monolayer. The electrodes (denoted as MHA/SAM modified electrodes, hereafter) were then thoroughly rinsed using ethanol to remove MHA adsorbed on the electrode surface and followed by drying under mild N_2 stream.

2.4. Analytical procedure

Different concentrations of Ag^+ were incubated in MOPS buffer (100 μL, pH 7.0) containing 150 mM of $NaNO_3$ and 20 nM of C-rich ssDNA probe for 10 min at room temperature. Then 20 μL of dispersed MWCNTs (0.1 mg/mL) was added to this mixture and incubated for 15 min under vibration. The resulting solution (10 μL) was dropped on the surface of MHA/SAM modified electrodes and incubated in a humid atmosphere at room temperature for 80 min. Subsequently, the electrode was thoroughly rinsed with ethanol and ultrapure water to remove MWCNTs weakly adsorbed on the electrode surface. Then the electrodes were dried under N_2 stream before electrochemical measurements. All electrochemical measurements were conducted in 20 mM PBS buffer solution (pH 7.0) containing 5 mM FcCOOH and 0.1 M $NaClO_4$. Cyclic voltammograms (CV) measurements were recorded using a step potential of 1 mV within the potential range from −0.2 V to +0.6 V at a scan rate of 100 mV/s. Differential pulse voltammogram (DPV) has been performed within the potential range from 0 V to +0.6 V under modulation amplitude of 50 mV and sample width 16.7 ms. The reported DPV curves were baseline correction. Electrochemical impedance spectroscopy (EIS) was performed in the frequency range from 0.1 Hz to 100 kHz with 10 mV as the frequency modulation at a bias potential of 0.24 V.

3. Results and discussion

3.1. Experiment principle

The principle for electrochemical detection of Ag^+ based on MWCNTs and un-labeled silver ion specific oligonucleotide was demonstrated in Fig. 1. The clean gold electrode was first modified with a dense MHA/SAM. The hydrophobic MHA/SAM isolated

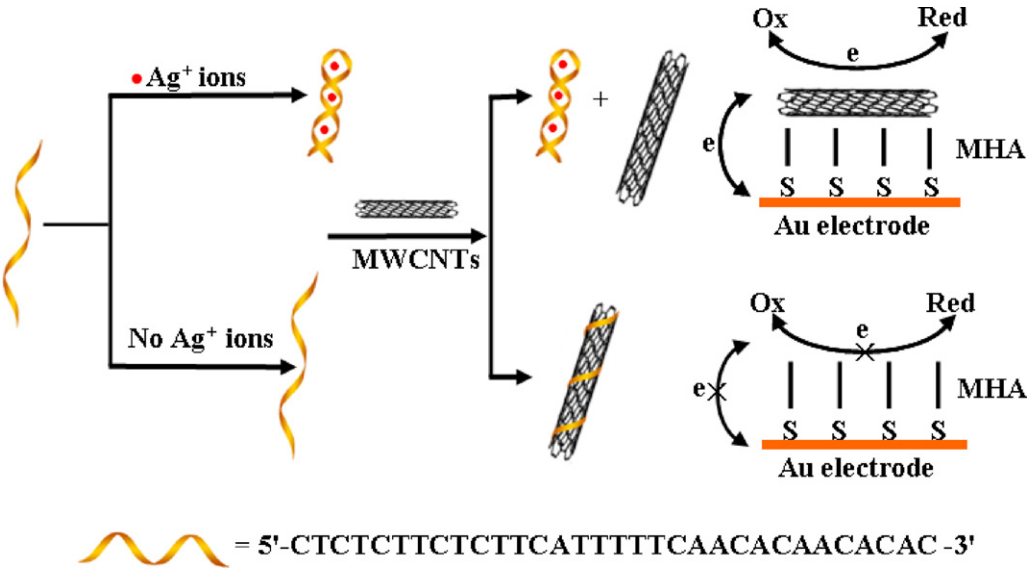

Fig. 1. Schematic illustration of the electrochemical assay for Ag^+ detection based on un-labeled C-rich ssDNA probe and controlled assembly of MWCNTs.

