Talanta 132 (2015) 613–618

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Highly sensitive colorimetric detection of lead using maleic acid functionalized gold nanoparticles

Nalin Ratnarathorn [a], Orawon Chailapakul [b], Wijitar Dungchai [a,*]

[a] Department of Chemistry, Faculty of Science, King Mongkut's University of Technology Thonburi, Prachautid Road, Thungkru, Bangkok 10140, Thailand
[b] Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Patumwan, Bangkok 10330, Thailand

ARTICLE INFO

Article history:
Received 5 August 2014
Received in revised form
6 October 2014
Accepted 10 October 2014
Available online 23 October 2014

Keywords:
Colorimetric sensing
Gold nanoparticles
Lead

ABSTRACT

Highly sensitive colorimetric detection for Pb^{2+} has been developed using maleic acid (MA) functionalized GNP. The –COOH on MA was used to modify GNP surface whereas the other –COOH functional group have strong affinity to coordination behavior of Pb^{2+} allowing the selective formation more than other ions. MA–GNPs solution changed from red to blue color after the addition of Pb^{2+} due to nanoparticle aggregation. The different optical absorption and discriminate of particle size between the MA–GNPs solution with and without Pb^{2+} were characterized by UV–visible spectroscopy and transmission electron microscopy (TEM), respectively. The color intensity as a function of Pb^{2+} concentration gave a linear response in the range of 0.0–10.0 $\mu g\,L^{-1}$ (R^2=0.990). The detection limit was found at 0.5 $\mu g\,L^{-1}$ by naked eye and can be completed the analysis within 15 min. The MA–GNPs aggregated with Pb^{2+} showed high selectivity when was compared to other metal ions (As^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}) and anions (Cl^-, NO_3^- and SO_4^{2-}). Our proposed method was also applied for the determination of Pb^{2+} in real drinking water samples from 5 sources. The result of real water samples were not statistically significant different from the standard methods at the 95% confidence level (pair *t*-test method). Moreover, we evaluated our proposed method for the determination of trace Pb^{2+} concentration in real breast milk samples. The recoveries were acceptable and ranged from 101 to 104% for spiked Pb^{2+} in real breast milk samples. Thus, MA–GNP colorimetric sensing provides a simple, rapid, sensitive, easy-to-use, inexpensive and low detection limit for the monitoring of Pb^{2+}.

1. Introduction

The present food and drinking water are often contaminated with harmful substances for humans, either as part of the production process, natural or caused by the additives added to it. Lead (Pb^{2+}) is a major environmental pollutant and ranks second in the list of toxic substances that cause renal malfunction and damage to the brain and kidneys [1]. It has also been classified as carcinogenic agents by the World Health Organization (WHO) and International Agency for Research on cancer. Moreover, the long-term exposure to low concentrations of these metals causes adverse health effects. Therefore, WHO controlled level of lead in drinking water is not over 10 $\mu g\,L^{-1}$ [2]. Several methods have been used for the detection of lead such as atomic absorption spectrometry (AAS) [3–5], inductively coupled plasma mass spectrometry (ICP/MS) [6], inductively coupled plasma atomic emission spectroscopy (ICP/AES) [7], electrochemical method [8] and X-ray fluorescence spectrometry [9]. Although, these methods can detect lead sensitively and accurately, but there are limits in their complicated sample preparation processes, expensive, and required any specialized as well as sophisticated instrumentation [10].

