



Colorimetric sensing of silver ions based on glutathione-mediated MnO₂ nanosheets



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ARTICLE INFO

Article history:

Received 18 April 2017

Received in revised form 14 July 2017

Accepted 17 July 2017

Available online 19 July 2017

Keywords:

MnO₂ nanosheets

Artificial oxidase

Colorimetric assay

Silver ions detection

GSH-mediated system

ABSTRACT

We described a rapid and highly sensitive colorimetric method for the detection and quantification of silver ions employing glutathione (GSH)-mediated MnO₂ nanosheets as an artificial oxidase. In this assay, the absorption intensity of the chromogenic reaction system enabled the quantification of silver ions. Under the optimum conditions, the linear response ranged for Ag⁺ was from 10 nM to 800 nM with a correlation coefficient of 0.996. Remarkably, limit of detection in aqueous solutions was 4.23 nM, which was well below United States Environmental Protection Agency (USEPA) permissible limit in drinking water (460 nM). This sensing assay had highly specificity because no significant interference occurred with 10-fold concentration of other metal ions. Moreover, the approach also could be employed to the Ag⁺ detection in real samples. And the recovery of Ag⁺ spiked in tap water ranged from 99.62% to 108.01%. Importantly, the oxidation reaction of TMB to oTMB by MnO₂ nanosheets completed instantaneously even by naked-eye readout. Therefore, the assay based on GSH-mediated MnO₂ nanosheets is simple, rapid, highly sensitive and selective for the quantification of Ag⁺ in water and practical samples.

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1. Introduction

Silver ions (Ag⁺) is one of the most hazardous pollutants [1], which is mainly used in electroplating, photography imaging, dental and medical products, and electronic equipment. The excess amount of silver ions would exert severe effects on the environment and pose adverse to human health [2,3]. As an important bioactive cation, Ag⁺ can bind with many metabolites, inactivate sulfhydryl enzymes, accumulate in the body and induce various disorders. Therefore, development of a sensitive and selective sensing platform for quantitative detection of Ag⁺ is of great importance to both human health and environment protection.

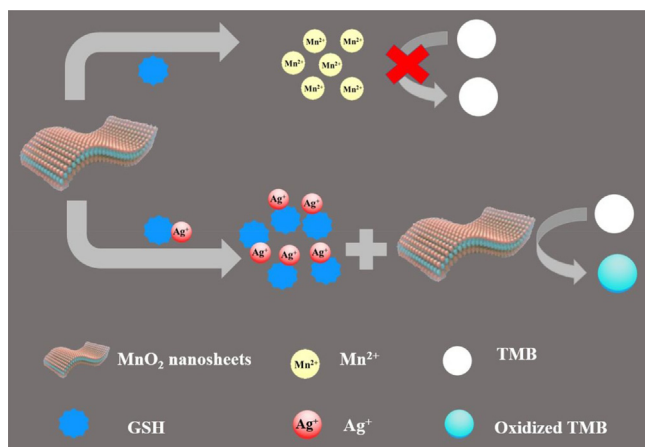
Traditional techniques for Ag⁺ detection mainly include inductively coupled plasma-mass spectrometry (ICP-MS) [4,5], and atomic absorption/emission spectroscopy [6,7]. In spite of the availability for detection of Ag⁺ at trace level, these approaches are costly, time-consuming, complicated, and the need of professional operation, which limits their practical applications. In response to the defects of traditional techniques, the colorimetric sensors have many advantages [8], and the exploration based

on functionalized gold nanoparticles (AuNPs) have gained popularity for the detection of Ag⁺ due to their high extinction coefficient and distance-dependent optical properties [9]. Various ligands including small organic molecules [10,11], peptides [12], and cytosine-(C)-rich oligonucleotides [13], have been reported for the quantification of Ag⁺. Although the colorimetric methods based on AuNPs aggregation are powerful, there is somewhat difficult for the analytes at the trace levels. Because it is insensitive to distinguish subtle color change induced by the aggregation degree of AuNPs by naked-eye readout. In addition, these strategies still suffer from tedious probe preparation, unsatisfactory selectivity and sensitivity [14,15]. Therefore, there are great challenges to obtain higher sensitivity and lower detection limit for Ag⁺ detection.

Recently, as one kind of redox active two-dimensional (2D) nanosheets, single-layer MnO₂ nanosheets have attracted considerable interest for their unique properties, including high specific surface area, higher chemical stability, and intrinsic oxidase-like activity [16–18]. Single-layer MnO₂ nanosheets have three atomic layers, that is one Mn layer sandwiched by two O layers. Each Mn coordinates to six O atoms to form an edge-sharing MnO₆ octahedral crystal lattice, which exhibits a broad absorption peak (200–600 nm) and excellent absorption capability ($9.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ molar extinction coefficient at 380 nm) [19]. The broad absorption is adaptable to use as effective fluorescence

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Scheme 1. Illustration of the colorimetric assay for silver ions detection by using GSH-mediated MnO₂ nanosheets.

quenchers or energy acceptors for the various targets such as H₂O₂ [20], T4 polynucleotide kinase [21], and ascorbic acid [22], glutathione [23,24], and Fe²⁺ [25]. MnO₂ nanosheets are reported to have intrinsic oxidase-like activity, which can catalyze colorless substrate TMB to blue oxidized product (oxTMB) at 650 nm [26]. The reaction system using dissolved molecular oxygen in the solution, overcoming the requirement for H₂O₂. The MnO₂ nanosheets coupled TMB provides an alternative nanomaterial for the development of novel colorimetric analysis [27]. Nevertheless, colorimetric sensor arrays based on MnO₂ nanosheets as an artificial enzyme are very rare. Accordingly, there have been great demands for the fabrication of colorimetric sensor arrays based on MnO₂ nanosheets.

