2021

A Convenient and Sensitive Colorimetric Iodide Assay Based on Directly Inducing Morphological Transformation of Gold Nanostars

Follow this and additional works at: <https://www.jfda-online.com/journal>

Part of the [Food Science Commons](#), and the [Medicinal Chemistry and Pharmaceuticals Commons](#)

This work is licensed under a [Creative Commons Attribution-Noncommercial-No Derivative Works 4.0 License](#).

Recommended Citation

Zhou, Rongju; Huang, Xiaohui; An, Qingxiao; Xu, Weizhen; Llu, Yi; Xu, Dong; Wang, Suyan; Lin, Qinlu; and Zhang, Jianglin (2021) "A Convenient and Sensitive Colorimetric Iodide Assay Based on Directly Inducing Morphological Transformation of Gold Nanostars," *Journal of Food and Drug Analysis*: Vol. 29 : Iss. 1 , Article 11.

Available at: <https://doi.org/10.38212/2224-6614.3139>

This Original Article is brought to you for free and open access by Journal of Food and Drug Analysis. It has been accepted for inclusion in Journal of Food and Drug Analysis by an authorized editor of Journal of Food and Drug Analysis.

A Convenient and Sensitive Colorimetric Iodide Assay Based on Directly Inducing Morphological Transformation of Gold Nanostars

Cover Page Footnote

This work was supported by funding from the National Natural Science Foundation of China (21505162, 31571874), the Grain-Oil Process and Quality Control 2011 Collaborative and Innovative Grant from Hunan province, Linyi Science and Technology Innovation Development Plan Project (201919044), and Training Program for Excellent Young Innovators of Changsha (kq1802043). We also gratefully acknowledge financial support from China Scholarship Council.

A convenient and sensitive colorimetric iodide assay based on directly inducing morphological transformation of gold nanostars

Rongju Zhou^a, Xiaohui Huang^b, Qingxiao An^a, Weizhen Xu^a, Yi Liu^c, Dong Xu^{a,*}, Qinlu Lin^{a,**}, Suyan Wang^a, Jianglin Zhang^d

^a National Engineering Laboratory for Rice and By-products Further Processing, College of Food Science and Engineering, Central South University of Forestry & Technology, Changsha, 410004, China

^b Hunan Edible Fungi Institute, Changsha, 410004, China

^c Women & Children's Health Care Hospital of Linyi. NO.1, Linyi City, Shandong Province, 276016, China

^d Department of Dermatology, Xiangya Hospital, Central South University, Changsha, 410008, China

Abstract

We propose a convenient and easy colorimetric assay for highly sensitive detection of iodide by using gold nanostars (GNSs) as probes. The assay relies on that iodide directly changes the morphology of GNSs and alters their longitudinal localized surface plasmon resonance (LSPR) without surface modifications and the use of other reagents. Upon increasing iodide concentration, GNSs gradually transformed to sphere gold nanoparticles, the absorbance at longitudinal LSPR decreased, and solution color varied from greenish blue to red, as confirmed by the UV-Vis absorption spectroscopy and transmission electron microscopy. With this strategy, as low as 0.005 μM of iodide can be determined due to the specific properties of GNS with plenty of tips and corners and high surface-to-volume ratio. The detection was simply achieved by mixing testing samples and GNS solution. Many ions like CO_3^{2-} , S^{2-} did not interfere with iodide detection since only iodide can trigger GNS geometry change through an electron injection process. The iodide contents in river water, table salt, seaweed, and complex vitamin tablet were quantified with great accuracy. The proposed assay shows great promises for environment protection and food safety. Moreover, GNSs are useful in developing colorimetric assays for biochemical analysis or clinical diagnosis.

Keywords: Colorimetric, Gold nanostar, Iodide detection, Morphological transformation

1. Introduction

Iodine plays a vital role in human growth and metabolism [1]. It is an essential ingredient for producing thyroid hormone for tuning body functions. Both its deficiency and abundance in the body would induce many health problems [2, 3]. For example, iodine deficiency would cause goiters, a public health issue in many regions on earth. On the other hand, its excess intake would cause hypothyroidism and hyperthyroidism [4].

High intake could cause thyroid papillary carcinoma and lead to acute poisoning symptoms, including abdominal pain, duodenal ulcer, and renal failure [5]. Still, the risks of iodine poisoning continually persist. A variety of products like germicides, antiseptics, contrast media, and medication contain iodine [6]. Although the spreading of iodized salt in cooking is an effective measure for preventing iodine deficiency, its irrational consumption however has become another crucial reason for its overdose in human

Received 9 August 2020; revised 3 November 2020; accepted 25 November 2020.
Available online 15 March 2021

* Corresponding author. National Engineering Laboratory for Rice and By-products Further Processing, College of Food Science and Engineering, Central South University of Forestry & Technology, Changsha, 410004, China Fax: +86 731 85623241.

