

Anodic stripping voltammetry of silver(I) based on Se nanoparticles doped carbon paste electrode

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Abstract

A simple and effective Se nanoparticles doped carbon paste electrode (nanoSe⁰/CPE) for Ag⁺ ions detection using anodic stripping voltammetry (ASV) has been demonstrated. NanoSe⁰/CPE has exhibited obvious advantages over CPE electrode in silver ion evolution owing to the enhanced determination sensitivity. The experimental parameters including pH value, amount of nanoSe⁰, reduction potential and time were optimized. Under optimal conditions, the peak current had a linear relationship with the concentration of Ag⁺ ions in the range from 0.0 to 75.0 μM ($I = 0.828C + 9.82$, $R^2=0.992$) on the nanoSe⁰/CPE.

Keywords

Se nanoparticle, Ag⁺ ions, carbon paste electrode, anodic stripping voltammetry

1. Introduction

Ag⁺ ions is widely used in industrial activities leading to increasing Ag⁺ ions content of ecological samples and biological organisms. [1-3]The toxicity of Ag⁺ ions has gradually potential to hamper human health and drawn remarkable attention. Therefore, Ag⁺ ions detection has considerable environmental and biological significance. Many innovative methods are continuously developed to detect Ag⁺ ions from aqueous solution, such as solid-phase extraction-Gas Chromatography-Mass Spectrum, [4] atomic absorption spectroscopy, [5] inductively couple plasma spectrometry-Mass Spectrum. [6] However, the applications of these methods suffer from practical problems of high cost and requirement of operating skills.

Electrochemical approaches are more favored over the above techniques owing to its low cost, remarkable sensitivity, fast response, as well as its smaller devices size and lower energy consumption. [7] Recently, electrochemical sensors have been widely used for detecting the concentration of heavy metals that are harmful to humans, such as Hg²⁺, [8, 9] Cu²⁺, [10] Pb²⁺. [11] Among all electrochemical technologies, anodic stripping voltammetry(ASV) is one of the most commonly used electrochemical analysis methods to detect ions. As a key part of ASV technology, a working electrode with wide electrochemical potential window, low background current, stable and sensitive electrical responds is generally required.

In this work, the Se nanoparticles doped carbon paste (NanoSe⁰/CPE) electrode is used as working electrode to detect Ag⁺ ions. We choose NanoSe⁰ because of its ultra high reaction activity with Ag⁺ ions. The result shows, the nanoSe⁰/CPE exhibited high sensitivity for the detection of Ag⁺ ions and the peak current had a good linear relationship with the concentration of Ag⁺ ions under optimal conditions.

2. Material and methods

2.1 Reagents and apparatuses.

Selenium dioxide, ascorbic acid (Vc), silver nitrate, potassium nitrate, natrium aceticum, acetic acid, potassium ferricyanide, graphite power and paraffin were used as received. All chemicals were analytical grade and were used in experiments without further purification. Double distilled water was used to prepare the solution.

2.2 Preparation of nanoSe⁰.

NanoSe⁰ sol was prepared by the reduction of SeO₂ with Vc (1:2 in molar ratio) and the nanoSe⁰ was spherical with an average diameter of 133 nm. [12]

2.3 Preparation of nanoSe⁰/CPE electrode.

The nanoSe⁰/CPE was prepared as follows. First, the nanoSe⁰/CPE was prepared by mixing graphite powder, liquid paraffin and a certain amount nanoSe⁰. The molar ratio (graphite powder: nanoSe⁰) was 20:1. Then, the nanoSe⁰/CPE was obtained by filling into a port of the glass tube (with 3 mm diameter) in which a copper wire was inserted. Prior to experiment, the surface of nanoSe⁰/CPE was polished with fine paper. Bare carbon paste electrode (CPE) was prepared as above.

2.4 Characterization.

The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out on a DY-2300 and PalmSence electrochemical workstation. A typical three-electrode system was used for all electrochemical experiments, which consisted of Ag/AgCl /saturated KCl as reference electrode, a Pt wire as auxiliary electrode and nanoSe⁰/CPE electrode as working electrode. The potential scan was carried out at 50 mV/s rate for all electrochemical experiments except illustrate.

