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The pH-dependent interaction of silver nanoparticles and hydrogen peroxide: A new platform for visual detection of iodide with ultra-sensitivity

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ABSTRACT

Considering the significance and urgency for the recognition and sensing of anions specifically, especially those of biological relevance, herein, a simple and reliable colorimetric iodide sensor that based on pH-dependent interaction of silver nanoparticles (AgNPs) and H_2O_2 was developed. In acidic medium, AgNPs reacted with H_2O_2 to produce Ag^+ and powerful oxidizing species. The powerful oxidizing species could etch AgNPs seriously. While, iodide acted as an antioxidant could protect AgNPs from oxidation-etching by the powerful oxidizing species. In neutral and alkaline medium, the reaction of AgNPs and H_2O_2 mainly produce Ag^+. The existence of iodide could complex with Ag^+, forming AgI, which paved the way for aggregation of AgNPs. Based on the different responses of iodide to these different products of the reaction between H_2O_2 and AgNPs in solutions with different pH, iodide with concentrations down to 1 nM in acidic medium, 6 nM in neutral medium, and 100 nM in alkaline medium could be detected by naked-eye. More importantly, urinary iodide had been detected successfully. This simple and speedy method, which also exhibited remarkable selectivity and outstanding sensitivity, not only innovated the field of iodide recognition but also opened up a novel insight of the application of AgNPs.

1. Introduction

Owing to the ubiquity of anions in the ecosystem and the pivotal roles they exert, there is great demand for extremely sensitive and selective analytical tools for detecting and monitoring them. In fact, in nature, over two thirds of cofactors and substrates involved in biological transformations are anionic [1]. Among the anions, the iodide has been attracting much attention in recent years given its biological activities, such as mental development, growth, and alkaline metabolism [2–4]. The deficiency of iodide or iodine may cause spontaneous abortion, increased infant mortality, and mental defects [5–7]. The World Health Organization (WHO) has stated that iodine deficiency is the biggest cause for mental retardation on a global scale [8]. Driven by the demand, it is significant and urgent to recognize and sense iodide.

However, it is well know that halogen contains F, Cl, Br, I. Their physical and chemical properties were similar. Moreover, iodide is characteristic of large ionic radius, low charge density, and low hydrogen-bonding ability. These notorious properties make the specific iodide recognition and sensing a challenge to be explored [9–12]. Currently available techniques for detecting iodide include the spectroscopic method [13–19] and the electrochemical method [20–22]. In the respect of the spectroscopic method, a plenty of chemosensors based on supramolecular chemistry capable of recognizing, sensing, separating anions have been developed [23–25]. In spite of the good selectivity, the usage of chemosensors based on supramolecular chemistry may suffer from several drawbacks, such as complicated organic synthesis procedure involved, water-incompatible properties, and a rather high detection limit. Though the electrochemical methods were sensitive, most of them suffered from interferences by Cl^-, CN^-, SCN^- and so on [26–28]. To improve the selectivity, electrodes needed to be modified [29], which made the detection tedious, cost-consuming and time-consuming. Hence, the design of new sensors for iodide is still fascinating and challenging.

Colorimetry based on gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs) has been reputed as a methodology for sensing and imaging of analytes due to the visual signal feedback and facile quantification, without the aid of advanced instruments [30–33]. However, compared to the maturely developed chromogenic chemosensors based on supramolecular chemistry for iodide detection, colorimetric sensors based on noble metal nanoparticles (NPs) (e.g., Au and Ag NPs) are still significantly limited and require much more attention to be paid. There was only one colorimetric assay based on iodide induced