** Corresponding author. Fax: +86 731 85623241.
E-mail addresses: philip198349@gmail.com (D. Xu), LinQL0403@163.com (Q. Lin).

<https://doi.org/10.38212/2224-6614.3139>

2224-6614/© 2021 Taiwan Food and Drug Administration. This is an open access article under the CC-BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

body. Especially for people living in the coastal area who eat much seaweed, the daily intake of iodine can reach as high as 50–80 mg, while the recommended daily intake of iodine is 150 μg for an adult [7]. Iodide (I^-) has the lowest valence among the chemical species, including I_2 , IO_3^- and IO_4^- . Normally, iodine content is quantified after converting other species to I^- or I_2 [8]. To date, traditional techniques including chromatography, electrochemical methods, and fluorescent assays, which usually require expensive instruments and operation skills, fail to meet the demand of the modern testing requirement such as on-the-spot analysis and simplicity [9, 10]. Therefore, the development of sensitive and simple analytical approaches for the detection of iodide is of great importance.

Due to the localized surface plasmon resonance (LSPR), gold nanomaterials such as gold nanoparticle, gold nanorod (GNR), gold nanocube, gold triangular nanoplate, and gold nanostar (GNS) with outstanding optical properties have been extensively applied as reporters for sensing analytes in modern analytical techniques [11–14]. However, comparing to other nanomaterials, GNS has specific properties originating from its geometry and is less employed in assays [15]. Composed of a quasi-sphere core and several branches, GNS processes both longitudinal and transverse LSPR modes. Its longitudinal LSPR could be readily regulated from visible to near-infrared region by tuning nanoparticle size and number and length of branches [16, 17]. The unique morphology with many corners and tips governs the arrangement of atoms, thus forming various facets including high-index facets. These features trigger a higher sensitivity to local changes in the dielectric environment [18], a more considerable enhancement of electric fields [16, 19], and a higher surface-to-volume ratio, as well as a better photothermal effect than that of GNRs [20]. Notably, a refractive index sensitivity of 703 nm/RIU is brought about for GNSs, more remarkable than other shaped nanoparticles like sphere gold nanoparticle (44 nm/RIU) [21]. Consequently, GNSs have gained broad applications in surface-enhanced Raman scattering [19, 22], refractive index sensing [23, 24], and photothermal imaging. However, their documents in colorimetric assays were rarely reported, probably because the general strategy of analyte-induced nanoparticle aggregation is not effective for GNSs since aggregation does not induce an apparent color change.

Iodide has specific interactions with gold. The affinity between iodide and gold is strong, making iodide spontaneously chemisorbed on the gold surface [25–27]. Based on this, labeling gold nanoparticles for radioactive imaging was implemented by mixing gold nanoparticles with iodine-125 [27]. Gold nanoparticle geometry has been adjusted to various shapes by adding different amounts of iodide to inhibit gold deposition on specific facets based on the difference of affinity between gold facets and iodide [28–30]. The iodide adsorption can neutralize surface charge, lower surface potential, and even induce gold nanoparticle aggregation. Accordingly several iodide colorimetric assays using gold nanoparticles have been proposed [31–33]. Furthermore, it was found that iodide can cause gold nanomaterials to fragment, fuse, and morphologically transform through an electron injection process [26]. Correspondingly, their LSPR properties depending on the geometry vary [34, 35]. Such variations were discovered on GNRs under the high concentration of iodide. Whether this phenomenon can take place on other gold nanomaterials at a low iodide level remains unknown.

In the present study, a novel and simple iodide colorimetric assay was proposed based on inducing the morphological transition of GNSs. This sensor is conveniently realized by just mixing GNS solution and testing samples without complex nanoparticle modification and the involvement of other reagents. The shape transformation of GNSs to sphere gold nanoparticles would change solution color and UV-Vis spectra that are highly dependent on nanoparticle geometry. Because of the unique morphology of GNSs and specific interaction between iodide and gold, the assay showed high sensitivity and selectivity toward iodide. Finally, the assay was validated to detect iodide content in various real samples.

2. Experimental

2.1. Chemicals and materials

4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), and ascorbic acid (AA) were bought from Sigma-aldrich. Potassium iodide (KI), sodium chloride (NaCl), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), sodium acetate trihydrate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$), potassium nitrate (KNO_3) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All the reagents were analytical grade and used without further purification.