Colorimetric sensors for Pb^{2+} determination attract much attention for their conveniences of visual observation and simple operations. They allow the direct analysis by the naked eyes without costly instruments compared with other methods. In recent year, gold nanoparticles (GNPs) have been widely used for colorimetric assays because their extinction coefficients are high relative to common organic compound [11–13]. GNPs have been extensively employed as colorimetric sensors for the detection of small concentrations of toxic metals such as arsenic, cadmium, cobalt, nickel and lead [14–16]. Kim et al. used GNPs capped with 11-mercaptoundecanoic acid to be capable of detecting Pb^{2+} through the coordination between the carboxylic groups and Pb^{2+} [17]. Moreover, Lu and co-workers reported a colorimetric sensor for Pb^{2+} detection using DNA-functionalized GNPs [18]. In 2010, GNPs capped with gallic acid (GA–GNPs) for the detection of Pb^{2+} has been reported. Huang and

* Corresponding author. Tel.: +66 2 470 9553; fax: +66 2 470 8840.
E-mail address: wijitar.dun@kmutt.ac.th (W. Dungchai).

http://dx.doi.org/10.1016/j.talanta.2014.10.024
0039-9140/

co-workers have also demonstrated the aggregation of GA–GNPs in aqueous solutions and its minimum detectable concentration for Pb^{2+} in drinking water is 10 nM or 2.1 μg L^{-1} [12]. The detection limits of GA–GNPs are lower than the maximum allowable contamination level of Pb^{2+} in drinking water (WHO). However, the European Food Safety Authority (EFSA) reported that even using a low concentration of Pb^{2+} in drinking water (2.1 μg L^{-1}), adverse effect children's intelligence development can be observed [19,20]. In the absence of a safe exposure limit of children to Pb^{2+} and because of its ability to accumulate in the body for a long time, a great interest in the evaluation of the adverse effects of Pb^{2+} in low concentrations has emerged. Moreover, Human Health State of the Science in Canada has studied the trace Pb^{2+} concentration in breast milk because it is good biomarkers of maternal and infant exposure to Pb^{2+}. The Pb^{2+} level in human milk was found in the range from 0.025 to 15.8 μg L^{-1} in 210 mothers cross Canada [21,22]. Therefore, a highly sensitive, selective, simple and rapid method for the detection and quantification of trace Pb^{2+} is still required not only for the acceptance criteria of food safety but also toxicology.

Maleic acid, which has two carboxylic groups ($HO_2CCH=CH-CO_2H$), should be suitable for the modification of nanoparticles surface. In the previous reports, GNPs was modified by thiol compounds such as glutathiol [10], cysteine [23], alkyl phosphate [24] and 11-mercaptoundecanoic acid [25] for the determination of Pb^{2+} in micromole level but maleic acid functionalized GNPs has been not investigated for the colorimetric detection of Pb^{2+}. Thus, the aim of this work was to develop the highly sensitive, selective, simple and rapid colorimetric sensor for trace Pb^{2+} determination using maleic acid modified GNPs. Maleic acid is easy to modify on GNPs surface within 1 h. MA–GNPs solution changed from red to blue color after the addition of Pb^{2+} and can be observed by the naked eye. The pH effect and the reaction time were studied in this work. The low limits of detection for Pb^{2+} at sub μg L^{-1} level with a short analysis time of 15 min were obtained by our proposed assay. Finally, our developed method was successfully applied for determination of trace levels of Pb^{2+} in drinking water samples and the human breast milk samples.

2. Experimental

2.1. Chemicals and materials

All chemicals used in experiment were analytical reagent (AR) grade and solutions were prepared using high pure water with a resistance of 18 MΩ cm^{-1}. Dithiothreitol (DTT), glutathione (Glu), homocysteine (Hcy), L-cysteine (L-cys), maleic acid (MA), metal ions (As^{3+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} using atomic absorption grade), KCl, KNO_3 and K_2SO_4 were bought from Sigma-Aldrich (St. Louis, Missouri). Whatman No. 1 filter paper was bought from Cole-Parmer (Vernon Hills, IL). All glassware was thoroughly cleaned with freshly prepared 1:1 HCl/HNO_3 and rinsed with high pure water prior to use. All metal ions stock solutions were prepared in 50 mM phosphate buffer pH 5.8.