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reorganization of atoms of the core/shell Cu@Au nanoparticles [34]. In this study, we have developed a novel sensing platform based on pH-dependent interaction of AgNPs and H_2O_2 for the determination of iodide with high selectivity over competing analytes and low detection limits of 0.5 nM in acidic medium, 2.5 nM in neutral medium, and 30 nM in alkaline medium obtained by the absorption method. We found that AgNPs could react with H_2O_2 and the products were correlated with the acidity of the experimental conditions. In acidic medium, AgNPs reacted with H_2O_2 to produce Ag^+ and powerful oxidizing species. The powerful oxidizing species could etch AgNPs seriously. While, iodide acting as an antioxidant could avoid the oxidation-etching of AgNPs by powerful oxidizing species. In neutral and alkaline medium, the reaction of AgNPs and H_2O_2 mainly produce Ag^+. The existence of iodide could complex with Ag^+ to form AgI on the surface of AgNPs, which led to aggregation of AgNPs. Based on the different responses of iodide to these different products by the reaction between H_2O_2 and AgNPs in solutions with different pH, a simple and fast colorimetric sensor to detect iodide was developed. This ultra-sensitive method was simple and speedy, which innovated the field of iodide recognition and opened up a new insight of the application of AgNPs.

2. Results and discussion

2.1. Sensing iodide in acidic, neutral and alkaline medium

As manifested in Fig. 1, after encountering iodide, a visual color change of AgNPs could be detected which was distinguished from that of the initial AgNPs suspension in the presence of H_2O_2 (0.2 mM). Even at iodide concentrations as low as 1 nM in acidic medium, 6 nM in neutral medium and 100 nM in alkaline medium, the color of AgNPs changed. When only adding iodide to AgNPs' solution, color change could not be identified until the concentrations of iodide reached 1 μM in acidic condition and 10 μM in neutral or alkaline medium (Fig. S1). The lowest concentrations of iodide that could be distinguished by naked-eye using AgNPs as probes in the absence of H_2O_2 (0.2 mM) were much higher than that when iodide and H_2O_2 were sequentially added to AgNPs solutions. Obviously, H_2O_2 could endow AgNPs with prominent sensitivity for iodide sensing.

The effects of H_2O_2 on the color and absorption changes of AgNPs in different media (acidic, neutral and alkaline solutions) were also investigated. When adding H_2O_2 (0.2 mM) to AgNPs in acidic medium (pH 2.2), the yellow AgNPs became pale pink with a remarkable decrease of absorbance from 1.327 to 0.068 (Fig. S2A). This indicated that there was obvious interaction between AgNPs and H_2O_2 in acidic medium. However, if adding iodide first, then H_2O_2 was added (0.2 mM) to AgNPs, the absorbance of AgNPs increased gradually with the increased concentration of iodide (Fig. 1A) compared to that of AgNPs after reaction with 0.2 mM H_2O_2. While in neutral or alkaline medium, changes in color and absorbance did not occur obviously after adding H_2O_2 (0.2 mM) to AgNPs (Fig. S2B, C). However, on adding iodide before the addition of H_2O_2 (0.2 mM) to AgNPs, the absorbance of AgNPs weakened with the increase of the concentration of iodide (Fig. 1B, C) compared to that of AgNPs after reaction with 0.2 mM H_2O_2. Though the absorption variation trends of AgNPs with the concentration of iodide in acidic and neutral/alkaline medium were different, the extents of the color change of AgNPs were all correlated with the iodide concentration, which provided a visible or spectroscopic avenue for the iodide assay.

Based on the phenomena found above, the feasibility of the strategy for visible and spectroscopic detection of iodide was examined. With the increase of the concentration of H_2O_2, the sensitivity for the detecting of iodide increased. Meanwhile, the response of the sensor to other interferents also became sensitive. That is, the corresponding selectivity of the method reduced. Take both sensitivity and selectivity into consideration, 0.2 mM H_2O_2 was chosen for iodide detection because at this concentration, the detection of iodide was not only sensitive but also selective. Different amounts of iodide were firstly mixed with AgNPs' solution under different solution media and then 0.2 mM H_2O_2 was added. The solution of AgNPs showed a quick color response from pale pink, orange, pale green to dark red in acidic medium with the increased concentration of iodide (Fig. 1). In the case of neutral medium, a color change from yellow, orange to pink was obtained after AgNPs reacted with increased concentration of iodide in the presence of H_2O_2 (Fig. 1). The color changed from yellow to orange in alkaline medium under the above same experiment conditions (Fig. 1). All these results demonstrated that the color change of AgNPs was sensitive to iodide, and AgNPs could be used as highly sensitive colorimetric probes for iodide. The lowest concentrations of iodide that could be detected with the naked eye in acidic (1 nM) and neutral medium (6 nM) in our study were at least a magnitude lower than the detection limits