Deionized ultra-filtered water was used throughout the experiments. UV-Vis spectroscopy of nanoparticle suspensions were performed using a UV-1800 spectrometer (SHIMADZU Ltd. Japan). The iodide concentrations were determined by an ICP-MS (iCAP-RQ, Thermo Fisher Scientific Inc, USA). Energy-dispersive X-ray (EDX) spectroscopy and transmission electron microscope (TEM) images were conducted on JEM-2100 from Electron Optics Laboratory Co., Ltd in Japan.

2.2. GNS synthesis

GNSs were prepared through mixing HAuCl_4 and HEPES solutions according to the reported method [36]. HEPES acts as both the reducing agent and the template for GNS formation. Briefly, 20 mL of 0.1 M HEPES at pH 7.4 mixed with 80 mL distilled water in a 100-mL volumetric flask, and then 823 μL of 24.28 mM HAuCl_4 was added to the mixture drop by drop. Then, the solution was kept undisturbed at room temperature for another 30 min. The color would change from light yellow to mauve to greenish-blue, indicating the formation of GNSs. To study the effect of GNS geometry on iodide detection, GNSs with various longitudinal LSPRs were prepared by changing HEPES concentrations from 25 mM to 200 mM in synthesis [16, 36, 37].

2.3. Sensitivity and selectivity

For iodide detection, the procedures are uncomplex and achieved by mixing testing samples with GNS solution without the engagement of other reagents. The longitudinal LSPR of GNSs, solution pH, and reaction time were optimized in advance. To detect iodide, 750 μL of GNS solution (pH 6.8) was added into a 2-mL centrifuge tube and then aliquots (750 μL) of iodide solution (ultimate concentrations: 0, 0.01, 0.05, 0.1, 0.5, 0.75, 1, 1.1, 1.2, 1.3, 1.4, 1.5, and 1.6 μM) were injected separately into each tube. After vortexing for 10–20 s and further incubation at room temperature for 120 min, UV-Vis spectra of the solutions were recorded to quantify iodide concentration. To investigate the selectivity of our assay, the above procedures were repeated by replaced iodide with 10 μM of ions, including CO_3^{2-} , S^{2-} , SO_4^{2-} , NO_3^- , Cl^- , CH_3COO^- , AA, K^+ , Na^+ , and Ca^{2+} .

2.4. Analysis of real samples

To evaluate the application of our assays, we tested iodine contents in river water, table salts, seaweed, and complex vitamin tablets. River water

from Xiang River at Changsha in Hunan province, China, was collected and filtered with a 0.2 μm membrane. The uniodized and iodized table salts and seaweed were bought from a supermarket. Complex vitamin tablets were purchased from a local pharmacy, on which the label shows it contains iodine 150 mg/Kg. In these samples, iodine species include organic iodine, IO_3^- , etc., rather than I^- . Thus, pretreating the samples and transforming other iodine species to iodide are necessary for the detection. For example, KIO_3 is usually used in iodized table salt, which can be transformed to iodide using the reducing reagents. Briefly, 1 g of iodized salt was weighed accurately and dissolved in distilled water with a final volume of 99 mL. Afterward, 1.0 mL of 20 mM AA was added and the mixture was kept at 50 °C for 20 min, ensuring IO_3^- is reduced to I^- [38]. The processing of seaweed and complex vitamin tablets was according to GB 5009.267-2016 with some modifications [39]. Briefly, 2–3 g of samples were put into a crucible, followed by adding 5 mL of 0.47 M Na_2CO_3 solution. Then, the crucible was heated on an electric furnace until there is no smoke. Subsequently, the carbonized samples were placed in a muffle furnace, heated and kept at 600 °C for 4 hours. Take them out after the furnace temperature drops to 200 °C. After cooling down, add 5 mL water to the ashed samples and transfer the mixture to a 100 mL volumetric flask, followed by washing twice. Followingly, 1.0 mL of 20 mM AA was added and the solution was kept at 50 °C for 20 min. After cooling down to room temperature, the volume was set to 100 mL by adding water. For iodide detection, 750 μL of sample solution mixed with 750 μL GNS solution (pH 6.8) thoroughly. After incubation for 120 min, the UV-Vis spectra were recorded. Additionally, if the detected iodide content exceeds the detection range, the samples should be diluted five times and re-detected. All the analytical results were repeated at least three times.

