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The Ag^+–G interaction inhibits the electrocatalytic oxidation of guanine – A novel mechanism for Ag^+ detection

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ABSTRACT

The heavy metal ions–nucleobases interaction is an important research topic in environmental and biochemical analysis. The presence of the silver ion (Ag^+) may influence the formation of oxidation intermediate and the electrocatalytic oxidation activity of guanine (G), since Ag^+ can interact with guanine at the binding sites which are involved in the electrocatalytic oxidation reaction of guanine. According to this principle, a new electrochemical sensor for indirectly detecting Ag^+ based on the interaction of Ag^+ with isolated guanine base using differential pulse voltammetry (DPV) was constructed. Among the heavy metal ions examined, only Ag^+ showed the strongest inhibitory effect on the electrocatalytic oxidation of guanine at the multi-walled carbon nanotubes modified glassy carbon electrode (CNTs/GC). And the quantitative study of Ag^+ based on Ag^+–G sensing system gave a linear range from 100 nM to 2.5 μM with a detection limit of 30 nM. In addition, this modified electrode had very good reproducibility and stability. The developed electrochemical method is an ideal tool for Ag^+ detection with some merits including remarkable simplicity, low-cost, and no requirement for probe preparation.

1. Introduction

The detection of toxic heavy metal ions can provide important information concerning environment pollution and control [1,2]. As an indispensable heavy metal in our daily life, silver (Ag) and its compounds have been used extensively in photography, batteries and semiconductor industry [3–5]. Moreover, silver compounds play an essential role in many medical applications such as pharmaceutical antibacterial and anti-HIV preparations, implanted prostheses, and water disinfection due to the anti-bacterial properties of Ag [6,7]. However, these widespread applications have led to increased silver content in environment (about 450 000 kg annually). Although only a small portion is biologically available, it has been found that silver accumulated in the skin, gum, liver and kidney of human may lead to grayish-blue skin discoloration (known as Argyria) [8]. According to the World Health Organization (WHO), the standard safe concentration of Ag^+ for human is <0.05 ppm [9]. The Environmental Protection Agency (EPA) approves certification of silver as a pesticide (EPA 73499-2) and limits the discharge concentration of soluble silver to 5 ppm [10]. Therefore, it is of great importance to develop techniques for routine and effective monitoring of the silver levels in a great variety of environmental and biological samples.

Towards this goal, various methods for the detection of Ag^+ have been developed based on different technologies. Traditional methods, such as inductively coupled plasma atomic emission spectrometry (ICP-AES) [11,12], inductively coupled plasma mass spectrometry (ICP-MS) [13,14] and flame atomic absorption spectrometry (FAAS) [15,16], are very efficient but normally require sample pretreatment and quite expensive instrument, which are not suitable for on-site applications. Recently, many DNA biosensors based on the interactions of Ag^+ and DNA bases have attracted substantial attention. It was reported that Ag^+ has great affinity to DNA bases, especially can exclusively combine with cytosine (C) to form C–Ag^+–C mismatch in DNA duplexes [17]. Based on this feature, some nucleic acid based Ag^+ sensors have been developed, such as colorimetric Ag^+ sensors using a G-quadruplex-based DNAzyme [18] or DNA–gold nanoparticle conjugate [19], fluorescent Ag^+ sensor with double-labeling [17], and electrochemical Ag^+ sensor based on Y-type DNA probe [20]. Another example of DNA base readily bound to Ag^+ is guanine, which can interact with Ag^+ through its N_7 and C_6O groups [21,22]. In comparison with plenty of biosensors based on Ag^+–C interaction, the application of Ag^+–G interaction in biosensing is scarce. Zhou et al. [23] successfully developed a new DNAzyme-based Ag^+ detection method which relied on this Ag^+–G interaction. All these applications demonstrated that the Ag^+–DNA bases interaction is a promising platform to develop new methods alternative to traditional Ag^+ assays. However, most of these sensors were fabricated by the oligonucleotide probes, suffering from the sophisticated and

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expensive DNA synthesis and modification. Developing Ag^+ biosensors straightforwardly dependent on nucleobase will significantly simplify the probe preparation and save the fabrication cost compared with DNA-based sensors. To the best of our knowledge, these nucleobase-based Ag^+ sensors are rare.