the electrode from the aqueous solution. Thus, the electron transfer between redox solutes and the electrode was blocked, with no electrochemical signal detected [28–30]. Upon the addition of Ag^+, the complexation of Ag^+ with the cytosine bases of C-rich ssDNA probe yielded a rigid hairpin structure, and Ag^+/C-rich ssDNA complex cannot be adsorbed efficiently on MWCNTs, the MWCNTs were "naked" and would be precipitated from the solution. When the mixture was dipped on the MHA/SAM electrode, the "naked" MWCNTs were assembled on the electrode by van der Waals and hydrophobic interaction. It will efficiently mediate the electron transfer between the electrode and the electroactive indicator. And then a strong redox current was generated. It was eT on state. In the absence of Ag^+, the C-rich ssDNA probe adsorbed on MWCNTs via π–π stacking interactions between DNA bases and MWCNTs to form a MWCNTs/C-rich ssDNA complex stably dispersed in the solution. Then it would not be adsorbed on the MHA/SAM due to strong electrostatic and hydration repulsions between the MWCNTs/C-rich ssDNA complex and the negatively charged SAM, keeping the MHA/SAM isolated with no background current signal being generated (eT off).

3.2. Characterization and feasibility investigation of the electrochemical assay

CV response was recorded using the MHA/SAM modified electrodes (Fig. 2A). No remarkable electrochemical peak was observed for FcCOOH at the MHA/SAM modified electrode (curve a), which indicated that a densely packed isolating layer on the electrode formed by the long chain alkanethiol completely blocked the electron transfer between the electrode and the electroactive indicators. Incubation of a suspension of the MWCNTs/C-rich ssDNA complex on the electrode had little effect on the CV response, and no significant increase of the redox current (curve b) was observed. It indicated that the adsorption of the MWCNTs/C-rich ssDNA complex on the MHA/SAM was precluded due to the strong electrostatic and hydration repulsion between the MWCNTs/C-rich ssDNA complex and the negatively charged MHA/SAM surface. However, in the presence of Ag^+ ions, a couple of well-defined redox peaks appeared at 0.25 and 0.35 V, characteristic electrochemical peaks of ferrocene derivatives. This demonstrated that the isolating nature of the MHA/SAM was altered due to the Ag^+/C-rich ssDNA complex cannot be adsorbed on MWCNTs. The "naked" MWCNTs were