3. Results and discussion

3.1. Iodide sensing by inducing GNS shape transition

The exposure to iodide leads to shape transformation for GNSs and results in a noticeable variation of longitudinal LSPR (Fig. 1). Typically, the as-synthesized GNSs have two typical absorption peaks at 632 and 526 nm, respectively, assigning to their longitudinal and transverse LSPR modes [16, 36, 37]. With the presence of 1 μM of I^- , the absorbance at the longitudinal LSPR reduced, while that

Fig. 1. (A) The UV-Vis spectra and (B) TEM images of gold nanostars (GNSs) in the presence of 0 (1), 1.0 (2), and 5.0 (3) μM of iodide after reaction for 60 min. Insets in (A) are the corresponding photos of solutions. (C) The UV-Vis spectra of GNR solution with and without 10 μM of iodide after incubation for 60 min. (D) The EDX spectrum of GNSs (Left) and elemental mapping images of one nanoparticle (Right) after exposure to 5 μM iodide for 60 min.

at the transverse LSPR slightly increased within 60 min. If the concentration of iodide is higher (e.g. 5 μM), the UV-Vis curve underwent a remarkable variation and only one absorption peak at 521 nm was observed. Correspondingly, the solution color turned red from greenish blue, indicating the formation of sphere gold nanoparticles. Such variations are only originating from iodide in solution [26]. For comparison, GNRs were prepared by the seed-mediated method [40] and their UV-Vis spectra before and after an exposure to 10 μM of iodide have no apparent difference (Fig. 1C). These results confirm that a low level of iodide can cause GNSs to undergo a morphological change instead of GNRs, probably because of the specific morphology of GNSs with many tips and corners on surface and the resultant high active facets. To further confirm these results, we obtained TEM images of GNSs in

the presence of 0, 1, and 5 μM of iodide ions, respectively. The morphology of nanoparticles has a drastic change from multi-branches to sphere. The original GNS has an outer and inner diameter of 38.1 nm and 20.3 nm with 2-5 branches. The sizes changed to 36.7 nm (outer diameter) and 21.2 nm (inner diameter) with the presence of 1.0 μM of iodide, respectively, indicating the shortened branches and the rounded tips. At a higher concentration of iodide (5.0 μM), all nanoparticles became quasi-spherical, with a diameter of 24.5 nm. The decreasing outer diameter and increasing inner diameter suggest that the shape transition is not due to etching. From the TEM images, the shape transition occurred independently and did not undergo nanoparticle aggregation, fusion, and reformation reported in previous literature [26]. The main reason is, HEPES can efficiently stabilize GNSs. These

GNSs were negatively charged and the further adsorption of iodide on surface would not lead to nanoparticle aggregation because the charge remained negative. Besides, the affinity between HEPES and gold surfaces is less than that for iodide, so that iodide can still reach gold surface and induce shape transformation. Furthermore, the EDX spectrum demonstrates the transformed GNSs are only composed of Au and I, which account for 89% and 11% in weight, respectively (Fig. 1D). The elemental imaging illustrates that iodide wrapped the outside of gold nanoparticles deformed from GNSs. The concentration of GNSs is 0.44 nM calculated based on nanoparticle size. The content of iodide adsorbed on GNS surface was determined by ICP-MS and it was found one GNS can keep ~1570 iodide ions. In the shape transformation, an electron injection progress plays the key role [26]. Hence, without the participation of other reagents, we established a very simple and convenient assay for iodide detection by inducing morphological change of GNSs (Scheme 1).

3.2. Parameters affecting iodide detection

Because of the simplicity of this reaction, the parameters that affect the quantification are relatively few. The longitudinal LSPR of GNSs, solution pH, and incubation time were optimized, as Fig. 2 shown. GNSs with different longitudinal LSPRs at

556, 638, 672, 703, and 712 nm were synthesized using 25, 50, 75, 100, and 200 mM of HEPES, respectively [16, 36, 37]. The TEM images of these GNSs without and with iodide were illustrated in Fig. 2A. The variation of $\Delta A/A_0$ (where $\Delta A/A_0 = 1 - A/A_0$, A_0 and A are the absorbances at longitudinal LSPR in the absence and presence of iodide) reached the maximum (Fig. 2B) when the longitudinal LSPR of GNSs was at 638 nm. Obviously, the length of branches on GNSs increases upon raising HEPES concentrations, accounting for longer LSPR wavelength. For GNSs with longer branches, the shape transformation requires the engagement of more iodide. The same amount of iodide could cause the GNSs with the longitudinal LSPR at 556 nm and 638 nm to deform to sphere nanoparticles instead of these GNSs with longer LSPRs. But GNSs prepared with 25 mM of HEPES have a smaller $\Delta A/A_0$ variation than 50 mM of HEPES. In fact, these nanoparticles could not be regarded as the typical GNSs, for one absorption peak is at 556 nm. Thus, GNSs with longitudinal LSPR at 638 nm have the best response toward iodide. The impact of solution pH on the detection was investigated over the range of 6.8–8.2, since it is the extent that HEPES can buffer [41]. The derivation of this range could unstabilize GNSs and result in nanoparticle precipitation during a three-day storage. Upon increasing pH value, $\Delta A/A_0$ descended (Fig. 2C). pH 6.8 is optimum for iodide testing. Longer reaction time caused larger

Scheme 1. Schematic illustration of colorimetric iodide detection by inducing shape transition of GNSs.