Herein, we present a novel and simple electrochemical experimental platform to study the influence of Ag^+ on the electrochemical event of guanine and quantitatively detect Ag^+ simultaneously based on Ag^+–G interaction. Guanine is an important target for DNA electrochemical analysis because it not only plays a key role in the oxidation damage of DNA by various types of oxidants and free radicals but also has the smallest redox potential among all nucleobases [24,25]. Although the electrochemistry of guanine is well understood, the electrochemical event of guanine interacted with Ag^+ is little known. Taking advantage of multiple-walled carbon nanotubes (CNTs) modified glassy carbon electrode [26], we demonstrated that the inhibitory effect of the Ag^+ on electrochemistry of guanine and developed the nucleotide-based Ag^+ sensor based on this phenomenon. The easy fabrication of the Ag^+–nucleobase complex and the intrinsic features of electrochemical sensors, including high sensitivity, simple instrumentation, low production cost, fast response and portability [27], will make the proposed sensor an effective approach for Ag^+ detection.

2. Experimental

2.1. Apparatus and chemicals

All the eletrochemical measurements were carried out on a CHI 660A electrochemical workstation (Chenhua Instrument Company of Shanghai, China) with conventional three-electrode cell. The bare glassy carbon (GC, 3 mm in diameter) or modified GC electrodes were used as working electrode. A saturated calomel electrode (SCE) and a platinum foil were used as the reference and counter electrodes, respectively. All potentials were referred to SCE.

The multi-walled carbon nanotubes (CNTs) with diameter of about 20–30 nm were purchased from Shenzhen Nanotech Port Company (Shenzhen, China). Guanine was purchased from Bio Basic Inc. (Shanghai, China). $AgNO_3$ was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Other reagents were of at least analytical reagent grade. 0.1 M acetate buffer solution (ABS, pH 5.0) was used as the electrolyte. Double distilled water was used throughout.

2.2. Fabrication of the CNTs modified glassy carbon electrode (CNTs/GC)

The CNTs were purified according to the procedure previously published in literature [28]. First the CNTs were sonicated in a mixture of concentrated sulfuric acid–nitric acid (3:1, v/v) for about 3 h. Then the treated CNTs were filtered and washed with double distilled water. The final precipitate was dried in oven. The resulting black powder was sonicated in double distilled water for about 2–3 h with a concentration of 0.5 mg mL^{-1}.

Prior to use, the glassy carbon electrode was polished to a mirror-like surface with 0.3 μm and then 0.05 μm alumina slurry. The electrode was then rinsed with double distilled water thoroughly. A 5.0 μL of CNTs suspension was cast onto the electrode surface and dried under an infrared lamp to form the CNTs modified electrode (CNTs/GC). The modified electrode was stored at 4 °C, when not in use.

2.3. Analytical procedure

0.1 M ABS (pH 5.0) containing 5.0 μM guanine and different concentrations of Ag^+ were first incubated for 20 min at room temperature. Then a CNTs/GC electrode or unmodified electrode was dipped into this reaction solution to accumulate at 0.3 V for 240 s. Differential pulse voltammetry (DPV) was performed from 0.6 to 1.1 V with an increment potential of 0.004 V, a pulse amplitude of 0.05 V, a pulse width of 0.05 s, a sample width of 0.0167s, a pulse period of 0.2 s and a quiet time of 2 s. Cyclic voltammograms were recorded between 0.6 and 1.1 V at a scan rate of 0.1 V s^{-1}.

