

COLORIMETRIC SENSOR FROM CITRATE CAPPED SILVER NANOPARTICLES FOR TRACE DETECTION OF ARSENIC (III) IN GROUNDWATER

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ABSTRACT. The arsenic (III) contamination in groundwater and some surface waters is a high-profile ecological problem due to the causing of acute toxicity. At neutral pH As (III) is usually present in the environment as an uncharged weak arsenious acid (H_3AsO_3). In this report a simple and effective colorimetric approach for trace detection of H_3AsO_3 is presented based on the localised change of surface plasmon resonance of silver nanoparticles. The nanoparticles were prepared by chemical reduction method from silver nitrate with trisodium citrate. They were tested for detection of various metal ions and anions, which usually occur in the chemical contents of the natural groundwater. In case of presence of low arsenic (III) concentrations (traces) perceptible shifts of the surface plasmon resonance of the silver nanoparticles have been observed, which were accompanied by colour change of the analytical sample due to the nanoparticle aggregation process.

Keywords: Silver nanoparticles, colorimetric sensor, arsenic detection

КОЛОРИМЕТРИЧЕН СЕНЗОР ОТ ЦИТРАТНО ПОКРИТИ СРЕБЪРНИ НАНОЧАСТИЦИ ЗА ОТКРИВАНЕ НА СЛЕДИ ОТ АРСЕН В ПОДПОЧВЕНИ ВОДИ

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РЕЗЮМЕ. Замърсяването на подпочвените и някои повърхностни води с арсен (III) е сериозен екологичен проблем, поради причиняването на остра токсичност. При неутрално рН арсен (III) се среща обикновено в околната среда, като слаба арсениста киселина (H_3AsO_3). В настоящия доклад е представен лесен и ефективен колориметричен подход за откриване на следи от арсен (III), на базата на локализираната на промяна на повърхностния плазмонен резонанс на сребърни наночастици. Наночастиците бяха получени чрез химична редукция на сребърен нитрат с тринатриев цитрат. Те бяха тествани за детекцията на различни метални йони и аниони, които обикновено се срещат в химичния състав на естествените подпочвени води. При наличие на ниски концентрации на H_3AsO_3 (следи) се регистрираха осезаеми промени в повърхностния плазмонен резонанс на сребърните наночастици, които бяха съпроводени с промяна на цвета на аналитичната проба, дължаща се на процеси свързани с агрегиране на наночастиците.

Ключови думи: сребърни наночастици, колориметричен сензор, откриване на арсен

Introduction

The contamination of groundwater and some surface waters with arsenic (III) has been a major problem in various countries mainly in Asia, Africa and South America due to the causing of acute toxicity (Smedley, Kinniburgh, 2002; Bhattacharya et al., 2002). In general, the soluble inorganic form of trivalent As is more prevalent and toxic than its organic form (Brinkel et al., 2009). The permissible level of arsenic in groundwater is 10 ppb (Shankar et al., 2014). This circumstance necessitates the development of a cheap and easy for performance monitoring system to save the ecosystem by restricting the As(III) concentration within the allowable range. The established analytical techniques for measuring the arsenic levels below 10 $\mu\text{g/L}$, such as hydride generation atomic absorption spectroscopy, atomic fluorescence spectroscopy, inductively coupled plasma mass spectroscopy, etc., are highly sensitive but expensive and require highly trained personnel in the laboratory (Yogarajah, Tsai, 2015). The developing nations do not have an appropriate infrastructure to perform complicated

analytical procedures with high reliability and throughput. In the light of these issues portable tests kits for simple but effective arsenic analysis are needed. Among the numerous analytical methods, the colorimetric detection seems the most popular among the users as a saviour in the context of saving time and expenditure as well. Recently, the nanostructured materials have attracted much attention for analysis of trace metal ions because of their novel optical properties, which could offer significant additional advantages over the commercial detection kits (Moghimi et al., 2015). Nanoparticle aggregation occurrence due to the interaction with the targeted heavy metal ions might change the original colour of nanoparticle suspension. This colour change is the basic principle of metal ions colorimetric detection by nanoparticles (Priyadarshini, Pradhan, 2017; Wang et al., 2013). The functionalised metal nanoparticles of gold and silver have attracted the interest of researchers for effective analysis of some toxic heavy metals due to their high extinction coefficients and unique optical properties (Rosi, Mirkin, 2005). The properties are attributed to the collective dipole oscillation, known as Surface Plasmon Resonance or SPR (Talpin et al., 2010). This phenomenon

makes the silver nanoparticles very desirable for colorimetric sensing of various heavy metal ions because of the interaction between the Ag nanoparticles and the analyte cause changes in the intensity and position of the absorption band in the visible spectrum. This process might be observed even with a naked eye (Hung et al., 2010).