In this paper, we propose an operationally simple and rapid colorimetric strategy for Ag⁺ detection based on GSH-mediated MnO₂ nanosheets (Scheme 1). The redox reaction between MnO₂ nanosheets and GSH decreases the produce of oxTMB. As a result, the reaction solution still keeps colorless. When Ag⁺ is added to the solution, the coordination between GSH and Ag⁺ [28] inhibits the decomposition of MnO₂ nanosheets, and the reaction solution changes to blue. There is a linear relationship between Ag⁺ concentration and blue oxTMB according to the mechanism. Importantly, GSH-mediated MnO₂ nanosheets system has been showed to be highly sensitive and selective detection of Ag⁺ than other metal ions. We also further demonstrated the analytical potential of this colorimetric sensing system for monitoring Ag⁺ in water samples.

2. Experimental section

2.1. Materials

Tetramethylammonium hydroxide (TMA⁺OH) and 3, 3', 5, 5'-tetramethylbenzidine (TMB) were obtained from Sigma-Aldrich (Saint Louis, USA). Manganese chloride tetrahydrate (MnCl₂·4H₂O) and methanol were purchased from Xilong Chemical Co., Ltd (Shantou, China). Silver nitrate, Ethylenediaminetetraacetic acid (EDTA) and hydrogen peroxide (H₂O₂, 30 wt%) were purchased from Beijing Chemical Works (Beijing, China). Acetic acid (HOAc) and sodium acetate (NaOAc) were purchased from Sangon Biotech. Co., Ltd. (Shanghai, China). L- glutathione reduced (GSH) was obtained from Beijing Biodee Biotechnology Co., Ltd (Beijing, China). All of the reagents and chemicals were at least analytical grade and used as received. The ultrapure water used throughout all experiments was purified by a Milli-Q system (Millipore, Bedford, MA, USA).

2.2. Instruments

Absorption spectra were recorded on SpectraMax[®]M2e Multi-Mode Microplate Reader (Molecular Devices, California, USA) at room temperature. The 96-well plates were produced from Costar (3590, USA). Transmission electron microscope (TEM) images were obtained on a Hitachi (H-7650, 80 kV) transmission electron microscope. Absorption spectra of MnO₂ was measured on UV-vis spectrophotometer (UV-2550, Shimadzu, Japan).

2.3. Synthesis of single-layer MnO₂ nanosheets

The single-layer manganese dioxide nanosheets were prepared as previous reports [29]. In brief, 12 mL of TMA⁺OH (1.0 M) and 2 mL of 30 wt% H₂O₂ were diluted to 20 mL mixture, then it was added into 10 mL of 0.3 M MnCl₂·4H₂O aqueous solution within 15 s. As the two mixtures were mixed, the solution became dark brown immediately. At room temperature, the obtained dark brown solution was stirred vigorously in the open air. The obtained bulk MnO₂ was centrifuged and washed three times with distilled water and methanol, then centrifuged at 12,000 rpm for 10 min. After that, the precipitate was dried in vacuum oven at 60 °C. To prepare single-layer MnO₂ nanosheets, 10 mg bulk MnO₂ was added into 20 mL ultrapure water and ultrasonicated for 10 h. Subsequently, the suspension was centrifuged at 2,000 rpm for 10 min and the supernatant was stored at 4 °C for further use. To calculate the concentration of resulting MnO₂ nanosheets, the absorption spectra of the supernatant was measured and the concentration was quantified according to Lambert–Beer's Law with the molar extinction coefficient of $9.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 380 nm [30].

2.4. Colorimetric detection of Ag⁺

Ag⁺ was prepared by dissolving silver nitrate (AgNO₃) in distilled water. First, 75 μL of 200 μM GSH solution was mixed with different concentration of Ag⁺ (50 μL). Then, 100 μL of MnO₂ (final concentration of 20 μM) and 225 μL of HOAc–NaOAc buffer solution (pH = 4.00) were added into the mixture, which was incubated with vigorous shaking for 5 min to react completely. Subsequently, 50 μL of TMB solution was added into the centrifuge tubes. Finally, 200 μL of the reaction mixtures were loaded into a 96-well plate by using the pipette (200 μL), respectively. The 96-well plates are produced from Costar (USA). The type of 96-well plates is 3590, and the maximum volume of each well is about 300 μL. The UV-vis absorption spectra of the work solutions were measured over the wavelength ranging from 500 nm to 800 nm, respectively.

2.5. Selectivity of Ag⁺ detection

To determine the selectivity of the detection method, the Ag⁺ and other metal ions with 10-fold concentrations were tested in a same way. We prepared other 13 kinds of metal ions, including Hg²⁺, Fe²⁺, Cu²⁺, Fe³⁺, K⁺, Zn²⁺, Na⁺, Cd²⁺, Ca²⁺, Ni²⁺, Co²⁺, Pb²⁺, Mn²⁺. The concentration of Ag⁺ was selected as 1.0 μM, and other metal ions were 10 μM.

2.6. Application to real samples

To investigate the detection performance of the sensing strategy in practical application, the tap water was collected and centrifuged at 12,000 rpm for 10 min. And then the supernatant was obtained to remove physical impurities. Subsequently, the Ag⁺ was dissolved in the tap water for further sensing. The assay condition was same as mentioned above for Ag⁺ sensing.

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