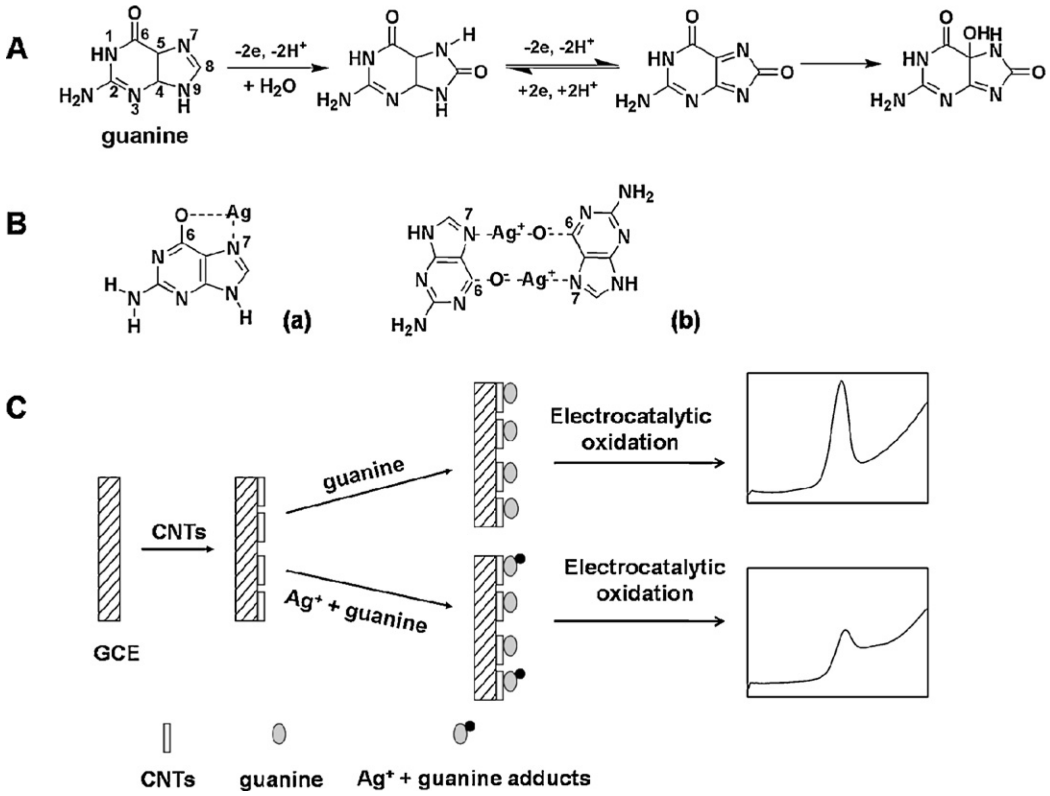
3. Results and discussion

3.1. Ag^+–G sensing system based on electrocatalytic oxidation of guanine

Ag^+ favors self-association with the N_7 and C_6O of guanine and its derivatives in dilute solution [29,30] (Scheme 1B), and N_7 of guanine is just the main reactive site involved in the electrocatalytic oxidation reaction of guanine [31,32] (Scheme 1A). Therefore, the adducts of Ag^+ with guanine may interfere with the formation of the 8-oxoderivative intermediate and then strongly influence the electrocatalytic oxidation activity of guanine (Scheme 1C). We expected to explore the effect of Ag^+–G interaction on the electrochemical event of guanine, and hypothesized that if the change in electrocatalytic oxidation activity of guanine is dependent on Ag^+ concentration, a new Ag^+–G sensing system might be developed.