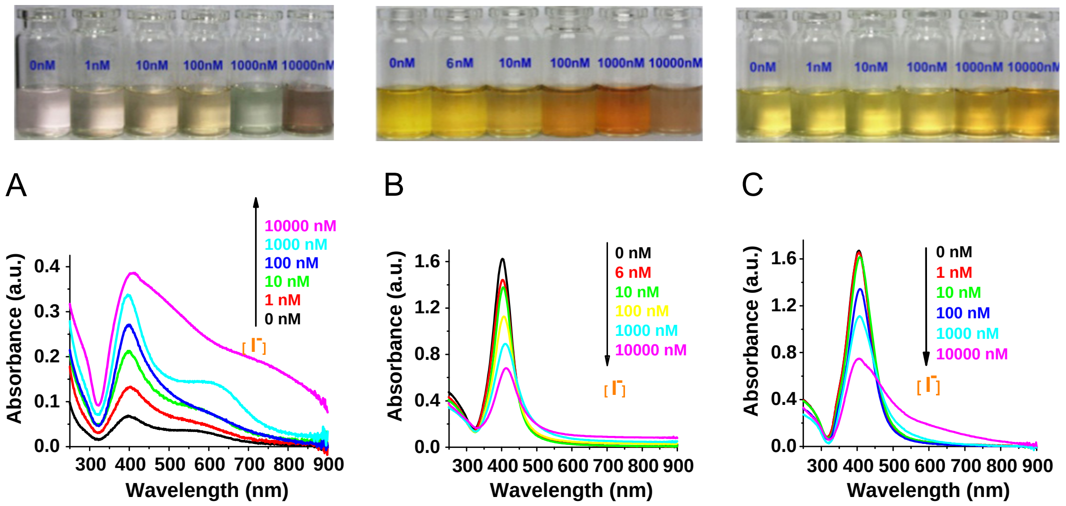


Fig. 1. Color change and corresponding absorption profiles of AgNPs solutions after interacting with different amounts of iodide (0–10 μM) and H_2O_2 (0.2 mM) in acidic (A), neutral (B) and alkaline (C) medium. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

obtained by reported methods, such as the spectroscopic method [13–19,23–25,34], and the electrochemical methods [20–22]. Furthermore, compared with the existing methods, this method was much simpler without the requirement of expensive and complicated instruments.

UV–vis spectroscopic measurements were also performed to determine iodide in addition to visual analysis. As shown in Fig. 1A (bottom part), with the increase of the concentration of iodide, the absorption band of AgNPs broadened and underwent a gradual enhancement in acidic medium. While the absorbance of AgNPs weakened gradually in neutral and alkaline medium with the increased concentration of iodide (Fig. 1B and C). The absorption intensity (A) showed a linear relationship with the logarithmic concentration of iodide (LogC) over the concentration range from 0.6 to 10,000 nM in acidic medium, with a correlation coefficient of 0.993 (Fig. S3A). Good linear correlations (0.999 and 0.996) between A_0–A (A_0 and A stand for the absorption intensity of AgNPs before and after reaction with iodide in the presence of H_2O_2) and the logarithm of iodide concentrations were found over the concentration range from 1 to 10,000 nM in neutral medium (Fig. S3B) and 10 to 10,000 nM in alkaline medium (Fig. S3C). The detection limits for iodide in our work were as low as 0.5 nM in acidic medium, 2.5 nM in neutral medium, and 30 nM in alkaline medium. Therefore, UV–vis spectra were fully consistent with the visual results, and UV–vis spectra could be another simple but sensitive approach for iodide sensing in our study.

