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Determination of mercury (II) by spectrophotometric method based on self assembly of gold nanoparticles

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Abstract

Due to the binding of the –COO- group with the mercury (II), gold nanoparticles functionalized with glutathione can self-assemble to form a supermolecular network in the HAc-NaAc buffer solution. The aggregation of functionalized gold nanoparticles and mercury (II) caused the shift of maximum absorption peak of the UV-Vis spectrum from 520 nm to 609 nm. Based on this principle, a simple spectrophotometric method for determination of mercury (II) was preliminarily established. The detection limit of the developed method for determination of mercury (II) was about 8.5×10^{-8} mol L^{-1}.

Keywords: Gold nanoparticles; Mercury (II); Spectrophotometer; Glutathione.

1. Introduction

Mercury is an environmental contaminant of global concern. Monitoring of mercury contamination was very important for protecting the global environment and human health. The most widely used methods for the determination of mercury are atomic absorption spectrometry with cold vapor (CV-AAS) [1, 2]. Inductively coupled plasma emission spectrometry coupled with mass spectroscopy (ICP-MS) [3], flow-injection analysis (FIA) [4], high-performance liquid chromatography (HPLC) [5], X-ray fluorescence spectrometry [6, 7], anodic stripping voltammetry [8] and neutron activation analysis [9] have also been employed for the determination of mercury. However, the common feature of these methods is that very expensive and sophisticated instruments are required. Moreover, for the neutron activation analysis, it is extremely expensive and unpractical to use for routine monitoring due to the requirement for a special instrument and license for working with neutrons.

In recent years, gold nanoparticle probes have attracted an increasing attention due to its application in biomedical analysis [10-12]. The increasing importance of gold nanoparticle probes have also been well embodied in environmental analysis of trace heavy metals [13]. In the present study, functionalized gold nanoparticle probes were prepared by the modification of gold nanoparticles with glutathione. Aggregation of functionalized gold nanoparticles in the presence of divalent mercury causes an easily measurable change of the UV-Vis absorption spectrum. Base on the principle, a simple colorimetric technique by using a very common UV-Visible spectrophotometer for the detection of mercury (II) in aqueous solution is preliminarily

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established. We hope the developed method is helpful for detection of divalent mercury in water samples.

2. Experimental

2.1. Reagents, chemicals and apparatus

Glutathione was purchased from Merck Chemicals, China. Tetrachloroauric acid ($HAuCl_4 \cdot H_2O$) was obtained from Sinopharm Group Chemical Reagent Co., Ltd. Trisodium citric, mercury (II) chloride, sodium chloride, and all the other reagents were analytical grade. Double-distilled deionized water was used throughout the whole experiment. A TU-1901 UV-Vis spectrophotometer was used for the absorbance measurements (Purkinje General Instrument Co. Ltd., Bejing, China). The pH values were measured by PHS-3C digital pH meter (Shanghai Weiye Instruments Plant, Shanghai, China). A WH-861 vortex mixer (Taicang Instrumental Co., Jiangsu, China) was used to blend the solutions.

2.2. Preparation of gold nanoparticles

In this experiment, gold nanoparticles were prepared according to the reference [14] with slight modification. In brief, trisodium citrate solution was used as reducing reagent of $HAuCl_4$. After boiling a 100 mL of the 0.1 g L^{-1} $HAuCl_4$ solution, 3.5 mL of the 10 g L^{-1} trisodium citrate solution was immediately added with simultaneous vigorous stirring for about 8 minutes. And then, the color of the solution changed to deep red. The solution was cooled naturally to room temperature and then diluted to the extent that the absorption of the solution was 1.000. After that, the solution was stored in refrigeration at about 4 °C for later use. The concentration of the gold nanoparticles was designed as 1X. The average diameter of the prepared gold nanoparticles was about 15 nm. The maximum absorption wavelength of UV-Vis spectrum was 520 nm.

2.3. Functionalization of gold nanoparticles

Functionalized gold nanoparticles were prepared as follows. 3.0 mL of gold nanoparticle solution (1X), 1.5 mL of 1.5 g L^{-1} aqueous glutathione solution were sequentially added into a 10 mL centrifugal tube, and diluted to 5.0 mL. The solution was thoroughly blended by vortex mixer, and laid naturally for 5 min. The solution was centrifuged with 8000 r.p.m for 27 min at about -5 °C in a frozen centrifugator and the upper clear solution was discarded. Then, the precipitate was cleansed by 5.0 mL Tris-HCl buffer solution (pH = 9.0) followed by three times' cleansing with 5.0 mL double-distilled deioned water. Finally, the obtained solution was diluted to the concentration that the absorption value was 0.200, and was preserved in a refrigerator at about 4 °C for later use.