The electrocatalytic oxidation response of guanine at different electrodes was studied first. Fig. 1 shows the cyclic voltammograms of the bare GC (A) and the CNTs/GC (B) electrodes in 0.1 M acetate buffer solution (pH 5.0) without (curve a) or with (curve b) 5.0 μM guanine at the scan rate of 0.1 V s^{-1}. In the absence of guanine, no obvious current peak signal was observed both at the bare GC and CNTs/GC electrodes. And the background current of the CNTs/GC electrode was found to be somewhat higher than that of the bare GC electrode, which can be ascribed to the large surface area of CNTs [33]. After 5.0 μM guanine was added, in the case of the CNTs/GC electrode, the oxidation of guanine showed a greatly increased current signal at +0.890 V in comparison with the bare GC electrode. In addition, there were no reduction currents observed within the investigated potential range, which indicated that the oxidation of guanine is an electrochemical irreversible process. The above presented experimental results demonstrated that CNTs played a critical role in the catalytic oxidation of guanine. This may be attributed to the following reasons: first, the functional groups (e.g. –COOH) and large specific surface area of CNTs can accumulation more guanine resulting in better current signals; then, the excellent electronic properties and subtle one-dimensional tubular structure of CNTs have the ability to promote the electron transfer rate [34].

Then to test the hypothesis mentioned above, the change of the electrocatalytic oxidation signal of guanine based on the interaction between Ag^+ and guanine was investigated by differential pulse voltammetry as it processes a higher sensitivity than cyclic voltammetry (Fig. 2). Firstly, we studied the DPV signals of 0.1 M acetate buffer solutions (pH 5.0) without (curve a) and with (curve b) guanine at the CNTs/GC electrode. In the absence of guanine, there was no obviously peak appeared, while a sharp oxidation peak at +0.814 V with a current of 10.5 μA can be observed in the present of guanine. However, after 4.0 μM Ag^+ was incubated with 5.0 μM guanine for 20 min at room temperature, the oxidation current of guanine at CNTs/GC electrode decreased obviously (curve c), suggesting that the reaction between Ag^+ and guanine can inhibit the electrocatalytic oxidation of guanine. For further comparison, only Ag^+ containing (curve d) buffer solution was also tested using the same procedure and no obvious oxidation peak observed. So we can conclude that the oxidation peak current was totally produced by guanine. All these experimental results demonstrated that our



Scheme 1. (A) Electrocatalytic oxidation of guanine. (B) The proposed structures for the monofunctional (a) and difunctional (b) adducts resulting from the interaction between Ag^+ and guanine. (C) Ag^+–G sensing system based on the inhibition of electrocatalytic oxidation of guanine by Ag^+.

prediction mentioned above is right, i.e. the presence of Ag^+ in the electrocatalytic oxidation reaction of guanine caused a decrease in electrochemical response. Therefore, a novel, simple, indirect Ag^+ detection sensor might be developed.

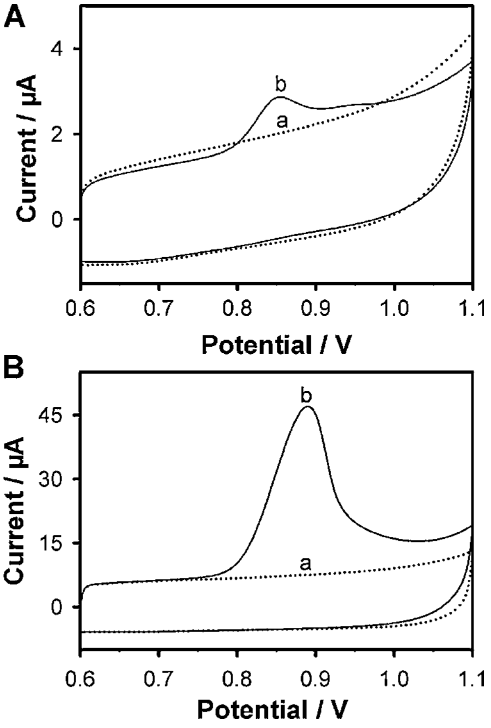


Fig. 1. Cyclic voltammograms of the bare GC (A) and CNTs/GC electrodes (B) in 0.1 M ABS (pH 5.0) without (a) and with (b) 5.0 µM guanine. Preconcentration time: 240 s. Scan rate: $0.1\,V\,s^{-1}$.