A big difficulty for detecting iodide was how to decrease the potential interference from Br^- and Cl^-. In order to examine selectivity of this method, the interaction of different anions (Br^-, Cl^-, F^-, IO_3^-, BrO_3^-, ClO_3^-, $C_2O_4^{2-}$, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, SO_3^{2-}, AC^-, CO_3^{2-}, SCN^-, $S_2O_3^{2-}$) with AgNPs was investigated. It was found that no anion investigated could elicit a similar response as iodide did, even their concentrations was as high as 0.2 μM in acidic medium, 2 μM in neutral medium and 10 μM in alkaline medium (Fig. S4). In summary, we fabricated a facile colorimetric sensor that allowed the detection of iodide with good selectivity.

As is known, iodide content in urine has been widely used as a marker for assessment of iodide deficiency disorder. According to the World Health Organization, for a healthy human being, urinary iodide should be in the range 100–200 μg L^{-1}; an iodide level in urine below 50 μg L^{-1} is defined as iodide-deficient [35]. To evaluate the efficacy of this sensor in biological samples, this sensor was applied to detect iodide anion in urine. As presented in Table 1, this sensor worked quite well in urine, with recoveries around 95%. Most importantly, the compositions in urine sample almost did not interfere with the detection of iodide, indicating the potential application of this sensor for the analysis of iodide in real samples.

2.2. The mechanism of iodide sensing

2.2.1. The mechanism of sensing iodide in acidic medium

When adding H_2O_2 (0.2 mM) to AgNPs in acidic medium, the color of AgNPs became pale pink concomitantly with a remarkable decrease of absorbance from 1.327 to 0.068 (Fig. S2A). This obvious decrease in the absorption intensity of AgNPs might due to the "oxidation-etching" of AgNPs by H_2O_2. However, the absorbance of AgNPs could be recovered in the presence of iodide (Fig. 1A). The increase in the absorption intensity of AgNPs in the presence of iodide might result from that iodide prevented "oxidation-etching" of AgNPs induced by H_2O_2.

Table 1
Recovery experiment in urine samples using this method.

Urine samples	Added (μM)	Found[a] (μM)	RSD (%)	Recovery (%)
1	0	1.31	3.6	–
2	1.0	2.26	3.9	95.0
3	10.0	10.88	4.7	95.7

RSD=relative standard deviation.

[a] The mean of three experiments.

Different analytical techniques, including resonance light scattering, dynamic light scattering and high-resolution transmission electron microscopy were combined to elucidate size changes of the AgNPs after interaction with H_2O_2 or iodide and H_2O_2 (Fig. 2). After the addition of H_2O_2 (0.2 mM), the resonance light scattering intensity of AgNPs significantly decreased (Fig. S2A), which indicated the decrease of the particle size of AgNPs due to "oxidation-etching" by H_2O_2. Meanwhile, the change of the hydrodynamic size of AgNPs from 76.8 to 63.1 nm resulted from the addition of H_2O_2 (0.2 mM) also proved the decrease of the particle size of AgNPs. However, when adding iodide first, then H_2O_2 (0.2 mM) was added to AgNPs in acidic medium, the resonance light scattering intensity in the whole wavelength ranged from 300–700 nm was gradually enhanced with the increase of the concentration of iodide (Fig. 2A). Meanwhile, hydrodynamic sizes of AgNPs also increased from 63.1 to 83.4, 110.3, 183.6, 219.4 and 252.8 nm when the concentration of iodide was raised from 0 to 10 μM. These results demonstrated that the "oxidation-etching" of AgNPs was inhibited more and more greatly with the increased concentration of iodide. The increase of particle size of AgNPs was also evidenced by TEM images, which revealed that the AgNPs (whose diameter was about 8 nm) after reacted with H_2O_2 were smaller in size and less in amount than the AgNPs after reacted with iodide and H_2O_2 (0.2 mM) (Fig. 2C, D).