2.5 Electrochemical analysis.

The detection of Ag⁺ ions was determined by anodic stripping voltammetry. The nanoSe⁰/CPE was immersed into a glass cell containing HAc-NaAc(0.1 M, pH=5) and AgNO₃ solution. The Ag/AgCl /saturated KCl electrode and Pt wire electrode was immersed into another glass cell. The two glass cell with connected with salt bridge. The anodic stripping voltammetry detection involved pre-concentration, electrodeposition at a certain voltage for a certain time, and stripping at a certain potential range.

3. Results and discussion

3.1 Electrochemical properties of nanoSe⁰/CPE.

The K₃Fe(CN)₆^{3-/4-} redox couple was used for electrode characterization and the electrochemical response from the Fe³⁺/Fe²⁺ redox couple could reflect the conductivity of the electrode interface. [7] The electrochemical behaviors of nanoSe⁰/CPE and CPE were investigated in a 5.0 mM K₃Fe (CN)₆^{3-/4-} + 0.1 M KNO₃ solution mixed solution. As shown in Fig 1.A. compared with the CV-response of K₃Fe (CN)₆^{3-/4-} on CPE, the redox peak current obviously decrease and potential difference was narrow on nanoSe⁰/CPE, indicating that the introduction of nanoSe⁰ could decrease the electrochemical activity of K₃Fe(CN)₆^{3-/4-} redox couple on CPE and the voltammetry of K₃Fe(CN)₆^{3-/4-} on nanoSe⁰/CPE was a typical surface-controlled process. This may be because nanoSe⁰ have semiconductor properties and poor electrical conductivity, which hinder the electron transfer rate.

Electrochemical impedance spectroscopy (EIS) was further used for the investigation of the modified electrodes, it can exhibit the impedance changes of the modification processes, and the results were consistent with those of the CV test. The radius of semicircle can reflect value of the electrode-transfer resistance. The larger the radius, the bigger the electron transfer impedance. As anticipated, the electron-transfer resistance of the CPE (Fig1.B) was smaller than nanoSe⁰/CPE, owing to poor electrical conductivity of nanoSe⁰ with semiconductor properties.

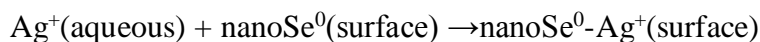
Based on CV and EIS analysis, nanoSe⁰/CPE was suitable for electrochemical applications due to their stable electrochemical response.

3.2 Cyclic voltammetric behavior of Ag⁺ ions on nanoSe⁰/CPE

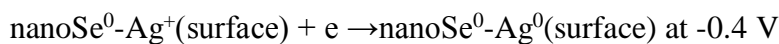
As shown in Fig.2 A, the CV response of Ag⁺ ions on nanoSe⁰/CPE was larger than that on CPE and the peak current had a good linear relationship with the concentration of Ag⁺ ions ($I=0.828 C + 9.82$, $R^2 = 0.992$, Fig.2 B), indicating can used to detect Ag⁺ ions with high sensitivity. Furthermore, the redox peak currents increased with the increase of the scan rate and a linear relationship between oxidation peak currents ($I_{pc}=867.8v+11.58$, $R^2=0.993$) at scan rate from 0.05 to 0.1 V/s (Fig.2A,

Inserts), indicating a typical adsorption-controlled process. From the literatures reported, [7] under the results of the experiments, electrochemical reaction mechanism of Ag^+ ions at the nanoSe⁰/CPE could be described as follows:

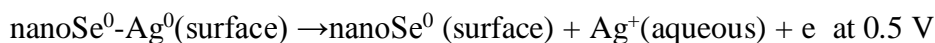
(1) Preconcentration step:



(2) Reduction step in negative potentials:



(3) Stripping step:



These results indicated that the introduction of nanoSe⁰ could enhance peak current of Ag^+ ions. It is well understood that nanostructures have larger surface area. Theoretically, the superior surface-to-volume ratio of nanostructures will undoubtedly increase the amount of the Ag^+ ions ion accumulated onto the nanoSe⁰/CPE. [7]