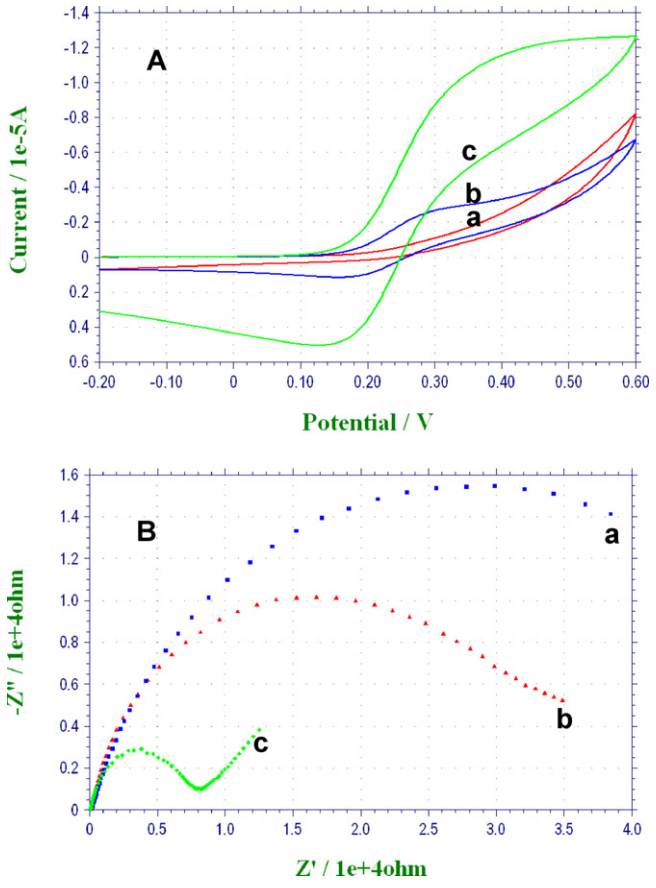

Fig. 2. Feasibility of the electrochemical assay. (A) CV of the MHA/SAM-modified electrode (a), CV of the MHA/SAM-modified electrode after incubation with the MWCNTs/C-rich ssDNA complex (b), CV of the MHA/SAM-modified electrode after incubation with the Ag^+/C-rich DNA complex and MWCNTs (c); (B) Nyquist plots of the MHA/SAM-modified electrode (a), Nyquist plots of the MHA/SAM-modified electrode after incubation with the MWCNTs/C-rich ssDNA complex (b), Nyquist plots of the MHA/SAM-modified electrode after incubation with Ag^+/C-rich ssDNA complex and MWCNTs (c) (250 nM Ag^+, 20 nM C-rich DNA).

assembled on the MHA/SAM, thus facilitating the electron transfer between the electrode and FcCOOH. In addition, EIS measurements were performed to further investigate the isolating properties of the MHA/SAM for the Ag^+ ions sensing (Fig. 2B). The MHA/SAM modified gold electrode exhibited large impedance (curve a) due to the hydrophobic isolating layer blocked electron transfer between the electrode and the electroactive indicators. Incubation of the MWCNTs/C-rich ssDNA complex on the electrode induced slightly decreased impedance, since there was trace dissociative MWCNTs in the suspension of the MWCNTs-C-rich ssDNA complex. However, incubation of the Ag^+/C-rich ssDNA complex and MWCNTs, MWCNTs on the electrode resulted in substantial decrease of electrochemical impedance (curve c). Because dsDNA formed via C–Ag^+–C base pairs cannot be absorbed on the MWCNTs. These "naked" MWCNTs could be assembled on the MHA/SAM, thus facilitating the electron transfer between the electrode and FcCOOH. EIS measurements and CV response both validated the mechanism of the developed electrochemical strategy for Ag^+ ions detection.

3.3. Optimization of experimental conditions

3.3.1. Effect of Na^+ concentration on the assay

Na^+ is very important to the stability and conformation of DNA [31,32]. Therefore, the effect of Na^+ concentration on the C-rich ssDNA probe based Ag^+ assay has been investigated. Fig. 3A shows DPV response of Na^+ ion concentration. The peak current increased rapidly with the Na^+ ion concentration increasing (curve a). While the concentration of Na^+ was over 150 mM, the current signal tended to increase slowly. Considering higher Na^+ concentration may affect the characteristics of C-rich ssDNA (easier to disassociate ssDNA from MWCNTs surface) and increase background current (curve b), 150 mM was then employed as the optimal Na^+ concentration to obtain a high Signal/Background (S/B) ratio.