After the addition of H_2O_2 (0.2 mM), AgNPs were oxidized by H_2O_2 to produce Ag^+ and powerful oxidizing species in acidic medium [36–37], an "oxidation-etching" process of AgNPs. And the produced powerful oxidizing species would continually oxidize AgNPs to Ag^+, still an "oxidation-etching" process of AgNPs. The above "oxidation-etching" processes of AgNPs gave rise to the great decrease of the absorbance of AgNPs after its interaction with

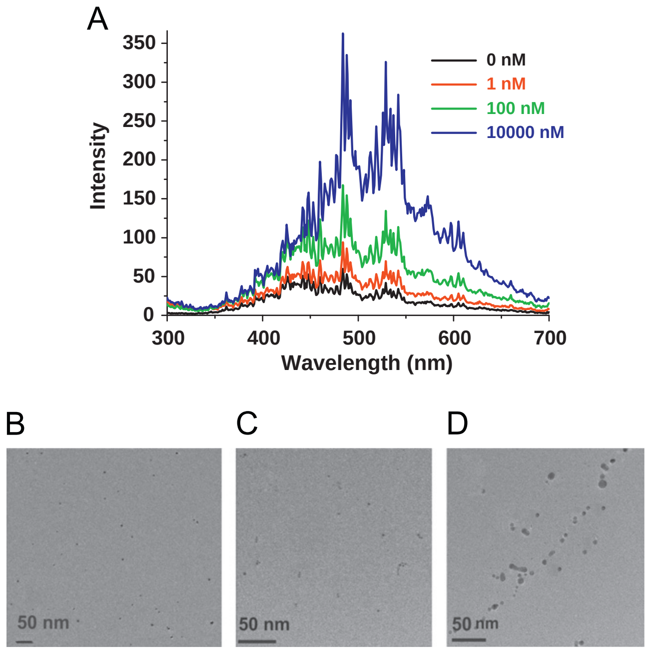


Fig. 2. Representative resonance light scattering spectra of AgNPs in the presence of increased iodide concentrations (0 nM, 1 nM, 100 nM, 10000 nM) and 0.2 mM H_2O_2 in acidic medium (A). The HRTEM images of AgNPs (B) and AgNPs before (C) and after (D) adding iodide (10 μM) in the presence of 0.2 mM H_2O_2 in acidic medium.

H_2O_2 (0.2 mM) in acidic medium (Fig. S2A). However, in the presence of iodide, the produced powerful oxidizing species from the reaction of AgNPs and H_2O_2 could instantly oxidized iodide on the surface of AgNPs to iodine, due to that the redox potential of I_2/I^- (0.54 V) was lower than that of Ag^+/Ag (0.799 V). The more concentration of iodide presented on the surface of AgNPs, the greater anti-etching effect for AgNPs could be obtained. Moreover, previous studies had reported that the iodide could readily scavenge a variety of powerful oxidizing species and played significant biological role as an inorganic antioxidant [38]. Because iodide could effectively scavenge powerful oxidizing species as an antioxidant to avoid the oxidation-etching of AgNPs by powerful oxidizing species, the absorbance of AgNPs after reaction with H_2O_2 in acidic medium was enhanced gradually when in the presence of increased concentration of iodide. It was found in our experiment that, only adding iodide ahead of H_2O_2 to AgNPs, the "oxidation-etching" of AgNPs could be avoided effectively, indicating that the absorption of iodide on the surface of AgNPs before the addition of H_2O_2 was favorable for its anti-etching effect. Exchange the addition sequence of iodide and H_2O_2, the effect of iodide for preventing the oxidation-etching of AgNPs would be greatly weakened. Meanwhile, substituted for iodide by Br^- or Cl^-, the effect to prevent the oxidation-etching of AgNPs was not as good as that of iodide, although their concentrations were as high as 0.2 μM (Fig. S4A). This was because the affinity of iodide for metal was greater than of Br^- or Cl^- [39–41]. In addition, the redox potentials of Br_2/Br^- (1.08 V) and Cl_2/Cl^- (1.358 V) were not as low as that of I_2/I^- (0.54 V).