In this report, a new colorimetric detection for As(III) with high sensitivity using citrate stabilised silver nanoparticles (Ag NPs) is presented. The colour change in the absorbance spectra is expected as a result of the interaction between Ag NPs and arsenic ions. In such a way, analysis of low trace of As(III) in the environment is possible. These simple and fast analytical methods for determination of soluble arsenic have potential application for As(III) analysis in drinking water and groundwater.

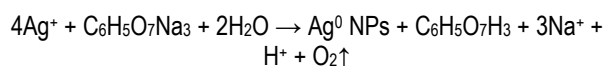
Experimental Procedures

Materials

All chemicals used were of analytical-reagent grade and all aqueous solutions were prepared with ultra-pure deionised water (Millipore Corp.). Silver nitrate (AgNO₃, 99.9 %) trisodium citrate (Na₃C₆H₅O₇), sodium hydroxide (NaOH, 99 %), hydrochloric acid (HCl) and salts of different cations (KCl, NaCl, CaCl₂, MgCl₂, FeCl₃, ZnCl₂, NiCl₂) were purchased from Wako, Japan (Wako Pure Chemical Corporation). Standard arsenic (III) solution of H₃AsO₃ was purchased from Merck (USA). Chromic acid (mixture made by adding of concentrated sulphuric acid and dichromate) was used for cleaning the glassware. After cleaning, the glassware was kept in an oven to dry for an overnight at 80 °C.

Synthesis of silver nanoparticles

The silver nanoparticles were prepared by the chemical reduction method with trisodium citrate as a reducing agent. For that purpose, silver nitrate and tri sodium citrate were dissolved in ultra-pure MilliQ water to prepare stock solutions of the precursors. In typical experiment 50 ml of 0.001 M AgNO₃ was heated to boil. 5 ml of 1 % trisodium citrate was added drop by drop to this solution. During this process, the reaction solution was mixed vigorously and heated until change of colour was evident (pale yellow). Then it was removed from the hot plate and stirred until cooled to room temperature. The reaction equation could be expressed as follows:



The colloidal solution of silver nanoparticles was characterised by using UV-VIS absorption spectroscopy and transmission electron microscope.

Selective colorimetric detection of arsenic (III)

To determine the selectivity of citrate functionalised Ag NPs as a nanosensor for As (III), some metal cations such as K⁺, Na⁺, Ca²⁺, Mg²⁺, Fe³⁺, Zn²⁺ and Ni²⁺ were taken for the test. In centrifuge Eppendorf, 1.0 ml of citrate capped Ag NPs were kept and mixed with 0.5 ml of the respective metal ion solution. The colour change is an evidence for the occurring of sensor reaction. It was observed by naked eye that only colour change

occurred (from yellow to blue) when Ag NPs were mixed with As (III) solution.

Analytical instrumentation

The absorbance spectra were measured in a quartz cuvette by UV-VIS Jasco analytical spectrophotometer (model No V-570). pH of all solutions was measured by conventional pH meter (EcoTestr pH1, Euttech Instruments). The zeta potential of the nanoparticles was measured by a ZetaPALS Zeta Potential Analyzed (Brookhaven Instrument Corporation). Transmission electron microscopy (TEM) images were obtained by FEI tecnai G2 20 at 120 kV accelerating voltage. The sample preparation of the nanoparticles observation in TEM was prepared as follows: an aqueous drop (1 μl) contained functionalised nanoparticles before and after sensing reaction (control and detection experiment) were injected by a micropipette on the support graphite film (15 nm in thickness) on a copper grid. The film must be strong, clean and must remain attached on the grid during this preparation step. After that the adsorbed nanoparticles on the support film were simply dried under vacuum and observed without any additional chemical staining.