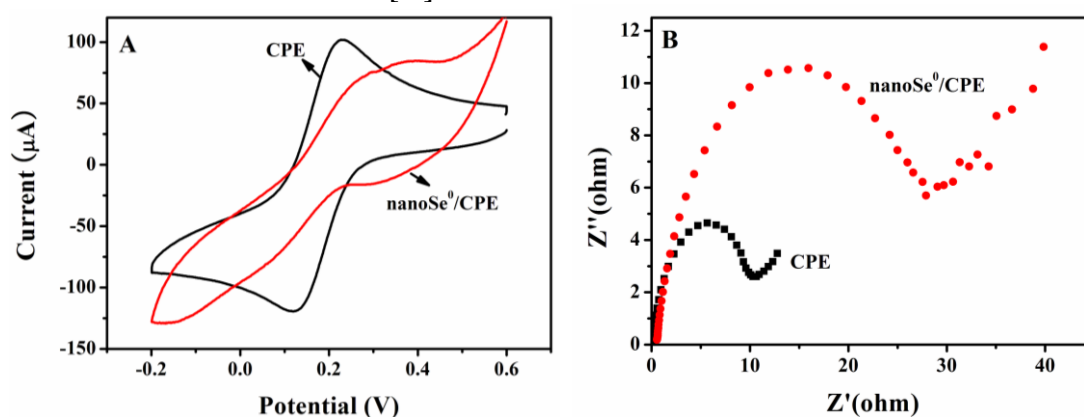


Fig 1. CVs (A) and EIS(B) of 5.0 mM $\text{K}_3\text{Fe}(\text{CN})_6$ 3-/4- in 0.1 M KNO_3 solution. Scan rate: 50 mV/s, Frequency range: 0.1 Hz to 50000 Hz.

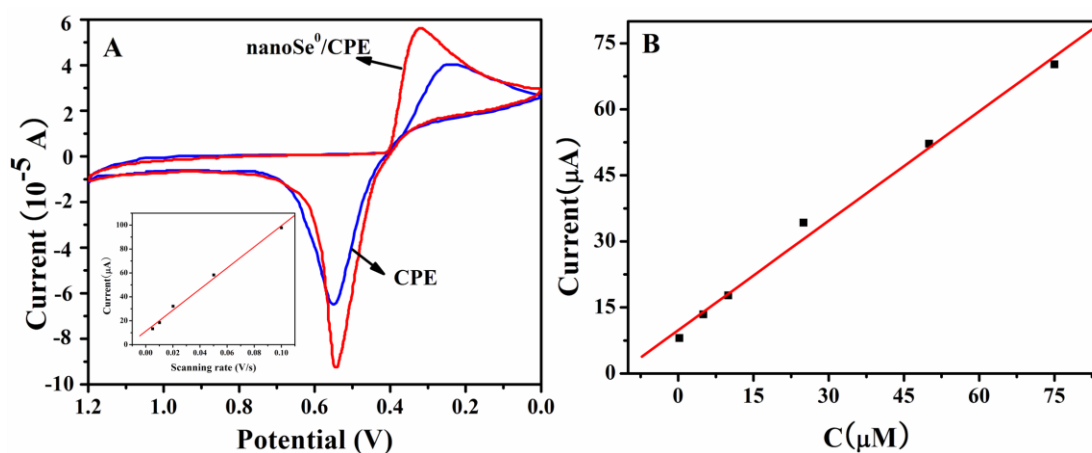


Fig. 2. CVs of Ag^+ ions (A) and the linear relationship of peak current and concentrations of Ag^+ ions (B) on nanoSe⁰/CPE in HAc-NaAc solution (0.1 M, pH=5), Scan rate: 50 mV/s.

Insert: Relationship of peak current and scan rate.

3.3 Optimization of detection conditions

To efficiently apply the electrochemical system to Ag^+ ions detection, several experimental parameters including pH value, scan rate, amount of nanoSe⁰, pre-concentration potential and time were optimized.

Effect of pH. Prior to testing the sensor, the pH value were optimized for the performance of hybridization process. The CV response signals were investigated with different pH value. As shown

in Fig. 3.A, the CV response increased from 2.0 to 5.0 and then decreased. The maximum current intensity was observed at pH 5.0. The influence of pH value on the peak current may be explained as follows. The pH value affects hybridization efficiency. [13]

Effect of amount of nanoSe⁰. The nanoSe⁰ can enhance redox peak current of Ag⁺ ions. Therefore, the amount of nanoSe⁰ was also one of the most significant parameters on detection of Ag⁺ ions. As shown in Fig 3.B, the peak current increased from 37.0 to 65.8 μ A when the amount of nanoSe⁰ increased from 10 to 100 μ L in graphite powder of 0.5 g. The results shows oxidation peak current of Ag was already comparable when the amount of nanoSe⁰ was 100 μ L in graphite powder of 0.5 g. Simultaneously, to get high efficiency, relative low-cost, flexibility operation, we selected 100 μ L nanoSe⁰ in graphite powder of 0.5 g in further experiments.