Fig. 2. (A) The TEM images of GNSs in the absence and presence of iodide, which were synthesized using HEPES concentrations of 25, 50, 75, 100, and 200 mM (from left to right), respectively. The corresponding longitudinal LSPR of these GNSs are from 556 nm to 712 nm. (B–D) The impact of longitudinal LSPR of GNSs (B), pH (C), and reaction time (D) on iodide detection. The detection conditions are: (A–B) pH 7.4 and reaction time of 30 min; (C) GNSs with longitudinal LSPR at 638 nm and reaction time of 30 min; (D) GNSs with longitudinal LSPR at 638 nm and pH 6.8, in which the iodide concentrations are 5 μM for (A) and 1.2 μM for (B–D).

optical signal variations and higher sensitivity. As Fig. 2D illustrated, prolonging the reaction time can decrease the absorbance at the longitudinal LSPR continually, but the rate would be fast initially and gradually decreased. In view of shorter time required for actual detection, 120 min was finally selected.

3.3. Sensitivity and selectivity

To evaluate the sensitivity of the proposed assay, the UV-Vis spectra of GNSs in the presence of iodide over the range of 0–1.6 μM were recorded (Fig. 3). As expected, with the increasing iodide concentration, the absorbance at the longitudinal LSPR of

Fig. 3. (A) The UV-Vis spectra of GNS solution in the presence of iodide over the range of 0–1.6 μM . (B) The plot of $\Delta A/A_0$ at 638 nm versus iodide concentration.

Fig. 4. The optical response of GNSs upon the addition of different ions. The red bars represent the addition of individual ions, while the green bars show the response to iodide in the presence of other ions. (1) Blank, (2) CO₃²⁻, (3) S²⁻, (4) SO₄²⁻, (5) NO₃⁻, (6) Cl⁻, (7) CH₃COO⁻, (8) AA, (9) K⁺, (10) Na⁺, and (11) Ca²⁺. The concentrations of these ions are 10 μ M except iodide (1.5 μ M).

GNSs continually descends, while that at the transverse LSPR rises. In particular, only single LSPR peak can be observed when iodide concentrations are in the range of 1.4–1.6 μ M, and increasing the concentration leads to a wavelength blueshift of transverse LSPR, demonstrating the geometry is approaching to sphere. Because of the blueshift of transverse LSPR, we did not use the absorbance ratio to quantify iodide concentrations. Obvious color changes could be distinguished by naked eyes when iodide concentration is above 0.1 μ M. Two linear relationships between the variation of absorbance at 638 nm ($\Delta A/A_0$) and C_{iodide} were established separately. With iodide concentration over the range of 0.01–0.9, a linear equation of $\Delta A/A_0 = 0.011 + 0.048 \times C_{\text{iodide}}$ was constructed, with a correlation coefficient (R^2) of 0.993. Another linear range is 0.9–1.6 μ M and the equation is $\Delta A/A_0 = -1.067 + 1.246 \times C_{\text{iodide}}$ with $R^2 = 0.998$. Because iodide can be chemisorbed on gold surface

spontaneously [25–27], two varying trends suggest there are two kinds of gold atoms with both high and low affinities sites on GNS surface. Indeed, it was documented that GNSs possess [321] high-index facets and [100], [111] low-index facets, having different interactions with iodide [42, 43]. The detection limit is 0.005 μ M obtained by 3σ , superior to many reported assays [31, 32, 44] and even comparable to ion chromatography [45]. The high sensitivity originates from the specific geometry of GNSs; many corners and tips contribute to the high chemical activity of some gold atoms on surface and the large surface-to-volume ratio. Moreover, the most important feature of the proposed assay is its simplicity. Neither surface modification nor other reagents are required. The testing can be realized by mixing the testing samples and GNS solutions.

The interference from other ions, including CO₃²⁻, S²⁻, Cl⁻, SO₄²⁻, NO₃⁻, CH₃COO⁻, AA, Na⁺, K⁺, and Ca²⁺ on the iodide quantification was investigated (Fig. 4). Other ions would not cause such dramatic variation of $\Delta A/A_0$ as iodide did because of the specific interaction between iodide with gold atoms. Iodide can be adsorbed onto gold surface and directly induce nanoparticle morphological variation [26], whereas other ions could not induce such change. For instance, S²⁻ has a high affinity with the gold but is unable to change nanoparticle geometry. Therefore, our essay demonstrated high selectivity toward iodide, facilitating its applications in real sample testing.