Results and discussion

Optical characterisation of silver nanoparticles in aqueous suspension

The presence of silver nanoparticles in aqueous suspension after reduction of AgNO₃ salt was proved by the exhibition of an intense peak in the visible region due to the surface plasmon excitation as shown on Figure 1A (solid red line). Ag nanoparticles have free electrons, which give an optical effect known as the so-called surface plasmon resonance absorption band. This effect of nanoparticles in aqueous suspension occurred due to the combined vibration of the electrons of the nanoparticles in resonance with the light wave. The obtained local surface plasmon resonance (SPR) is a characteristic phenomenon of metal nanoparticles (particularly of Ag NPs) that depends on dielectric constant of its surrounding environment. The absorption band between 350 nm to 500 nm in the visible range of the light is typical for the silver nanoparticles. With increasing of Ag NPs diameter, the plasmon absorption shifts toward lower energy wavelength, i.e. red shifting. The prepared Ag NPs demonstrated stability in the colloidal solution one week after preparation. However, a week later the absorbance spectrum showed a little red shift (within 10-15 nm) with the decrease in absorbance intensity value. At the same time the absorption peak becomes broader which is an indication for suspension growth and occurring of aggregation. As the dielectric constant changes due to the presence of target analyte in the sample solution, we have observed red shift in localised SPR peak.

Colorimetric detection of As (III)

Citrate functionalised Ag NPs have negative surface charges. When As (III) ions are introduced with these functionalised nanoparticles, then a specific reaction between heavy metal ions and nanoparticle organic shell occurred in the analytical solution. After the proceeding of the detection reaction, alteration of the authentic SPR spectra was observed.

As shown on the figure, the UV-VIS absorption spectra revealed that arsenic containing Ag NPs have two absorption peaks – one at 420 nm and another around 585 nm (blue dashed line). Thus, as the surrounding environment was changed with the presence of As (III), a red shift in nanoparticles SPR and consequent colour change from yellowish to bluish was measured. Such red-shifted secondary absorption peak was not observed in the test experiments with other metal ions. This result implies that the achieved sensing unit has arsenic selective capability in a complex solution obtained from contaminated groundwater. The limit of detection was obtained in linear range as shown on Figure 1 B. The detection limit of citrate capped Ag NPs was found to be around 6 ppm. Lineal correlation (R^2) ~ 0.995 was observed between absorbance A_{585} and concentration of As (III) ranging from 6 to 14 ppm. The sensor reaction of the functionalised Ag

NPs toward As(III) detection is due to the specific reaction with hydroxyl (-OH) and carboxylic groups (-COOH) on the nanoparticles surface (Ag NPs are functionalised with citric acid ligands), which act as binding sites with the soluble arsenic ions in the media. Because of this specific interaction aggregation of the Ag NPs takes place as shown on Figure 1 C and D.

To determine the selectivity of citric capped Ag NPs toward other metal ions, 1.5 ml test tubes with pH = 7.5 contained chlorides of Na^+ , Ca^{2+} , Mg^{2+} , Fe^{3+} , Zn^{2+} , and Ni^{2+} were prepared. Functionalised Ag NPs were added to the tubes, mixed and observed for colour change. It was proved that only the arsenic containing sample showed prominent colour change of the test from yellow to bluish. In the other test no colour changes were observed in the visible range of the light spectrum.

