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Sensitive and selective detection of Ag^+ in aqueous solutions using Fe_3O_4@Au nanoparticles as smart electrochemical nanosensors

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ABSTRACT

Owing to the selective deposition reaction on the surface of magnetic nanoparticles, we reported a simple and selective magnetic electrochemical method for the detection of Ag^+ ions in aqueous solutions. The analyte deposited on the nanoparticles was brought to the surface of a homemade magnetic electrode and detected electrochemically in 0.1 mol/L KCl solution based on the reaction of Ag_0 transferred to AgCl. Under the optimal conditions, the linear response range of Ag^+ ions was 0.117–17.7 μmol/L ($R^2=0.9909$) with a detection limit of 59 nmol/L (S/N=3). A series of repeatability measurements 1.0 μmol/L Ag^+ gave reproducible results with a relative standard deviation (RSD) of 4.5% ($n=11$). The interference from other metal cations can be eliminated by adding EDTA as a co-additive to mask the metal cations. The recoveries ranging from 98.6% to 103.99% after standard additions demonstrate that this sensor has great potential in practical applications. The advantages of this developed method include remarkable simplicity, low cost, and no requirement for probe preparation, among others.

1. Introduction

Silver ions are considered to be one of the heavy metal ions. Its potential toxicity for environments and human body has drawn people attention. 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 [1]. The standard safe concentration of Ag^+ for human is <0.05 ppm according to the World Health Organization (WHO) [2]. Traditional methods, such as inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrometry (F-AAS), atomic emission spectroscopy (AES), spectrophotometry, ion exchange chromatography (IEC) as well as laser excited atomic fluorescence spectrometry, had been used to detect trace levels of Ag^+ in aqueous media. However, these methods are normally performed in the laboratory and not suitable for on-site applications. Other drawbacks include the need for somewhat sophisticated and expensive instrumentation that can be time consuming to operate. The development of simple, low cost, sensitive and selective methods for detection of trace amounts of Ag^+ in environmental and food related samples is of great importance.

Owing to the advantages such as low cost, high sensitivity, straightforwardness, low sample volume, ease of operation and the ability to carry out speciation, electrochemical methods offer advantages for the determination of metal ions. There are several examples of electrochemical methods applied to the determination of Ag^+ in aqueous samples [3–14]. The performance such as the limit of detection and the linearity range of several electrochemical techniques for the detection of Ag^+ are summarized and compared in Table 1. Modified working electrodes were generally used to enhance the sensitivity and selectivity of electrochemical analysis techniques. The modifiers used include complexing reagents and special electrode-film coatings. The modification methods include chemisorption, covalent binding, polymer film coating, and composite. However, these methods for the determination of silver still suffer from more or less drawbacks such as the sophisticated pretreatment process, slow mass transport of the metal ions from bulk solution to the electrode surface, and matrix interferences, which limit their wide application [15,16].

Previous researches have been demonstrated that the incorporation of magnetic nanoparticles (MNPs) into sensors can enhance sensor performance [17–19]. First, the MNPs can be easily separated from the reaction mixtures with a magnet and re-dispersed immediately following removal of the magnet. It can effectively minimize the

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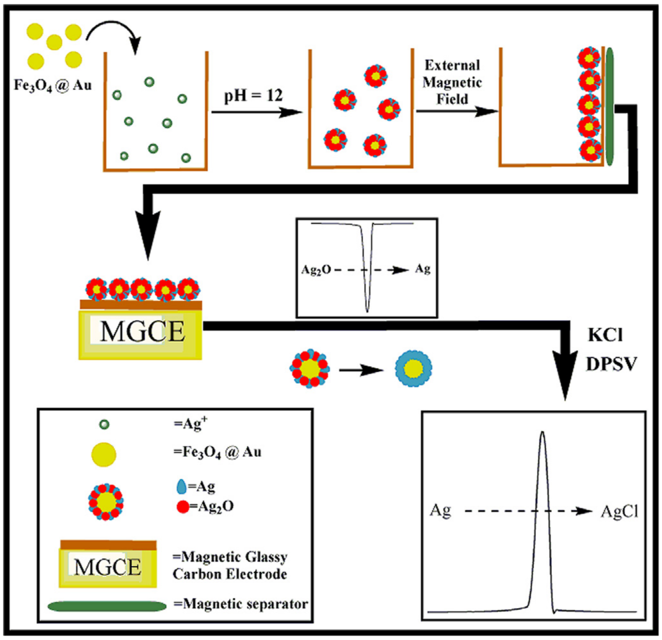
Table 1
Comparison of performance for electrochemical detection of Ag^+.