2.4. Spectrophotometric determination of Hg^{2+}

In a 10 mL volumetric test tube, 1.5 mL of functionalized gold nanoparticles (absorption = 0.200), 0.5 mL of 0.02 mol L^{-1} HAc-NaAc buffer solution and 222 μL 1 μmol L^{-1} of Hg^{2+} solution was added sequentially, the solution was blended thoroughly with a vortex mixer. After incubation for 40 min at ambient temperature, the UV-Vis absorption intensity was determined at the wavelength of 609 nm. The blank solution was prepared according to the same procedure except that the 222 μL Hg^{2+} solution was substituted by 222 μL double-distilled water, and the blank solution was determined at the same condition as the sample solution.

3. Results and discussion

3.1. Formation of supermoleucular network

The single dispersed gold nanoparticle solution (15 nm) appeared red color due to the excitation of free electrons in plasma on the surface of gold nanoparticles and the maximum absorption wavelength was 520 nm. In the experimental condition, the –SH group could covalently linked to the surface of gold nanoparticles, two $–COO^-$ group could form chelation with one Hg^{2+} ion. Thus, aggregation occurred and the supermoleucular network formed as shown in Fig.1.

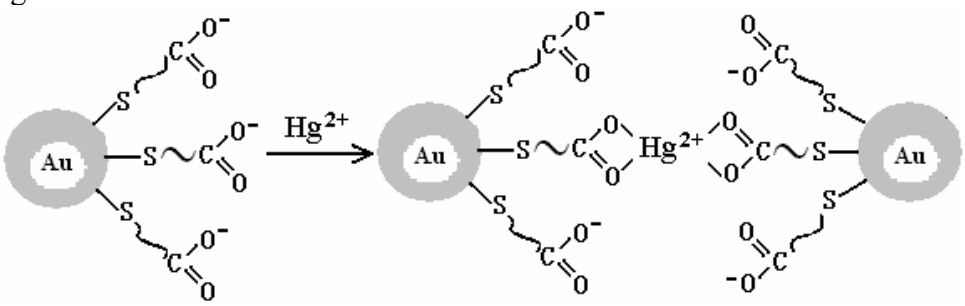

Fig.1. Self-assemble of Hg^{2+} and gold nanoparticles functionalized with glutathione.

This change has lead to the red shift of maximum absorption wavelength from 520 nm to 609 nm (Fig.2), and also we noticed that the color of the solution changed from red to blue.

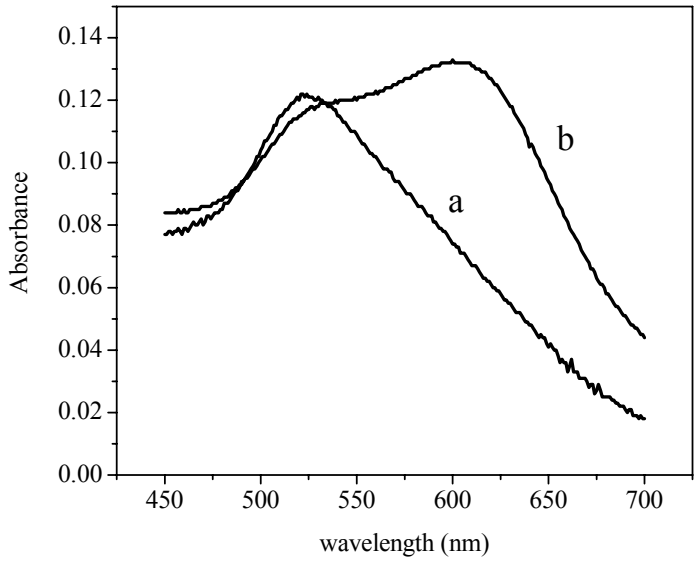

Fig. 2. UV-Visible spectra of (a) gold nanoparticles functionalized with glutathione and (b) functionalized gold nanoparticles and Hg^{2+}. Functionalized gold nanoparticles: 0.14X; HAc-NaAc: 0.02 mol L^{-1} (pH 5.9); Hg^{2+}:1 μmol L^{-1}; incubation time: 40 min.

3.2. Effect of pH value

The pH of solution was an important factor for determination of mercury (II). The optimization of pH is investigated over the pH range from 5.0 to 6.2. Seen from the Fig. 3, the absorption intensity of Hg^{2+} and functionalized gold nanoparticles decreases slowly with the increasing pH of the solution. The absorption intensity of functionalized gold nanoparticles (without addition of Hg^{2+} solution) also descends with the increasing of the pH value. The margin of them reaches maximum at pH 5.9. Thus, pH 5.9 was finally selected for determination of Hg^{2+}.