3.2. *Optimizing the Ag^+–G sensing system for Ag^+ assay*

In order to get the most sensitive detection of the Ag^+–G sensing system, the influencing factors, such as scan rate, preconcentration time, solution pH and incubation time of Ag^+ with guanine were studied.

The cyclic voltammograms of the electrocatalytic oxidation of guanine at the CNTs/GC electrode at different scan rates (υ) were investigated (Fig. S1). The results showed that the oxidation peak current increased simultaneously with the scan rate increase (Fig. S1A). In the range of 0.03–0.3 $V\,s^{-1}$, the peak current (I_{pa}) versus the square root of scan rate ($\upsilon^{1/2}$) obeyed the linear regression equation $I_{pa}\,(\mu A) = 185.5\upsilon^{1/2} - 14.32$ ($R^2 = 0.999$), which suggested that the electrocatalytic oxidation of guanine at the CNTs/GC electrode was a diffusion-controlled process,

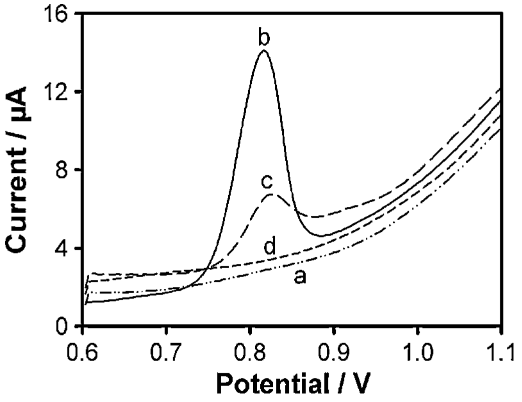


Fig. 2. Differential pulse voltammograms of CNTs/GC electrode in 0.1 M ABS (pH 5.0) with blank (a), 5.0 µM guanine (b), 5.0 µM guanine + 4.0 µM Ag^+ (c) and 4.0 µM Ag^+ (d). Preconcentration time: 240 s.

not a surface-controlled process [35]. In addition, the oxidation peak potential (E_p) of guanine shifted positively with the scan rate increase and the resulting regression equation was E_p (V) = 0.063 log υ + 0.96 (R^2 = 0.987) (Fig. S1B). Since it was an irreversible oxidation process, the peak potential (E_p) can be represented by the following equation [36,37]:

$$E_p = A + \frac{2.3RT}{[(1-\alpha)nF]\log \upsilon}$$

where A is a constant related to the formal electrode potential (E_0) and the standard rate constant of E_0, and υ is the scan rate. The transfer coefficient (α), which characterizes the effect of the electrochemical potential on the activation energy of an electrochemical reaction, was calculated to be 0.53.

The effect of preconcentration time on the oxidation current response of guanine at the CNTs/GC electrode was investigated (Fig. S2). The peak current increased rapidly with the preconcentration time, and then, slowly, up to 240 s. With a preconcentration time more than 240 s, the peak current decreased. This may be attributed to the adsorption of guanine at the CNTs/GC electrode which was saturated enough to block the successive adsorption of the diffused guanine. So we finally chose 240 s as the optimal preconcentration time.

At the CNTs/GC electrode, the electrochemical event of guanine without and with Ag^+ in 0.1 M ABS with various pH from 3.0 to 8.0 was investigated by DPV. The results showed that the oxidation peak potential of guanine shifted negatively with the increment of the solution pH (Fig. S3), indicating that protons were involved in the electrode reaction [38]. Moreover, in acidic condition (pH from 3.0 to 6.0), a good linear relationship was established between E_p and the solution pH with the linear equation as E_p (V) = −0.064 pH + 1.139 (R^2 = 0.995). The slope of 64 mV/pH suggests that the electron transfer was accompanied by an equal number of protons in the electrode reaction [39,40]. All these results consist with the mechanism shown in Scheme 1A. As shown in Fig. 3A, in the absence of Ag^+ (curve a), the maximum current response of guanine was obtained at pH 5.0. However, the reaction between Ag^+ and guanine might be affected by the solution pH. Curve b in Fig. 3A shows the influence of pH on the oxidation peak current of guanine in the presence of Ag^+. The results were similar to that of guanine without Ag^+. The maximum peak current response can still be obtained at pH 5.0. The difference between the oxidation currents of guanine in the absence and in the presence of the Ag^+ ($\Delta i = i_{\text{without Ag+}} - i_{\text{with Ag+}}$) at different pH values is shown in Fig. 3B, from which we can find that the maximum difference of the current was 6.75 μA at pH 5.0, indicating that the effect of Ag^+ on the oxidation of guanine was greatest at pH 5.0. Hence, in order to get the highest sensitivity for Ag^+ detection, we finally chose pH 5.0 as the best sensing condition.

