Analytica Chimica Acta xxx (2018) 1–6

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

Cu(II) triggering redox-regulated anti-aggregation of gold nanoparticles for ultrasensitive visual sensing of iodide

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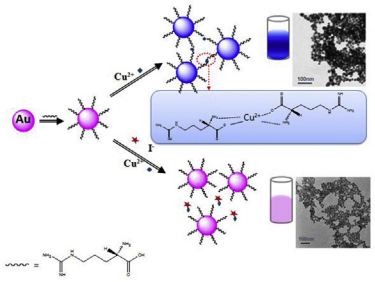
HIGHLIGHTS

- A facile and sensitive colorimetric assay for detecting of I^- in water was proposed.
- The strategy was based on a redox-regulated anti-aggregation of AuNPs in the presence of Cu^{2+}.
- The anti-aggregation process can be monitored through UV-vis spectrophotometer or by the naked-eye.
- This assay showed high sensitivity and exhibited good selectivity towards I^- over other anions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 May 2018
Received in revised form
13 June 2018
Accepted 29 June 2018
Available online xxx

Keywords:
Gold nanoparticles
Anti-aggregation
Colorimetric sensor
Iodide ion

ABSTRACT

In this study, we proposed a novel anti-aggregation of gold nanoparticles (AuNPs) strategy for colorimetric sensing of iodide ions (I^-) regulated by the redox reaction between the target ions and the ion cross-linking agent. Cu^{2+} as interlinking ion can induce aggregation of arginine capped AuNPs (Arg-AuNPs) due to the formation of Arg-Cu^{2+}-Arg analogous structure resulting from the chelation between Cu^{2+} and arginine, with a clear color change of solution from red to blue. In the presence of I^-, however, Cu^{2+} would be readily reduced owing to the formation of CuI, AuNPs underwent a transformation from an aggregation to a dispersion state depending on the concentration of I^-, leading color changes from blue to red. The corresponding color variation in the process of anti-aggregation of AuNPs can be monitored through UV–vis spectrophotometer or by the naked-eye, making quantitative analysis of I^- feasible in a convenient colorimetric or visual way. The assay only took 5 min, showing high sensitivity with a lowest detectable concentration of 10 nM and excellent selectivity for I^- over other anions tested, which was successfully applied for the detection of I^- in drinking water and table salt samples.

1. Introduction

Iodine is a key nutrient in the synthesis of thyroid hormones which are important for healthy metabolism, growth, and development [1]. Human body does not produce iodine, so it must be obtained from food, water or a supplement. Improper intake of

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https://doi.org/10.1016/j.aca.2018.06.080
0003-2670/

iodine remains a major concern in public health, because iodine deficiency and iodine excess are both associated with adverse health consequences. For example, iodine deficiency during pregnancy leads to insufficient maternal thyroid hormone, subsequently causing irreversible adverse effects on the neurological and cognitive functions of the offspring, while excess iodine intake might increase the prevalence of subclinical hypothyroidism [2]. Therefore, a facile, sensitive and selective method to monitor the levels of I^- in daily diet is highly required. A number of methods such as fluorescence method [3–6], atomic absorption spectrometry [7], capillary electrophoresis [8], electrochemical [9–11] and chromatographic method [12] have been well developed for detecting of I^-, however, all of which rely on expensive instruments and require sophiscated procedures. Hence, the development of simple and economical assay for point-of-care detection iodide is still appealing.

Colorimetric sensing methods are extremely attractive for biological and chemical analysis since targeted events can be transferred to a visual color change, allowing straightforward readout without any equipment. Metal nanoparticles, especially gold nanoparticles (AuNPs) [13–19] and silver nanoparticles (AgNPs) [16,20–23], have been extensively used to design visible sensing approaches based on their instinct optical properties that depend on their size, shape, and morphology. Typically, an aggregation of AuNPs or AgNPs induced by targets will lead to a visible color change of solution from red to blue, and the corresponding absorbance is related to the concentration of target analytes. For example, Lee et al. [24] proposed a colorimetric assay for the determination of I^- based on the aggregation of AuNPs in the presence of I^-, and the detection limit was as low as 15 nM; Shilpa et al. [25] developed a AgNPs-based colorimetric nanosensor for detection of I^- where Cu^{2+} was employed as interlinking agent, exhibiting good sensitivity with a detection limit of 0.24 μM. It should be noted that in these assays, the aggregation of AgNPs or AuNPs not only depended on concentration of I^-, but also was highly sensitive to various external factors, such as pH values, ionic strength and environmental temperature etc. [25,26]. Therefore, the selectivity of the aggregation-based chromogenic assay is always a challenge.