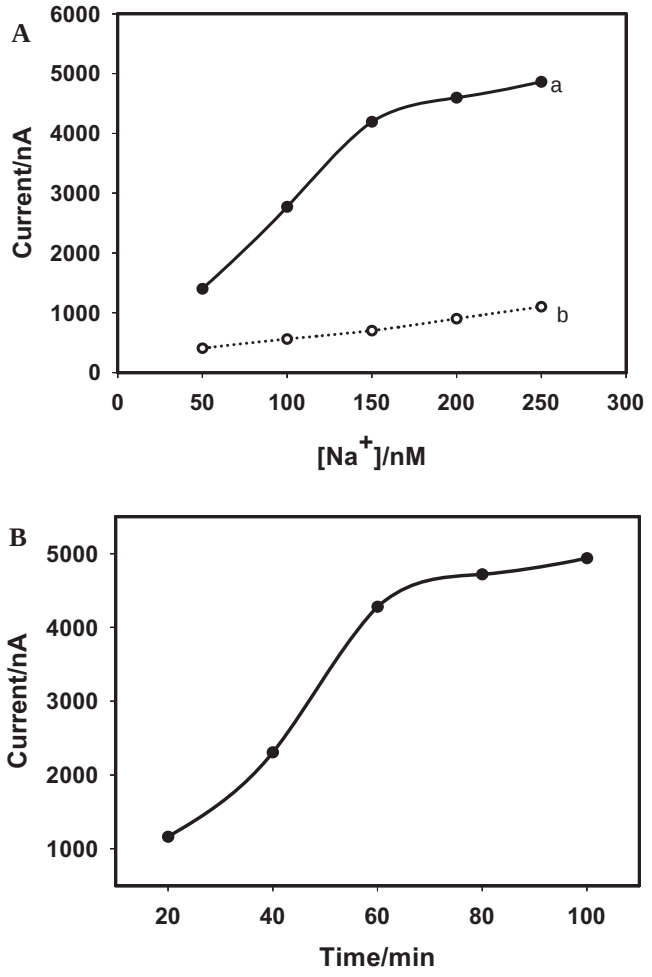

Fig. 3. (A) Optimization of Na^+ concentration on the electrochemical assay for Ag^+ detection (Na^+ concentration: 50–250 nM). (B) Optimization of the incubation time of MWCNTs on the MHA/SAM modified gold surface (50 nM Ag^+, 20 nM C-rich DNA).

3.3.2. Effect of incubation time of MWCNTs/Ag^+/C-rich ssDNA mixture with MHA/SAM modified electrode

As we described in the principle, in the presence of Ag^+, the complexation of Ag^+ with the cytosine bases of C-rich ssDNA yielded a rigid hairpin structure, and Ag^+/C-rich ssDNA complex cannot be adsorbed efficiently on MWCNTs. Then the MWCNTs would be precipitated from the solution. Therefore, when the mixture was dipped on the electrode, it took time for MWCNTs to interact with MHA fully. The incubation time of MWCNTs/Ag^+/C-rich DNA mixture with the electrode was also an important influence factor to the peak current. Fig. 3B shows that when the incubation time was over 80 min, the peak current increased to a platform. Thus, 80 min was chosen as the appropriate incubation time in the following experiments.

3.4. Sensitivity of the electrochemical assay

The detection performance of the electrochemical Ag^+ assay was evaluated by exposing the sensor to a series of Ag^+ concentrations under the same experimental condition. The electrochemical response to different concentrations of Ag^+ was shown in Fig. 4. As can be seen from Fig. 4A, the peak current increased with the increasing Ag^+ concentration within a range from 10 to 500 nM. Fig. 4B shows Δi value plotted against the concentration of Ag^+ with error bar (standard deviation from the mean, $n = 3$). Δi equals the detection value subtracted the blank value. Linear relationship between the peak current and the Ag^+ concentration was observed in the range of 10–60 nM with a correlation factor 0.9833. The linear regression equation was $i = 108.42\ [Ag^+] - 116.14$ (Fig. 4B (inset)). Meanwhile, the detection limit was 1.3 nM as calculated according to the rule of three times standard deviation over the background signal. With respect to sensitivity, this electrochemical assay for Ag^+ detection was better than some previous reported Ag^+ assay [15,17,23,33].

3.5. Selectivity of the electrochemical assay

The selectivity of the electrochemical assay was determined by challenging it with different environmentally relevant metal ions (Li^+, Cd^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+}, Co^{2+}, Ca^{2+}, Mg^{2+}, Hg^{2+}, Pb^{2+}, and Fe^{2+}) with a concentration of 500 nM concentrations, which was 10-fold higher than that of Ag^+ ions. The DPV responses of the electrochemical assay to all the ionic species investigated were summarized in Fig. 5. Among the various metal ions studied, Ag^+ showed the highest signal gain change compared with the other metal ions. It was obvious that the specific recognition of C–C mismatch bases for Ag^+ endowed the electrochemical assay with the high selectivity.