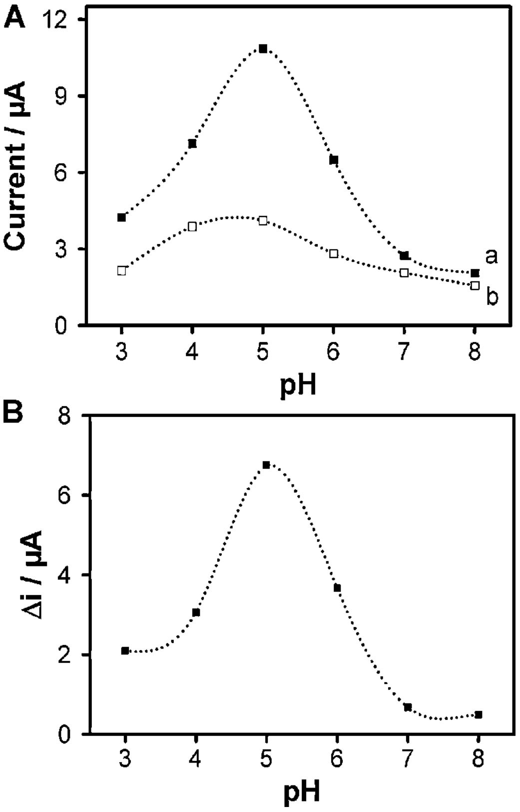


Fig. 3. (A) Effect of pH on the electrocatalytic oxidation current of 5.0 μM guanine without (a) and with 2.5 μM Ag^+ (b) in 0.1 M ABS at the CNTs/GC electrode. (B) The dependence of the oxidation peak current difference (Δi) of guanine with and without Ag^+ on the solution pH. Experiment conditions were as in Fig. 2.

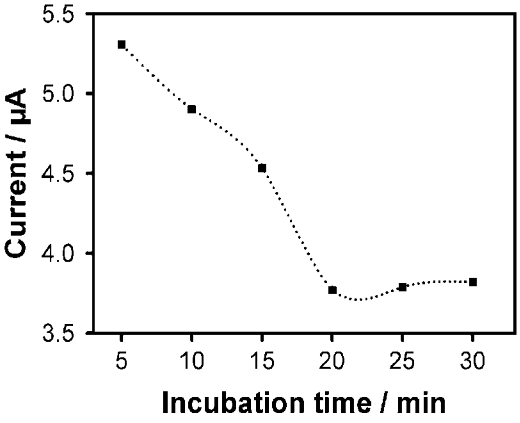


Fig. 4. Effect of incubation time between 5.0 μM guanine and 2.5 μM Ag^+ on the electrocatalytic oxidation peak current of guanine in 0.1 M ABS (pH 5.0) at the CNTs/GC electrode. Experiment conditions were as in Fig. 2.

The extent of the binding of Ag^+ to guanine can be easily controlled by the incubation time. As shown in Fig. 4, the oxidation current of guanine decreased rapidly with the incubation time of Ag^+ and guanine, the value of the intensity diminishing from 0 to 20 min incubation time, and a minimum current response was obtained at 20 min. Afterwards, as the binding between Ag^+ and guanine has achieved the maximum, the oxidation current did not change significantly and exhibited a platform. Therefore, an incubation time of 20 min was chosen for the further experiments.