Fortunately, the strategy of target-induced anti-aggregation was found to be quite a good solution, which involved the process of re-dispersion from aggregation of AuNPs with the introduction of target analyte. This dispersion-dominated colorimetric assay was able to improve selectivity since the re-dispersion of AuNPs was induced by the specific coordination between target analytes and ion chelating agent such as Hg^{2+} [27]. As a result, biosensors relied on Hg^{2+} mediated anti-aggregation of AuNPs have been well-developed for detection of biothoils such as glutathione (GSH) in complex biological samples, where the aggregation of amino acids capped-AuNPs was inhibited by the specific interaction between GSH and Hg^{2+} with the introduction of GSH [28–30]. The colorimetric sensing of I^- detection based on Hg^{2+} mediated anti-aggregation of AuNPs also exhibited high sensitivity with a low detection limit of 10 nM [31]. Nonetheless, using the highly toxic Hg^{2+} during the above experiments is always unfavorable.

From the perspective of greener approach, Cu^{2+} is a good alternative as ion chelating agent. Moreover, Cu^{2+} would be easily reduced in the presence of I^- as the formation of highly stable CuI. Therefore, herein we proposed a novel redox-regulated anti-aggregation of AuNPs strategy for colorimetric detecting I^-. Rather than the coordination between I^- and Hg^{2+} in previous studies [27,29–32], the present assay showed an anti-aggregation principle based on the redox nature of target ion of I^- and chelating agent of Cu^{2+}. Namely, when Cu^{2+} was added, the arginine capped AuNPs aggregated immediately induced by the coordination between Cu^{2+} and amino acids, with a concomitant red-to-blue color change. While in the simultaneous presence of I^- and Cu^{2+} in the system, the redox reactions between Cu^{2+} and I^- inhibited the aggregation of Arg-AuNPs, and the color changed from blue to red. A colorimetric assay for the determination of I^- was thus established. The proposed assay exhibited desirable selectivity and sensitivity towards I^- when it was applied for I^- screening in real samples.

2. Experimental

2.1. Chemicals and solutions

Chloroauric acid ($HAuCl_4 \cdot 3H_2O$), citrate trisodium, NaF, KCl, NaBr, $NaNO_3$, Na_2SO_4, Na_2CO_3, NaAc, $NaHCO_3$ and polyvinylpyrrolidone (PVP, M.W. 40000) were received from Sinopharm Chemical Reagent Co., Ltd., China. KI, L-Arginine and $CuCl_2$ were purchased from Aladdin. All of the reagents were of analytical grade and used without further purification. Ultrapure water was used throughout the experiments.

Standard stock solutions of Cu^{2+} (10 mM) and different concentration of I^- from 10^{-2} mM to 10 mM were prepared by dissolving an appropriate amount of $CuCl_2$ and KI in Milli-Q water, respectively.

2.2. Instrumentation

UV–vis absorption spectra were measured on SP-2500 UV–vis spectro-photometer. Transmission electron microscopy (TEM) analysis was performed using a transmission electron microscope (Tecnai G2 F20, America). The dynamic light scattering (DLS) analysis on a Malvern Nano ZS90 instrument. All glasswares used in the following procedure were cleaned with aqua regia, rinsed with ultrapure water and dried in air in sequence.

2.3. Preparation of citrate-capped AuNPs

Citrate-capped gold nanoparticles (approximately 13 nm diameter) were prepared by the classical citrate reduction of $HAuCl_4$ based on the reported method [33]. In a typical procedure, a 100 ml water solution containing 1 mM $HAuCl_4$ was heated to reflux with vigorous stirring in a three-necked flask fitted with a reflux condenser. Followed by the rapid addition of 10 ml solution containing 38.8 mM sodium citrate to the boiled solution, the mixed solution was heated under reflux for an additional 15–20 min and the color changed to wine red, indicating the formation of AuNPs. The obtained solution was allowed to cool at room temperature. The citrate capped AuNPs were stable at least for two months when stored at 4 °C.

2.4. Synthesis of arginine modified AuNPs (Arg-AuNPs)

It is well-known that amino acids can bind AuNPs through their amino groups, arginine was accordingly assembled on the surface of citrate-capped AuNPs. Briefly, the modified AuNPs were prepared by mixing 1 ml of 1 mM arginine solution and 10 ml AuNPs solution. The mixture of the solution was incubated for 60 min on shaking table at room temperature then left overnight without any disturbance.

2.5. Colorimetric detection of I^- using Arg-AuNPs

For the detection of I^-, the different concentrations of I^- were added to the Arg-AuNPs (1 ml) and diluted to 2 ml with phosphate-buffered saline (PBS pH = 7.4), followed by addition of 14 μL of Cu^{2+}

Please cite this article in press as: R. Peng, et al., Cu(II) triggering redox-regulated anti-aggregation of gold nanoparticles for ultrasensitive visual sensing of iodide, Analytica Chimica Acta (2018), https://doi.org/10.1016/j.aca.2018.06.080