3.4. Applications in real sample detection

We applied our assay to detect iodine content in river water, table salt, seaweed, and complex vitamin tablets. However, two issues must be solved for real sample detection. One is, the chemical iodine forms in real samples are different and other iodine species should be converted to iodide before testing. The other is, high

Table 1. Detection of iodide content in real samples ($n = 3$).

Sample	Added (μ mol/L or μ mol/Kg)	Detected (μ mol/L or μ mol/Kg)	Recovery (%)	RSD (%)
River water	0	ND	/	/
	0.10	0.11	110.0	6.7
	0.40	0.43	107.5	5.2
Uniodized table salt	0	ND	/	/
Table salt (spiked)	150	157.8	105.2	3.7
Iodized table salt	0	228.1	/	4.5
Seaweed	0	185.7	/	5.9
Complex vitamin tablet	0	1204.8	/	7.8

Note: ND denotes not detected. The concentration unit is μ mol/L for liquid and μ mol/Kg for solid.

ionic strength can disrupt GNS stability. It is widely recognized that KIO_3 is utilized to iodize salt, while organic iodine is present in seaweed and complex vitamin tablets. Therefore, seaweed and complex vitamin tablets were ashed at high temperatures. Then, the incubation with AA would convert other iodine species to iodide. To eliminate the effect from high ionic strength, the table salts were diluted by 100 times using distilled water prior to testing in view of the high sensitivity of our assay. The final NaCl concentration is 0.085 mol/L, which would not trigger nanoparticle aggregation and precipitation. The content in iodized salt in China is allowed in the range of 20–30 mg/Kg (157.5–236.2 $\mu\text{mol/Kg}$) [46], which is customarily determined by titration that is labor-intensive [47]. The iodide content in river water and iodized salt, spiked table salt, seaweed, and complex vitamin tablets were precisely quantified, as Table 1 shown. The iodized salt contained 228.1 $\mu\text{mol/Kg}$ of iodide, meeting the requirement of the standard. Seaweed contain iodine as high as 185.7 $\mu\text{mol/Kg}$ (23.58 mg/Kg), demonstrating the foods made of seaweed are a good choice for iodine supplement. The complex vitamin tablets contained 1204.98 $\mu\text{mol/Kg}$ (153.0 mg/Kg) of iodine, slightly higher than the label shows. Our assay has good recoveries of 105.2–110.0% for spiked samples and a small relative standard deviation (RSD) in the range of 3.7–7.8%. The results demonstrated excellent accuracy and great promise in real sample detection.

4. Conclusion

A simple and convenient colorimetric assay toward iodide was proposed based on it induces the shape transition of GNSs. As low as 0.005 μM of iodide can be detected. Such high sensitivity is probably due to the specific geometry of GNSs with multiple tips and corners and the resultant high surface-to-volume ratio and gold atoms with high chemical activities. Our assay exhibited excellent selectivity over other ions including CO_3^{2-} , S^{2-} , SO_4^{2-} , and *etc.*, since only iodide can induce GNS morphology transformation. More importantly, the detection is simply achieved by mixing GNS solution and the samples without the use of other reagents. The iodide content in real samples could be measured with good recoveries and high accuracy. Our assay shows a great prospect in the fields of environment protection and food safety. Moreover, GNSs with unique properties are valuable as a signal transducer for developing other sensitive sensors.

Acknowledgements

This work was supported by funding from the National Natural Science Foundation of China (21505162, 31571874), the Grain-Oil Process and Quality Control 2011 Collaborative and Innovative Grant from Hunan province, Linyi Science and Technology Innovation Development Plan Project (201919044), and Training Program for Excellent Young Innovators of Changsha (kq1802043). We also gratefully acknowledge financial support from China Scholarship Council.