3.6. Reproducibility and stability of the Ag^+ sensing assay

The repeatability of the electrode preparation has been investigated. The current signals of 250 nM Ag^+ in 20 mM PBS buffer solution (pH 7.0) containing 5 mM FcCOOH and 0.1 M $NaClO_4$, was measured with five different electrodes, changed with a RSD of 7.2%. This demonstrated that the repeatability of the electrode preparation was good. In addition, the repeatability and reproducibility of

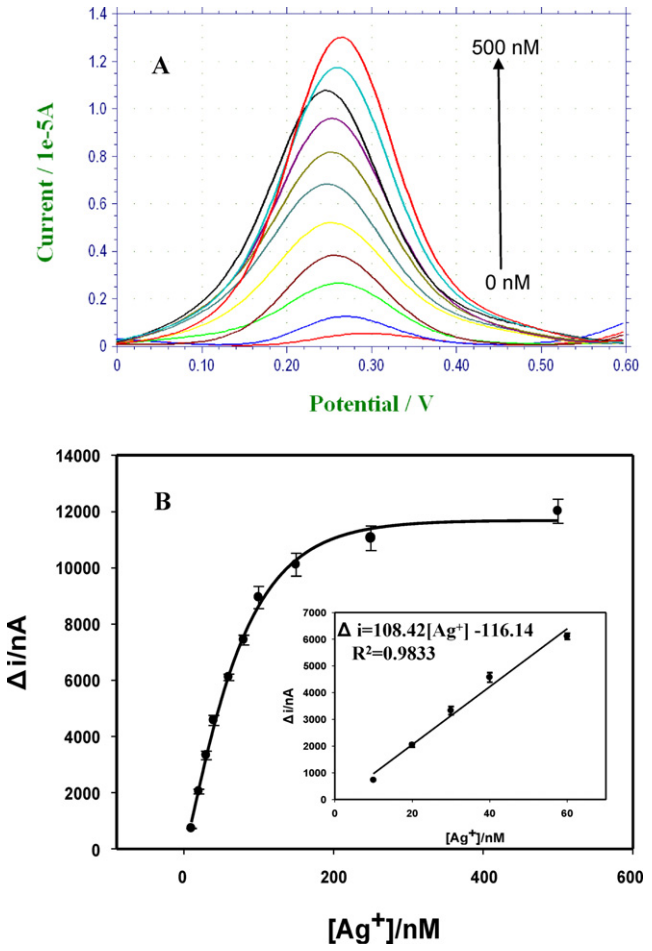

Fig. 4. (A) Typical DPV responses of the electrochemical assay with a series of concentrations of Ag^+ (0 nM, 10 nM, 20 nM, 30 nM, 40 nM, 60 nM, 80 nM, 100 nM, 150 nM, 250 nM, 500 nM). (B) Δi value plotted against the concentration of Ag^+ with error bar (standard deviation from the mean, $n = 3$). Δi equals the detection value subtracted the blank value ($\Delta i = i_{\text{with } Ag^+} - i_{\text{without } Ag^+}$).

the measurements for one modified electrode was measured. Continuous detections of 250 nM Ag^+ in 20 mM PBS buffer solution (pH 7.0) containing 5 mM FcCOOH and 0.1 M $NaClO_4$ were performed five times with the same electrode, and an acceptable reproducibility with a 6.5% relative standard deviation (RSD) was obtained.

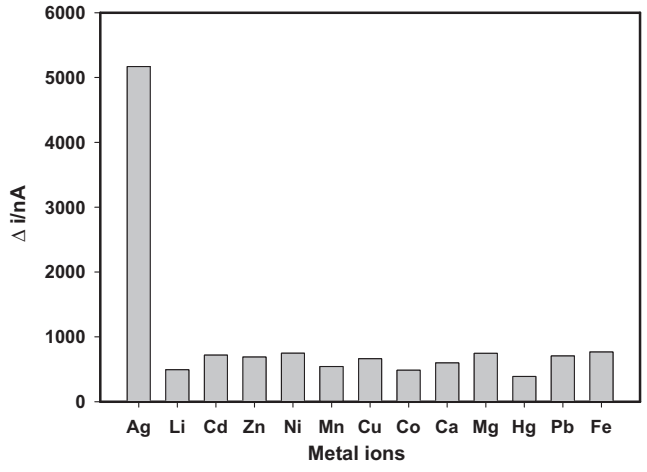

Fig. 5. Selectivity of the electrochemical assay. Ag^+ was 50 nM, all other competing ions were 500 nM.