3.3. Sensitivity of the Ag^+–G sensing system

Under the optimal conditions, the sensitivity of the Ag^+ sensing system was measured in 0.1 M ABS (pH 5.0) by differential pulse voltammetry due to its high sensitivity. As shown in Fig. 5, the oxidation peak current of guanine continuously decreased with the increasing concentrations of Ag^+ from 0 to 4.0 μM with the current signal change of 7.33 μA. A linear relationship was obtained for Ag^+ concentrations ranging from 100 nM to 2.5 μM with a peak current change of 6.48 μA. The linear regression equation was I_{pa} (μA) = −2.24C (μM) + 9.30 (R^2 = 0.990). The detection limit of Ag^+ was calculated to be 30 nM (S/N = 3). Since the WHO standard safe concentration for human is 0.05 ppm (460 nM), which is located in the linear range of the proposed method (100 nM to 2.5 μM), our method can be directly used for safe assessment of Ag^+ without dilution or enrichment of the sample. Therefore, all results suggested that this method has high sensitivity and a relatively broad linear range for the indirect quantitative detection of Ag^+.

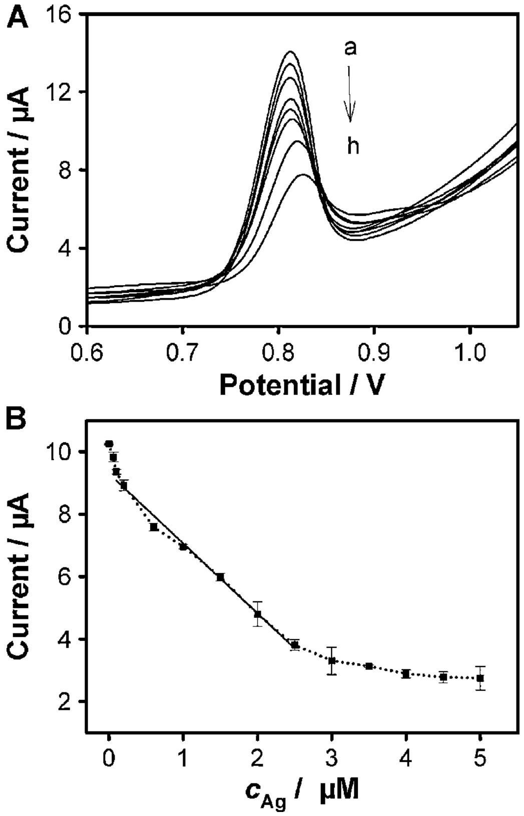


Fig. 5. (A) Differential pulse voltammograms at CNTs/GC electrode in 0.1 M ABS (pH 5.0) containing 5.0 μM guanine and different concentrations of Ag^+ (a–h): 0, 0.1, 0.2, 0.6, 1.0, 1.5, 2.0, 4.0 μM. (B) Ag^+ concentration (ranging from 0 to 5.0 μM) dependent change in the electrocatalytic oxidation peak current of guanine. Experiment conditions were as in Fig. 2.

3.4. *Selectivity of the Ag^+–G sensing system*

An important criterion for a metal ion sensor is the ability to recognize a specific metal ion in the presence of other metal ions since they are usually coexistent. Therefore, testing the selectivity of this Ag^+–G sensing system is essential. Some common metal ions were tested, including Ca^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Pb^{2+}, Co^{2+}, Cd^{2+}, Mg^{2+}, Sr^{2+}, Zn^{2+}, Cu^{2+}, Al^{3+}, Hg^{2+}. As shown in Fig. 6, with the same procedure as Ag^+ assay, none of the tested metal ions except Hg^{2+} caused obvious decrease in the oxidation peak current of guanine. This may be contributed to the interaction between Hg^{2+} and the N_1, N_7 or C_2NH_2 site of guanine [41]. The interference from Hg^{2+} can be eliminated by adding EDTA as a co-additive to mask the Hg^{2+}. These results implied that the Ag^+ induced oxidation peak current decrease of guanine is highly selective.