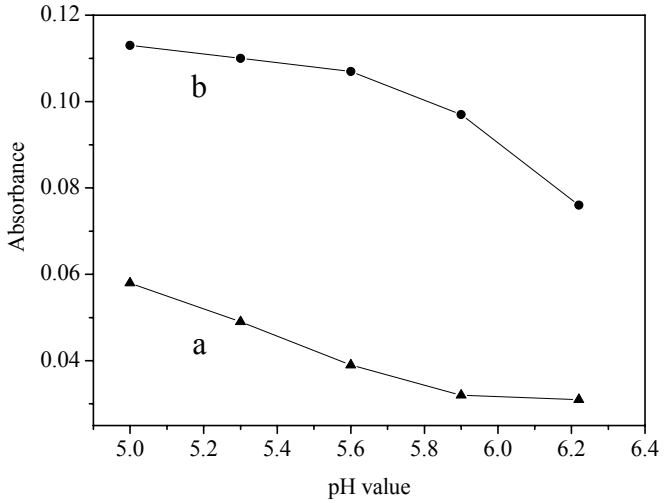

Fig. 3. Effect of pH on the absorption of (a) functionalized gold nanoparticles and (b) Hg^{2+} and functionalized gold nanoparticles. Functionalized gold nanoparticles: 0.14X; Hg^{2+}: 1 μmol L^{-1}; incubation time: 40 min; HAc-NaAc: 0.02 mol L^{-1}; λ= 609 nm.

3.3 Effect of incubation time

The influence of incubation time on UV-Vis absorption intensity was investigated in a period of 80 min immediately after mixing the Hg^{2+} solution and functionalized gold nanoparticles in HAc-NaAc buffer solution at pH 5.9. As shown in Fig. 4, the UV-Vis absorption intensity of conjugates (Hg^{2+} and functionalized gold nanoparticles) reaches a plateau in about 20 min and keeping stable for at least 60 min. The UV-Vis absorption intensity of the functionalized gold nanoparticles (without addition of Hg^{2+} solution) at pH 5.9 became slightly stronger with the time prolong before 40 min. As stated above, the incubation time of 40 min was finally selected for the determination of Hg^{2+}.

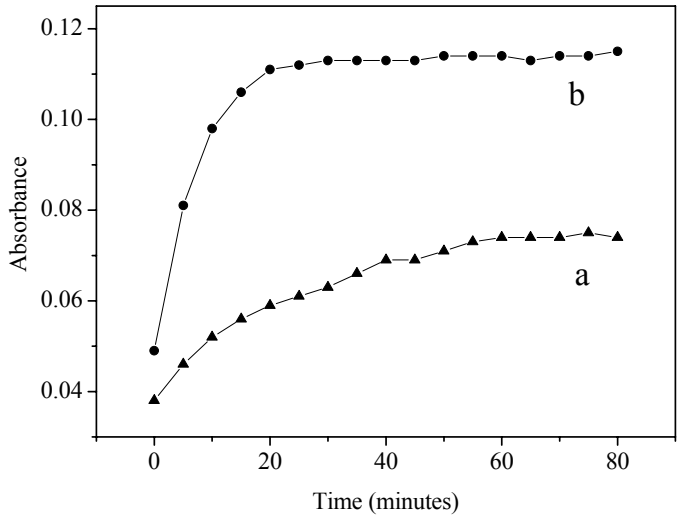

Fig. 4. Influence of incubation time on the absorption of (a) gold nanoparticles functionalized with glutathione and (b) functionalized gold nanoparticles and Hg^{2+}. Functionalized gold nanoparticles: 0.14X; HAc-NaAc: 0.02 mol L^{-1} (pH 5.9); Hg^{2+}:1 μmol L^{-1}; λ= 609 nm.

3.4 Validation of method

A series of standard Hg^{2+} solutions was prepared and determined by the proposed method, each solution was tested three times and the average value was calculated. According to the general procedure, the calibration curve for determination of Hg^{2+} was established under the optimal conditions. The results showed that the relationship between the UV-Vis absorbance and the concentration of Hg^{2+} solution presented a good linearity in the range from 0.20 μmol L^{-1} to 0.60 μmol L^{-1}. The standard regression equation is A609 = 0.0313 + 0.145 with regression coefficient of 0.9992. The relative standard deviation (RSD) for 11 measurements of the blank is 1.6%. The detection limit of the developed method for determination of mercury (II) was about 8.5×10^{-8} mol L^{-1} (0.20 μmol L^{-1} 3σ).

3.5 Comparison with the resonance light scattering technique

The resonance light scattering (RLS) technique was tested for the purpose of comparison with the established UV-Vis absorption method. The applied wavelength of RLS equipment was 545 nm. Other condition by RLS technique was the same as that of UV-Vis method. The results obtained from the comparison showed that the UV-Vis absorption method could achieve the approximately same high sensitivity as RLS technique, which indicating the simple UV-Vis absorption method was satisfactory for determination of mercury (II).

4. Conclusion

In this study, a simple spectrophotometric method for determination of mercury (II) was preliminarily established. The detection limit of the developed method for determination of mercury (II) was about 8.5×10^{-8} mol L^{-1}. The developed method is helpful for detection of divalent mercury in water samples.

Acknowledgements

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