Table 1
Detection of Ag^+ in water samples ($n = 5$).

Sample	Added (nM)	Found (nM)	Recovery
Lake water	25	26 ± 3	104%
	35	36 ± 3	103%
	80	79 ± 2	102%
	100	96 ± 4	96%
River water	25	24 ± 1	96%
	40	43 ± 4	108%
	90	92 ± 3	102%
	120	118 ± 5	98%

These results demonstrated that this Ag^+ sensing system had a good reproducibility. The stability of the Ag^+ sensing assay was also studied. The current response of 250 nM Ag^+ in 20 mM PBS buffer solution (pH 7.0) containing 5 mM FcCOOH and 0.1 M $NaClO_4$ was measured at a MWCNTS/MHA gold electrode which was stored for 14 days at 4 °C. The oxidation peak currents retain 92% of their initial response values. All these experimental results demonstrated that this sensing system has a very good repeatability, reproducibility and stability.

3.7. Practical application of the Ag^+ sensing assay

Practical application of the present method has been investigated. Ag^+ was analyzed in real samples (lake water and river water) using the standard addition method. All samples were first filtered by a 0.22 μm membrane to remove particulate matters. Then the concentration of Ag^+ in the samples was analyzed by the proposed method (Table 1). The recoveries ranging from 96% to 108% after standard additions are satisfactory, these results demonstrated that this sensor can be challenged by real water samples and has great potential in practical applications.

4. Conclusions

In conclusion, a novel signal on electrochemical assay for Ag^+ detection based on Ag^+-induced conformational change of cytosine-rich ssDNA probe and controlled assembly of MWCNTs has been developed. Compared with other Ag^+ detection methods, merits can be listed as follows. First, it achieved higher sensitivity through the signal amplification of easy produced MWCNTs. Second, one un-labeled C-rich ssDNA probe was employed, which cut down its cost and simplified the experiment procedure in practical detection. What's more, the MHA/SAM electrode can be a common detection platform based on carbon or other nanomaterial for signal transduction in electrochemical sensing. We believe that this strategy could be a generalized platform for DNA-based other heavy metals sensing and will find great application in real environmental analysis.

Acknowledgments

This work was supported in part by the Key Project of Natural Science Foundation of China (90606003, 21175039, and 21190044), International Science & Technology Cooperation Program of China (2010DFB30300), Key Technologies Research and Development Program of China (2011AA02a114), Research Fund for the Doctoral Program of Higher Education of China (20110161110016) and project supported by Hunan Provincial Natural Science Foundation and Hunan Provincial Science and Technology Plan of China (10JJ7002, 2011FJ2001).

