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

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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 \text{mM} 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 \text{CO}_3^{2-}, \text{S}_2^{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...
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 progress [26]. Correspondingly, their LSPR properties depending on the geometry vary [34, 35]. Such variations was 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 (HAuCl₄·3H₂O), and ascorbic acid (AA) were bought from Sigma-aldrich. Potassium iodide (KI), sodium chloride (NaCl), sodium hydroxide (NaOH), sodium carbonate (Na₂CO₃), potassium carbonate (K₂CO₃), sodium acetate trihydrate (CH₃COONa·3H₂O), potassium nitrate (KNO₃) 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 HAuCl₄ 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 HAuCl₄ 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 CO₃²⁻, S²⁻, SO₄²⁻, NO₃⁻, Cl⁻, CH₃COO⁻, AA, K⁺, Na⁺, and Ca²⁺.

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, IO₃⁻, etc., rather than I⁻. Thus, pretreating the samples and transforming other iodine species to iodide are necessary for the detection. For example, KIO₃ 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 IO₃⁻ 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 Na₂CO₃ 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. Subsequently, 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 retested. 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
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 \( \Delta A/A_0 = 1 - A/A_0 \), \( A \) and \( A_0 \) 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
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...
GNSs continually descends, while that at the transverse LSPR rises. In particular, only single LLSPR peak can be observed when iodide concentrations are in the range of 1.4-1.6 mM, 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 mM. Two linear relationships between the variation of absorbance at 638 nm ($\Delta A/A_0$) and $C_{\text{iodide}}$ 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 mM 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 μM 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 $\text{CO}_3^{2-}$, $\text{S}_2^{2-}$, $\text{Cl}^-$, $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{CH}_3\text{COO}^-$, $\text{AA}$, $\text{Na}^+$, $\text{K}^+$, and $\text{Ca}^{2+}$ 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, $\text{S}_2^{2-}$ 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

| Sample                  | Added (μmol/L or μmol/Kg) | Detected (μmol/L or μmol/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                           |              |         |
| 0.10                    |                           | 0.11                         |              |         |
| 0.40                    |                           | 0.43                         |              |         |
| Table salt (spiked)     | 0                         | 150                          | 157.8        | 3.7     |
| 0.10                    |                           | 157.8                        | 105.2        | 4.5     |
| 0.40                    |                           | 228.1                        |              | 5.9     |
| 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 μmol/L for liquid and μmol/Kg for solid.
ionic strength can disrupt GNS stability. It is widely recognized that KIO₃ 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 μmol/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 μmol/Kg of iodide, meeting the requirement of the standard. Seaweed contain iodine as high as 185.7 μmol/Kg (23.58 mg/Kg), demonstrating the foods made of seaweed are a good choice for iodine supplement. The complex vitamin tablets contained 1204.9 μmol/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 CO₃²⁻, S²⁻, SO₄²⁻, 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.

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