Besides, from Fig. 2C we could find that after adding H_2O_2, AgNPs were closer to each other, which might have resulted from oxidation-etching of AgNPs after adding H_2O_2 in the absence of iodide. Because of oxidation-etching, the shape of AgNP particles would be asymmetry. In the case of anisotropic surfaces, the asymmetry would induce AgNPs to be closer to each other [42]. When after adding iodide and H_2O_2 (0.2 mM) to AgNPs, they were still dispersed although certain particles' morphology underwent some changes with some of them losing their spherical shape and aggregating to form elongated structures. The absorption of iodine, produced from the oxidation of iodide by powerful oxidizing species on the surface of AgNPs, would enhance van der Waals attractive force, leading to the increase of the surface stress of AgNPs [43] and resulting in the aggregation of AgNPs [44]. Thus, it was explicitly seen that the quantity and size transformation of AgNPs were the reasons responsible for the enhancement and broadening of absorbance of AgNPs when in the presence of increased concentration of iodide.

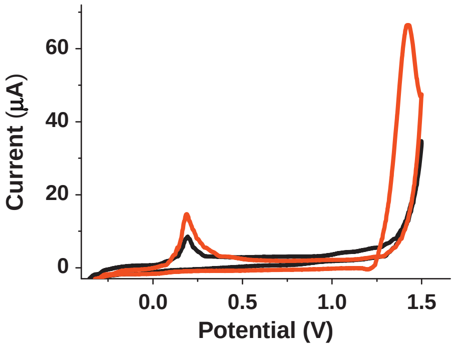


Fig. 3. Cyclic voltammograms of AgNPs after reaction with 0.2 mM H_2O_2 in the absence (black curve) and presence (red curve) of 10 μM iodide in acidic condition. The scan rate was 100 mV s^{-1}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The exploration of the detection mechanism of the method was assisted by the cyclic voltammogram studies (Fig. 3) to give insight into the products of AgNPs after reaction with H_2O_2 in the absence and presence of iodide. As shown in Fig. 3, only one oxidative peak appeared at about 0.2 V was found for AgNPs in the absence of iodide after its reaction with H_2O_2 in acidic medium. Thus, the oxidative peak at about 0.2 V resulted from the oxidation of AgNPs. However, after the reaction of iodide with AgNPs in the presence of H_2O_2, a new strong oxidative peak was seen at around 1.3 V. To understand what this new strong oxidative peak represented, iodide (10 μM) or iodine (10 μM) was added to AgNPs in acidic medium and their cyclic voltammograms were measured under the same experimental conditions. Results were shown in Fig. S5 and Fig. S6. Comparing Fig. 3 with Fig. S5 and Fig. S6, we could find that the strong oxidative peak emerged at around 1.3 V in Fig. 3 should be ascribed to the oxidization of iodine. So, it was speculated that I^- was oxidized to I_2, which prevented the "oxidation-etching" of AgNPs by H_2O_2 in acidic medium. He et al. [36]. had proposed that the reaction between AgNPs and H_2O_2 was similar to Fenton reaction, which could produce powerful oxidizing species such as hydroxyl radical (•OH). The as-generated powerful oxidizing species, such as •OH, had strong oxidant ability and oxidized iodide to iodine easily. From Eqs. (1) and (2) we could find that the production of powerful oxidizing species such as •OH was controlled by the pH of solution. The production of •OH was favored in acidic medium. The lower of the solution pH, the more •OH would be produced. However, in neutral and alkaline medium, •OH produced would be transformed into superoxide in a fast manner [36,37].

Tertiary butanol (TBA), a frequently-used scavenger for •OH, could be used to prove the generation of •OH indirectly [36]. In acidic medium, AgNPs reacted with H_2O_2 to produce •OH and Ag^+. The •OH with powerful oxidation ability ($E^0 = 2.8$ V) would continuously "oxidation-etching" of AgNPs seriously, leading to