Effect of reduction potential and time. ASV electrochemistry methods including pre-concentration step and reduction step in negative potentials and stripping step. Therefore, reduction potential and time is essentially required to detection of Ag⁺ ions. As shown in Fig. 3.C, the CV response increased from -0.5 to -0.1V and then decreased. The potential of -0.4 V was selected in further experiment to avoid the interference ions. As shown in Fig 3.D, the peak current increased from 37 to 53.01 μ A as the reduction time increased from 0 to 180 s. In order to low time consumption and avoid reduction of other metal ion, we selected reduction time of 180 s in further experiment.

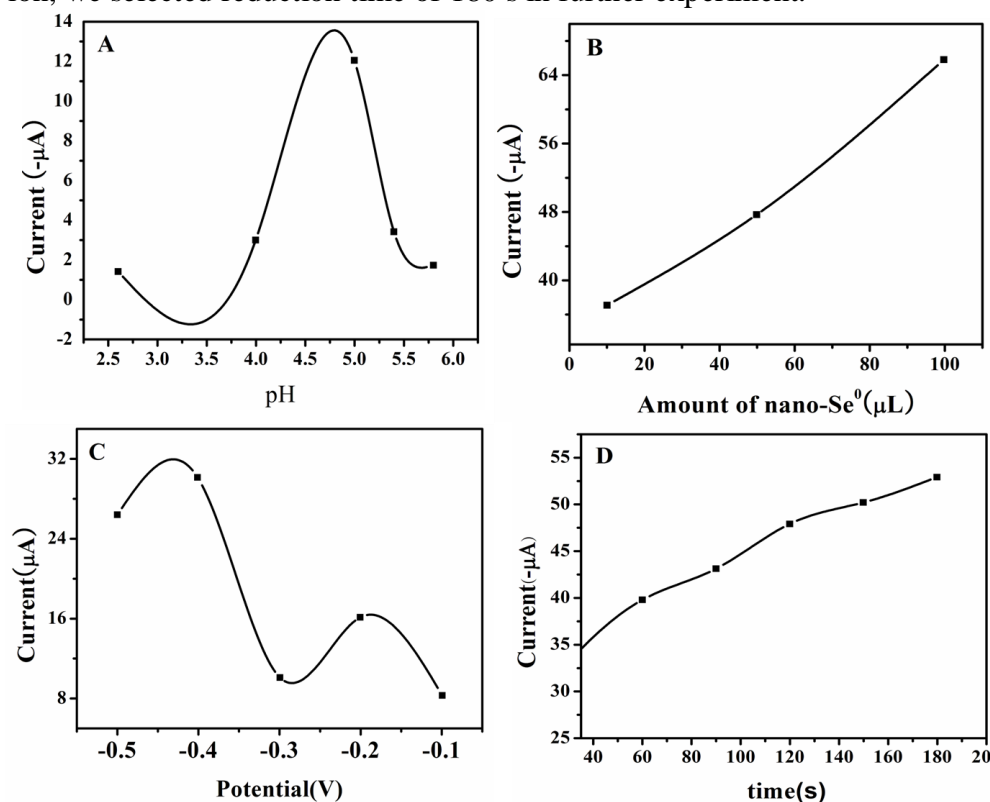


Fig 3. Effects of the pH (A), amount of nanoSe⁰(B), reduction potential (C) and time(D) on the peak current of Ag⁺ ions on nanoSe⁰/CPE at scan rate 50 mV/s.

3.4 Electrochemical detection of ions

Fig 2.B shows the CV response-concentration curves of Ag⁺ ions on nanoSe⁰/CPE at optimization condition. As the concentration of Ag⁺ ions increased, the CV response signal increased accordingly. The corresponding calibration plot of peak currents versus the concentrations of Ag⁺ ions was linear in the range from 0.0 to 75.0 μ M, which is suitable for quantitative analysis of low levels of metal ions. The nanoSe⁰/CPE electrode has comparable sensitivity and a wide linear range. Low-cost nanoSe⁰, without any electrode processing is a competitive candidate for detecting Ag⁺ ions.

4. Conclusion

In this study, Se nanoparticles doped carbon paste electrode (nanoSe⁰/CPE) was developed and successfully applied for the determination of Ag⁺ ions. The experimental parameters including pH value, scan rate, amount of nanoSe⁰, reduction potential and time were optimized.

Acknowledgements

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