References

- [1] Ahad F, Ganie SA. Iodine, iodine metabolism and iodine deficiency disorders revisited. *Indian J Endocrinol Metab* 2010;14:13–7.
- [2] Zimmermann MB, Boelaert K. Iodine deficiency and thyroid disorders. *Lancet Diabetes Endocrinol* 2015;3:286–95.
- [3] Leung AM, Braverman LE. Iodine-induced thyroid dysfunction. *Curr Opin Endocrinol. Diabetes Obes* 2012;19: 414–9.
- [4] Bürgi H. Iodine excess, best practice and research. *Clin Endocrinol Metab* 2010;24:107–15.
- [5] Clark MN. A fatal case of iodine poisoning. *Clin Toxicol* 1981;18:807–11.
- [6] Diosady L, Alberti J, Mannar MV, FitzGerald S. Stability of iodine in iodized salt used for correction of iodine-deficiency disorders. II. *Food Nutr Bull* 1998;19:240–50.
- [7] Li M, Waite KV, Ma G, Eastman CJ. Declining iodine content of milk and re-emergence of iodine deficiency in Australia. *Med J Aust* 2006;184:307.
- [8] Choengchan N, Uraisin K, Choden K, Veerasai W, Grudpan K, Nacapricha D. Simple flow injection system for colorimetric determination of iodate in iodized salt. *Talanta* 2002; 58:1195–201.
- [9] Yu Y-y, Chen Y-y, Gao X, Liu Y-y, Zhang H-y, Wang T-Y. Nanoparticle based bio-bar code technology for trace analysis of aflatoxin B1 in Chinese herbs. *J Food Drug Anal* 2018; 26:815–22.
- [10] Dervisevic M, Dervisevic E, Çevik E, Şenel M. Novel electrochemical xanthine biosensor based on chitosan–polypyrrole–gold nanoparticles hybrid bio-nanocomposite platform. *J Food Drug Anal* 2017;25:510–9.
- [11] Jans H, Huo Q. Gold nanoparticle-enabled biological and chemical detection and analysis. *Chem Soc Rev* 2012;41: 2849–66.
- [12] Bonanni A. M.J.A.c.a. Del Valle, Use of nanomaterials for impedimetric DNA sensors: a review. *Anal Chim Acta* 2010; 678:7–17.
- [13] Jin W, Maduraiveeran GJT. Electrochemical detection of chemical pollutants based on gold nanomaterials. *Trends Environ Anal Chem* 2017;14:28–36.
- [14] Liu Y, Deng Y, Dong H, Liu K, He NJSCC. Progress on sensors based on nanomaterials for rapid detection of heavy metal ions. *Sci China Chem* 2017;60:329–37.
- [15] Aad G, Abbott B, Abdallah J, Abdelalim AA, Abdessalam A, Abidinov O, et al. Nanostars shine bright for you : colloidal synthesis, properties and applications of branched metallic nanoparticles. *Curr Opin Colloid Interface Sci* 2011;16: 118–27.
- [16] Liu XL, Wang JH, Liang S, Yang DJ, Nan F, Ding SJ, et al. Tuning plasmon resonance of gold nanostars for enhancements of nonlinear optical response and raman scattering. *J Phy Chem C* 2014;118:9659–64.
- [17] Hao F, Nehl CL, Hafner JH, Nordlander P. Plasmon resonances of a gold nanostar. *Nano Lett* 2007;7:729–32.