References

[1] J.B. Brower, R.L. Ryan, M. Pazirandeh, Environ. Sci. Technol. 31 (1997) 2910–2914.
[2] H.T. Ratte, Environ. Toxicol. Chem. 18 (1999) 89–108.
[3] J.L. Barriada, A.D. Tappin, E.H. Evans, E.P. Achterberg, Trends Anal. Chem. 26 (2007) 809–817.
[4] A. Schedle, P. Samorapoompichit, X.H. Rausch-Fan, A. Franz, W. Fureder, W.R. Sperr, W. Sperr, A. Ellinger, R. Slavicek, G. Boltz-Nitulescu, P. Valent, J. Dent. Res. 74 (1995) 1513–1520.
[5] E. Hidalgo, C. Dominguez, Toxicol. Lett. 98 (1998) 169–179.
[6] K.M.V. Poon, A. Burd, Burns 30 (2004) 140–147.
[7] S. Dadfarnia, A.M.H. Shabani, M. Gohari, Talanta 64 (2004) 682–687.
[8] Q.S. Pu, Q.Y. Sun, Z.D. Hu, Z.X. Su, Analyst 123 (1998) 239–243.
[9] M. Krachler, C. Mohl, H. Emons, W. Shotyk, Spectrochim. Acta Part B 57 (2002) 1277–1289.
[10] K. Ndung, M.A. Ranville, R.P. Franks, A.R. Flegal, Mar. Chem. 98 (2006) 109–120.
[11] C.-Z. Lai, M.A. Fierke, R.C. Costa, J.A. Gladysz, A. Stein, P. Bühlmann, Anal. Chem. 82 (2010) 7634–7640.
[12] A. Coskun, E.U. Akkaya, J. Am. Chem. Soc. 127 (2005) 10464–10465.
[13] J. Wang, J.G. Liang, Z.H. Sheng, Microchim. Acta 167 (2009) 281–287.
[14] C.K. Wu, C. Xiong, L.J. Wang, C.C. Lan, L.S. Ling, Analyst 135 (2010) 2682–2687.
[15] Y.Q. Wen, F.F. Xing, S.J. He, S.P. Song, L.H. Wang, Y.T. Long, D. Li, C.H. Fan, Chem. Commun. 46 (2010) 2596–2598.
[16] H.L. Li, J.F. Zhai, X.P. Sun, Langmuir 27 (2011) 4305–4308.
[17] Y.H. Lin, W.L. Tseng, Chem. Commun. 43 (2009) 6619–6621.
[18] X.H. Zhou, D.M. Kong, H.X. Shen, Anal. Chem. 82 (2010) 789–793.
[19] A. Ono, S. Cao, H. Togashi, M. Tashiro, T. Fujimoto, T. Machinami, S. Oda, Y. Miyake, I. Okamoto, Y. Tanaka, Chem. Commun. 39 (2008) 4825–4827.
[20] T. Li, L.L. Shi, E.K. Wang, S.J. Dong, Chem. Eur. J. 15 (2009) 3347–3350.
[21] X.H. Zhou, D.M. Kong, H.X. Shen, Anal. Chim. Acta 678 (2010) 124–127.
[22] C. Zhao, K.G. Qu, Y.J. Song, C. Xu, J.S. Ren, X.G. Qu, Chem. Eur. J. 16 (2010) 8147–8154.
[23] L. Wang, J.Q. Tian, H.L. Li, Y.W. Zhang, X.P. Sun, Analyst 136 (2011) 891–893.
[24] S.N. Kim, J.F. Rusling, F. Papadimitrakopoulos, Adv. Mater. 19 (2007) 3214–3228.
[25] H.L. Li, J.Q. Tian, L. Wang, Y.W. Zhang, X.P. Sun, J. Mater. Chem. 21 (2011) 824–828.
[26] L. Zhang, C.Z. Huang, Y.F. Li, S.J. Xiao, J.P. Xie, J. Phys. Chem. B 112 (2008) 7120–7122.
[27] M. Zheng, A. Jagota, E.D. Semke, B.A. Diner, R.S. Mclean, S.R. Lustig, R.E. Richardson, N.G. Tassi, Nat. Mater. 2 (2003) 338–342.
[28] Y.H. Wang, D. Maspoch, S.J. Zou, G.C. Schatz, R.E. Smalley, C.A. Mirkin, Proc. Natl. Acad. Sci. U. S. A. 103 (2006) 2026–2031.
[29] H.G. Nie, S.J. Liu, R.Y. Yu, J.H. Jiang, Angew. Chem. Int. Ed. 48 (2009) 9862–9866.
[30] L.Q. Guo, N. Yin, D.D. Nie, F.F. Fu, G.N. Chen, Chem. Commun. 47 (2011) 10665–10667.
[31] M.T. Record Jr., C.P. Woodbury, T.M. Lohman, Biopolymers 15 (1976) 893–915.
[32] A.A. Zinchenko, K. Yoshikawa, Biophys. J. 88 (2005) 4118–4123.
[33] X.X. Liu, W. Li, Q.P. Shen, Z. Nie, M.L. Guo, Y.T. Han, W. Liu, S.Z. Yao, Talanta 85 (2011) 1603–1608.