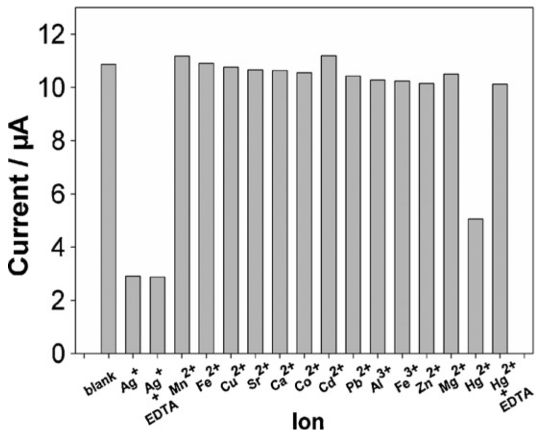


Fig. 6. The electrocatalytic oxidation peak current change of guanine in the presence of 4.0 μM of commonly met metal ions. The guanine concentration was 5.0 μM in 0.1 M ABS (pH 5.0). Experiment conditions were as in Fig. 2.

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

Sample	Added (μM)	Found (μM)	Recovery
Pond water	0.45	0.47 ± 0.04	104%
	0.80	0.84 ± 0.03	105%
	1.30	1.34 ± 0.03	103%
	1.70	1.67 ± 0.04	98%
Well water	0.45	0.43 ± 0.01	96%
	0.90	0.94 ± 0.03	104%
	1.50	1.55 ± 0.05	103%
	2.00	2.03 ± 0.04	102%

3.5. *Reproducibility and stability of the Ag^+–G sensing system*

The reproducibility of the modified electrode was measured. Continuous detections of 5.0 μM guanine and 4.0 μM Ag^+ in 0.1 M ABS (pH 5.0) were performed five times with the same electrode, and an acceptable reproducibility with a 2.7% relative standard deviation (RSD) was obtained. In addition, the current signals of 5.0 μM guanine and 4.0 μM Ag^+ in 0.1 M ABS (pH 5.0), measured with five different electrodes, changed with a RSD of 3.4%. These results demonstrated that this Ag^+–G sensing system had a good reproducibility. The stability of the Ag^+–G sensing system was also studied. The current response of 5.0 μM guanine and 4.0 μM Ag^+ in 0.1 M ABS (pH 5.0) was measured at a CNTs/GC electrode stored for 14 days at 4 °C. The oxidation peak currents retain 90% of their initial response values. All these experimental results implied that this sensing system has a very good reproducibility and stability.

3.6. *Analytical applications*

In order to evaluate the practical utility of the present method, Ag^+ was analyzed in real samples using the standard addition method. All pond water and well water samples were first filtered by a 0.45-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 105% after standard additions are satisfactory, suggesting that the Ag^+–G sensor could be efficiently used for the detection of Ag^+ content in the real samples.

4. Conclusions

A novel and simple method for the sensitive detection of Ag^+ based on the Ag^+–G sensing system has been presented in this paper. Ag^+ inhibits the electrocatalytic oxidation of guanine by interacting with guanine, revealing an obvious current response decrease. This sensor enables the selective detection of Ag^+ with a linear range of 100 nM to 2.5 μM and a detection limit of 30 nM. Moreover, as the first example of Ag^+ detection method based on its interaction with isolated base, this work demonstrated a new kind of analytical function of DNA bases and a new approach for studying the toxic action of heavy metal ions to DNA. Compared with traditional DNA-based biosensors, this method using isolated base – guanine is more simple and economical for its low-cost, easy preparation and time saving. Therefore, the interaction of metal ions and DNA bases in combination with the intrinsic electrochemistry of DNA bases provides a promising platform for developing simple, indirect, sensitive and selective analytic methods for heavy metal ions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.06.061.

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