- [18] Dondapati SK, Sau TK, Hrelescu C, Klar TA, Stefani FD, Feldmann J. Label-free biosensing based on single gold nanostars as plasmonic transducers. *ACS Nano* 2010;4: 6318–22.
- [19] Esenturk EN, Walker ARH. Surface-enhanced Raman scattering spectroscopy via gold nanostars. *J Raman Spectrosc* 2010;40:86–91.
- [20] Rodr-Guez-Oliveros R, Snchez-Gil JA. Gold nanostars as thermoplasmonic nanoparticles for optical heating. *Opt Express* 2012;20:621–6.
- [21] Chen H, Kou X, Yang Z, Ni W, Wang J. Shape- and size-dependent refractive index sensitivity of gold nanoparticles. *Langmuir* 2008;24:5233–7.
- [22] Hrelescu C, Sau TK, Rogach AL, Jckel F, Feldmann J. Single gold nanostars enhance Raman scattering. *Appl Phys Lett* 2009;94:153113.
- [23] Miao X, Wang T, Chai F, Zhang X, Wang C, Sun W. A facile synthetic route for the preparation of gold nanostars with magnetic cores and their reusable nanohybrid catalytic properties. *Nanoscale* 2011;3:1189–94.
- [24] Zhou ZY, Tian N, Li JT, Broadwell I, Sun SG. Nanomaterials of high surface energy with exceptional properties in catalysis and energy storage. *Chem Soc Rev* 2011;42:4167–85.
- [25] Wang J, Li YF, Huang CZ. Identification of Iodine-induced morphological transformation of gold nanorods. *J Phy Chem C* 2008;112:11691–5.
- [26] Cheng W, Dong S, Wang E. Iodine-induced gold-nanoparticle fusion/fragmentation/aggregation and iodine-linked nanostructured assemblies on a glass substrate. *Angew Chem Int Ed* 2003;42:449–52.
- [27] Walsh AA. Chemisorption of iodine-125 to gold nanoparticles allows for real-time quantitation and potential use in nanomedicine. *J Nanopart Res* 2017;19:152.
- [28] Jessl S, Tebbe M, Guerrini L, Fery A, Alvarez-Puebla RA, Pazos-Perez N. Silver-assisted synthesis of gold nanorods: the relation between silver additive and iodide impurities. *Small* 2018;14:1703879.
- [29] Millstone JE, Wei W, Jones MR, Yoo H, Mirkin CA. Iodide ions control seed-mediated growth of anisotropic gold nanoparticles. *Nano Lett* 2008;8:2526–9.
- [30] Chung PJ, Lyu LM, Huang MH. Seed-mediated and iodide-assisted synthesis of gold nanocrystals with systematic shape evolution from rhombic dodecahedral to octahedral structures. *Chem - Eur J* 2011;17:9746–52.
- [31] Zhang J, Xu X, Yang C, Yang F, Yang X. Colorimetric iodide recognition and sensing by citrate-stabilized core/shell Cu@Au nanoparticles. *Anal Chem* 2011;83:3911–7.
- [32] Deng H-H, Li G-W, Lin X-H, Liu A-L, Chen W, Xia X-H. An IMPLICATION logic gate based on citrate-capped gold nanoparticles with thiocyanate and iodide as inputs. *Analyst* 2013;138:6677–82.
- [33] Wei S-C, Hsu P-H, Lee Y-F, Lin Y-W, Huang C-C. Selective detection of iodide and cyanide anions using gold-nanoparticle-based fluorescent probes. *ACS Appl Mater Interfaces* 2012;4:2652–8.
- [34] Yang X-H, Ling J, Peng J, Cao Q-E, Ding Z-T, Bian L-C. A colorimetric method for highly sensitive and accurate detection of iodide by finding the critical color in a color change process using silver triangular nanoplates. *Anal Chim Acta* 2013;798:74–81.
- [35] Zhen S, Wu T, Huang X, Li Y, Huang C. Facile synthesis of gold nanoflowers as SERS substrates and their morphological transformation induced by iodide ions. *Sci China Chem* 2016;59:1045–50.
- [36] Xie J, Lee JY, Wang DIC. Seedless, Surfactantless, High-yield synthesis of branched gold nanocrystals in hepes buffer solution. *Chem Mater* 2007;19:2823–30.
- [37] Dam DH, Lee JH, Sisco PN, Co DT, Zhang M, Wasielewski MR, et al. Direct observation of nanoparticle-cancer cell nucleus interactions. *ACS Nano* 2012;6:3318–26.
- [38] Machado A, Mesquita RBR, Oliveira S, Bordalo AA. Development of a robust, fast screening method for the potentiometric determination of iodide in urine and salt samples. *Talanta* 2017;167:688–94.
- [39] Li X, Cao X, Li J, Xu J, Ma W, Wang H, et al. Effects of high potassium iodate intake on iodine metabolism and antioxidant capacity in rats. *J Trace Elem Med Biol* 2020;126575.
- [40] Gole A, Murphy CJ. Seed-mediated synthesis of gold nanorods: role of the size and nature of the seed. *Chem Mater* 2004;16:3633–40.
- [41] Gari D, Humbert L, Fils-Aim N, Korah J, Zarfabian Y, Lebrun J-J, et al. Development of buffers for fast semidry transfer of proteins. *Anal Biochem* 2013;441:182–4.
- [42] Niu W, Chua YAA, Zhang W, Huang H, Lu X. Highly symmetric gold nanostars: crystallographic control and surface-enhanced Raman scattering property. *J Am Chem Soc* 2015; 137:10460–3.
- [43] Pu Y, Zhao Y, Zheng P, Li M. Elucidating the growth mechanism of plasmonic gold nanostars with tunable optical and photothermal properties. *Inorg Chem* 2018;57:8599–607.
- [44] Chen L, Lu W, Wang X, Chen L. A highly selective and sensitive colorimetric sensor for iodide detection based on anti-aggregation of gold nanoparticles. *Sens. Actuators, B* 2013;182:482–8.
- [45] Ito K. Determination of iodide in seawater by ion chromatography. *Anal Chem* 1997;69:3628–32.
- [46] Fan L, Su X, Shen H, Liu P, Meng F, Yan J, et al. Iodized salt consumption and iodine deficiency status in China: a cross-sectional study. *J Glob Health* 2017;1:23–37.
- [47] Sheng-Min L, Li-Jun X, Rong-Hua Z, Chong Z-S, Li-Hui J, Jing M, et al. Control of iodine deficiency disorders following 10-year universal salt iodization in Hebei Province of China. *Biomed Environ Sci* 2009;22:472–9.