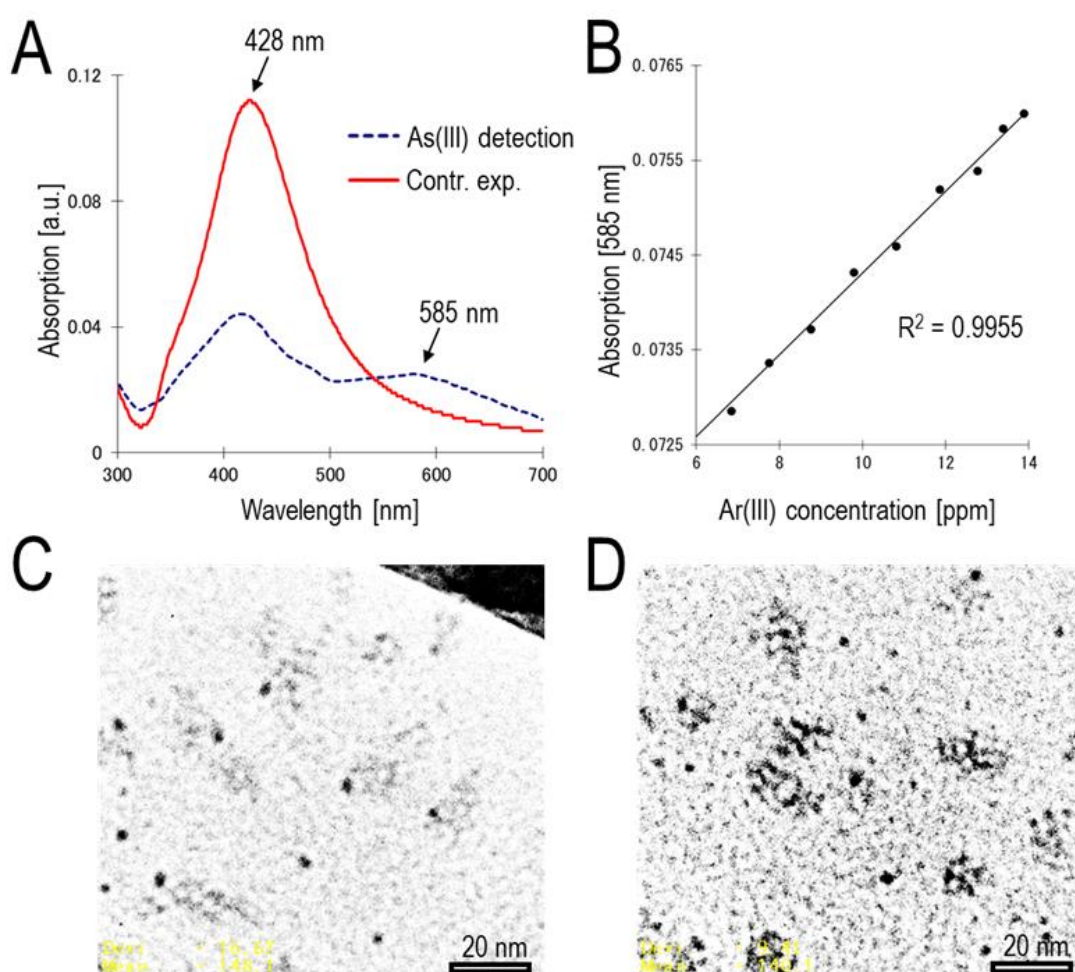


Fig. 1. Silver nanoparticles as colorimetric nanosensor for trace detection of arsenic (III) at pH = 7.5. (A) Absorbance spectra of citrate capped Ag NPs (red solid line) and nanoparticles reacted with As (III) ions (blue dashed line). (B) Detection limit of citrate capped Ag NPs for analysis of arsenic. Transmission electron microscope image of (C) monodispersed bare citrate capped Ag NPs and (D) nanoparticle aggregations formed due to sensor reaction with As (III); scale bar for C and D = 20 nm

Electron microscopic analysis of the nanoparticles

The diameter and size distribution of Ag NPs and Ag NPs adsorbed with As(III) were determined using 120 kV transmission electron microscope (TEM). The nanoparticle size histogram (Fig. 2) was obtained by measuring at least 350 NPs. Nanoparticles with different sizes and homogenous spherical shapes (as shown on Fig. 1 C) were obtained by the synthesis described above using sodium citrate reduction. However, the

use of a single reagent as sodium citrate for Ag NPs synthesis results in nanoparticles with a broad range of sizes between 1.5 nm to 8 nm. Surprisingly, bigger nanoparticles with a diameter bigger than 10 nm were not found in the sample during TEM observation. Even the change of reaction conditions, for example increasing the temperature, does not produce uniform in size Ag NPs. After interacting with arsenic the aggregations of Ag NPs were obtained. As shown on TEM

photo (Figure 1 D) the formed aggregations were also heterogeneous but with various sizes. The aggregations are

not stable in the suspension and there is precipitation on the tube bottom after keeping for a few days.