Electrode	Method	Linear range	LOD	Ref.
DNA film modified gold electrode	EIS	100–800 nM	10 nM	[4]
Carbon paste electrode	ASV	0.05–150 μg L^{-1}	0.05 μg L^{-1}	[5]
LB/PAn-PTSA/GCE	LSSV	$6.0 \times 10^{\times -10}$–$1.0 \times 10^{-6}$ mol L^{-1}	4.0×10^{-10} mol L^{-1}	[6]
LB-TCA/GCE	DPASV	5.0×10^{-9}–2.0×10^{-6} mol L^{-1}	3.0×10^{-9} mol L^{-1}	[7]
Au-MBT SAM	SWV	5.0×10^{-8}–8.0×10^{-7} and 1.0×10^{-6}–1.0×10^{-5} M	1.0×10^{-8} M	[8]
CNTs/GCE	DPV	100 nM–2.5 μM	30 nM	[9]
MHA/SAM modified gold electrode	DPV	10–500 nM	1.3 nM	[10]

LB/PAn-PTSA/GCE: Polyaniline doped with p-toluenesulfonic acid Langmuir–Blodgett film modified glassy carbon electrode; LB-TCA/GCE: Langmuir–Blodgett film of p-tert-butylthiacalix [4] arene modified glassy carbon electrode; Au-MBT SAM: Gold 2-mercaptobenzothiazole self-assembled monolayer; CNTs/GCE: Carbon nanotubes modified glassy carbon electrode; MHA/SAM modified gold electrode: 16-mercaptohexadecanoic acid self-assembled monolayer modified gold electrode; EIS: Electrochemical impedance spectroscopy; ASV: Anodic stripping voltammetry; LSSV: Linear scanning stripping voltammetry; DPASV: Differential pulse anodic stripping voltammograms; SWV: Square wave voltammograms; DPV: Differential pulse voltammograms.

matrix effect from the samples. Second, the MNPs provide a larger surface area than that of a flat solid phase, thus permitting a large amount of analyte to be captured, leading to increased detection sensitivity. Third, the analyte can be captured by MNPs and then brought to a sensing surface by magnetic electrode for direct detection without the need for further processing. This can reduce the complexity and time required for the sensing application. Forth, MNPs and magnetic separators enabling automated handling of the MNPs are commercially available. Due to these advantages, several MNPs-based electrochemical methods for metal ions sensing have been recently presented by attaching the chelating reagents onto MNPs surface to effectively capture metal ions [20–23]. The selectivity of these methods above also depends on the binding interaction of metal ions and complexing agent.

Herein, we introduce a new concept of utilizing commercial Fe_3O_4@Au nanoparticles as the smart electrochemical nanosensors, which serve as the active element and direct electroanalytical quantification of analytes. The novelty of this work not only resides in the description of a chemical deposition process but also includes the ability to search, reduce, trap and detect Ag^+ ions from water in a selective manner. The schematic design is depicted in Scheme 1. (1) The Fe_3O_4@Au were dispersed into the sample and hence brought directly to the analyte. (2) The Ag^+ ions could be reduced to Ag_0 by the residual hydroxylamine groups on the surface of Fe_3O_4@Au composites, where the Fe_3O_4@Au acted as the catalyst. Meanwhile, the Ag_2O were also formed in aqueous base. Both species deposited on the surface of Fe_3O_4@Au nanoparticles. (3) The Fe_3O_4@Au was brought to the electrode surface by a magnetic electrode, then, the Ag_2O were electrochemically reduced to Ag_0. Finally, the amount of analyte was detected electrochemically in 0.1 mol/L KCl solution based on the reaction of Ag_0 transferred to AgCl.



Scheme 1. Illustration of the procedure used to detect the Ag^+ ions in aqueous solution.

2. Experimental

2.1. Material and reagents

All reagents and chemicals were of analytical grade. A 0.117 mol/L stock solution of Ag^+ were prepared by dissolving the appropriate amounts of $AgNO_3$ (Merck, Germany), and were stored at 4 °C for further use. Fe_3O_4@Au nanoparticles (50 nm) and magnetic separation racks were purchased from Shanxi Life Gen Co., Ltd. (Xi'an, China).

2.2. Apparatus

Cyclic voltammograms (CVs) and differential pulse voltammetry (DPV) were performed in a Gaoss Union electrochemical analyzer (Wuhan, China). All measurements were carried out at room temperature (25 ± 1 °C) in a 2.5 mL electrochemical cell with a normal three-electrode configuration. A homemade magnetic glassy carbon electrode was used as working electrode [24]. A platinum wire counter electrode and a saturated calomel reference electrode (SCE) were used in the three electrodes configuration. The pH of all buffer solutions was measured by an Orion pH meter (United Initiators Co., Ltd., America). The solutions were prepared by the use of ultra pure water, which was obtained through a Cascada Lab Water System (USA). An Oscillator (Kylin-Bell Lab Instruments Co., Ltd., Jiangsu, China) was utilized to disperse magnetic particles.

2.3. Analytical procedure

Fe_3O_4@Au nanoparticles were firstly added into the samples and hence brought directly to the analyte. The pH of mixture solutions were then adjusted to 12.0, after which the mixture solutions were incubated for 5 min at room temperature. A magnetic separation rack was used to separate the magnetic particles from the solution phase, and the supernatant was discarded. The Fe_3O_4@Au nanoparticles were washed three times with ultra pure water to remove residual matrix.