2.2. Instrumentation

UV–visible absorption spectra were recorded in a quartz cuvette (1-cm pathlength) using a UV–visible spectrometer (Lambda 35, Perkin Elmer Instruments, USA). Size distribution of particles was recorded by Transmission Electron Microscope (TEM, TECNAI T20 G^2, FEI, Netherland). Photographic results were recorded using a digital camera (PowerShot S95, 10.1 Megapixels, Canon). An atomic absorption spectrometer (AAS) with a hollow cathode lamp and standard air/acetylene flame (Analyst 300, Perkin Elmer Instruments, USA) was used for atomic absorbance measurements. A hollow cathode lamp was used under the following operations conditions: wavelength: 283.3 nm; slit-width: 0.7 H nm; lamp current: 10 mA.

2.3. Synthesis of GNPs

100 mL of $HAuCl_4$ (0.01%) was added into a 250 mL Erlenmeyer flask and then boiled. After that, 3.5 mL of trisodium citrate (1%) was added and further rapidly stirred for 15 min. We continually stirred for 30 min without heating. The solution was cooled to room temperature which was stored in the refrigerator 4 °C before further use [15].

The MA–GNPs solution was prepared using self-assembly of the organic compound on the GNP surface. A red of GNP solution (~20 nm in diameter) was first prepared from GNPs stock solution. Then, 0.20 mL of 0.01 M MA was added into 0.40 mL of GNP solution to generate MA–GNPs. Organic compound was self-assembled on to the surface of GNPs by incubating the GNPs with the MA solutions for 1 h at room temperature. After this step, the GNP aggregation was characterized using UV–visible Spectrometry.

2.4. Detection of lead

0.60 mL of MA–GNP solution in the eppendrof was mixed with 0.40 mL of metal ion solutions (As^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}) and anions solutions (KCl, KNO_3 and K_2SO_4) in 50 mM phosphate buffer at pH 5.8. For background (Bg), 0.40 mL of buffer was mixed 0.60 mL of MA–GNP solution (Bg–MA–GNPs). Then, the mixture was incubated for 15 min at the room temperature and analysis by the spectrometer and TEM.

2.5. Sample preparation for transmission electron microscopy (TEM)

Transmission electron microscope (TEM) measurements were performed on TECNAI T20 G^2 instrument which operated at an accelerating voltage of 120 kV and the 25000× magnification. The sample solutions for TEM studies were prepared by placing a drop of GNPs, MA–GNPs, Bg–MA–GNPs and Pb^{2+}–MA–GNPs on a formvar coated copper grid. The films on the TEM grids were allowed to dry for 1 h. The size of nanoparticle studies was performed in aqueous solution by Center of Nanoimaging, Mahidol University.

2.6. Applications

To evaluate the utility of our proposed method, the Pb^{2+} in the drinking water samples from five different sources was quantified. Our method was validated against AAS. Prior to analysis by AAS, preconcentration was carried out on all samples. 1.5 L of sample was mixed with 1 mL of 0.1 M HCl and then heated to evaporate excess water until 5.0 mL of samples remained. For AAS, samples were adjusted to a final volume of 10 mL with deionized water. For our proposed method, 0.60 mL of MA–GNP solution in the eppendrof was mixed with 0.40 mL of the water sample without any pretreatment. Then, the mixture was incubated for 15 min at the room temperature and analysis by spectrometer. For testing of trace levels of Pb^{2+} in the human breast milk, the sample was divided two parts. The first was analyzed by our method without spiking Pb^{2+} and the second was spiked with the standard Pb^{2+} solution at 10.0, 25.0 and 50.0 μg L^{-1} to obtain the final concentration at 1.0, 2.5 and 5.0 μg L^{-1}, respectively. Prior to analysis, spiked samples were precipitated the protein by adding 0.75 mL of sample with 0.15 mL of 10% w/v TCA (Tri chloroacetic acid). After that, samples were stored at 4 °C for 15 min and then subjected to centrifugation at 14,500 rpm for 10 min. The precipitate was removed from the supernatant and kept only supernatant for analysis.