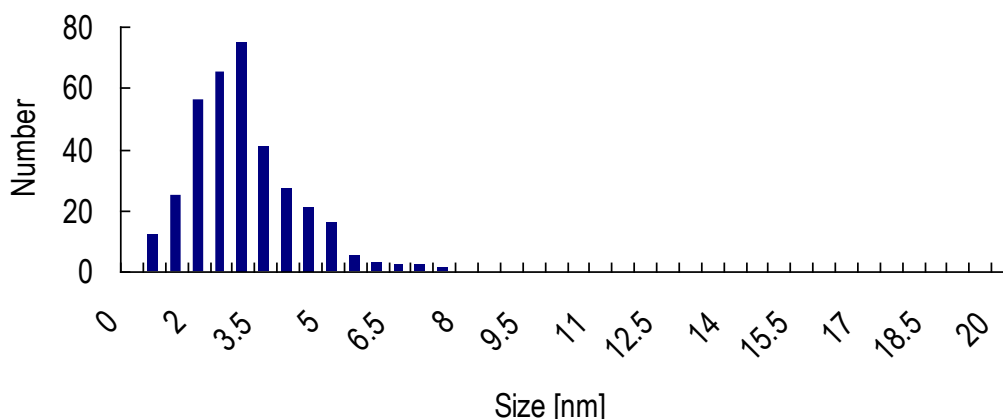


Fig. 2. Size distribution of silver nanoparticles capped with citric acid by number

Effect of pH on the detection reaction

The pH of analysed sample solution influenced both the solubility of metal ions and the stability of citrate capped Ag NPs. In acid conditions ($\text{pH} < 4$) neutralisation of nanoparticle surface occurred, which results in the change of SPR absorption band. This process happened in the absence of analytes. The experiments have proved that the optimum pH for effective colorimetric sensing was in the range between 5 and 9. Based on the obtained results a pH at 7.5 (using HEPES buffer) was selected for all experiments in order to obtain reproducible analyses. At this pH value the citrate ligands on the nanoparticle surface exhibit negative charges.

Conclusion

We have developed a colorimetric detection of arsenic (III) in aqueous medium by detection with citrate functionalised silver nanoparticles. The limit of detection was found to be around 6 ppm. It was measured in a linear range with a linear correlation (R^2) of 0.99. The proposed colorimetric approach is very simple, sensitive and cost effective. In addition, it required a small amount of reagents and cheap equipment to perform.

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References

Bhattacharya, P., G. Jacks, K. M. Ahmed, J. Routh, A. A. Khan. 2002. Arsenic in groundwater of the Bengal Delta

- Plain aquifers in Bangladesh. – *Bulletin of Environmental Contamination and Toxicology*, 69, 538–545.
- Brinkel, J., M. H. Khan, A. Kraemer. 2009. A systematic review of arsenic exposure and its social and mental health effects with special reference to Bangladesh. – *International Journal of Environmental Research and Public Health*, 6, 1609–1619.
- Hung, Y. L., T. M. Hsiung, Y. Y. Chen, Y. F. Huang, C. C. Huang. 2010. Colorimetric detection of heavy metal ions using label-free gold nanoparticles and alkanethiols. – *The Journal of Physical Chemistry C* 114, 16329–16334.
- Shankar, S., Shanker, U., Shikha. 2014. Arsenic contamination of groundwater: a review of sources, prevalence, health risks, and strategies for mitigation. – *Scientific World Journal*, 304524.
- Moghimi, N., M. Mohapatra, K. T. Leung. 2015. Bimetallic nanoparticles for arsenic detection. – *Anal. Chem.*, 87, 5546–5552.
- Priyadarshini, E., N. Pradhan. 2017. Gold nanoparticles as efficient sensors in colorimetric detection of toxic metal ions: a review. – *Sensors and Actuators B* 238, 888–902.
- Rosi, N. L., C. A. Mirkin. 2005. Nanostructures in biodiagnostics. – *Chem. Rev.*, 105, 1547–1562.
- Smedley, P. L., D. G. Kinniburgh. 2002. A review of the source, behaviour and distribution of arsenic in natural waters. – *Applied Geochemistry*, 17, 517–568.
- Talapin, D. V., J.-S. Lee, M. V. Kovalenko, E. V. Shevchenko. 2010. Prospects of colloidal nanocrystals for electronic and optoelectronic applications. – *Chem. Rev.*, 110, 389–458.
- Wang, C. C., H. T. Yau, C. C. Wang. 2013. Chaotic and subharmonic motion analysis of floating ring gas bearing system by hybrid numerical method. – *Mathematical Problems in Engineering*, 145716.
- Yogarajah, N., S. S. H. Tsai. 2015. Detection of trace arsenic in drinking water: challenges and opportunities for microfluidics. – *Environ. Sci. Water Res. Technol.*, 1, 426.