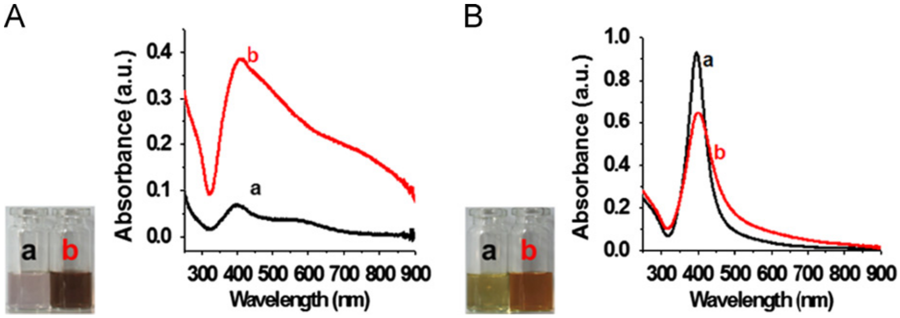
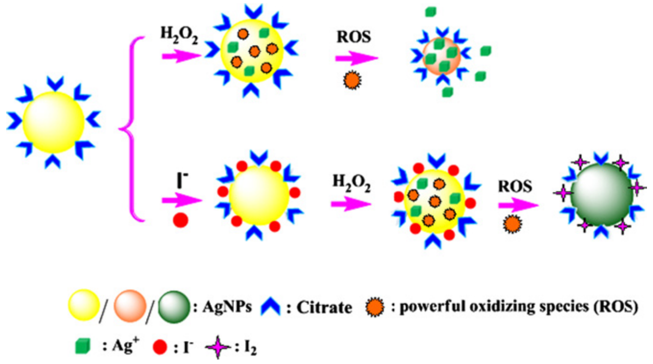


Fig. 4. UV–vis absorption spectra and the corresponding color of the solutions in acidic medium: (A) $AgNPs+H_2O_2$ (a), $AgNPs+I^-+H_2O_2$ (b); (B) $AgNPs+TBA+H_2O_2$ (a), $AgNPs+I^-+TBA+H_2O_2$ (b). TBA: 0.2 mL (95%), I^-: 10 μM, H_2O_2: 0.2 mM. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

greatly decreased absorbance (with absorption intensity of 0.068) of AgNPs (Fig. 4A, a). Iodide could inhibit the "oxidation-etching" of AgNPs, resulting in the absorbance enhancement of AgNPs (Fig. 4A, b). However, this absorbance variation tendency of AgNPs induced by iodide and H_2O_2 was contrary to that in the presence of TBA (Fig. 4B). It could be found that in the presence of TBA, the absorbance of AgNPs after reaction with H_2O_2 was still 0.93, which greater than that (0.068) in the absence of TBA. This might due to that the $\bullet$OH produced from the reaction of AgNPs and H_2O_2 (0.2 mM) in acidic medium was scavenged by TBA. Thus, the "oxidation-etching" of AgNPs by $\bullet$OH was inhibited. The above results gave insight into the generation of $\bullet$OH by the reaction of AgNPs and H_2O_2 in acidic medium indirectly. In the presence of TBA, the absorbance of AgNPs decreased and red-shifted after reaction with iodide and H_2O_2 compared to that when AgNPs reacted with H_2O_2. This was because AgNPs was still etched by H_2O_2 as Eq. (1) shown. Due to the scavenge of $\bullet$OH by TBA, iodide added was not oxidized to iodine by $\bullet$OH and still existed in the form of iodide. The presence of iodide could promote the oxidation-etching of AgNPs by H_2O_2. Because of the lower K_{sp} of AgI (9.3×10^{-17}), the produced Ag^+ from the oxidation of AgNPs by H_2O_2 could be fast complexed by iodide, forming AgI. The formation of AgI promoted the "oxidation-etching" of AgNPs by H_2O_2 as previous study demonstrated that the "oxidation-etching" of AgNPs could be accelerated by a complex agent [45]. Moreover, the absorption of AgI could neutralize the negative charges of citrate molecules on the surface of AgNPs and induced aggregation of AgNPs in solution. As a result, red shift and decrease in the absorbance of AgNPs after reaction with iodide and H_2O_2 occurred due to the formation of aggregates of nanoparticles.

$$\mathrm{AgNP}+H_2O_2\rightarrow Ag^{+}+\bullet OH+OH^{-}+\mathrm{intermediates} \quad (1)$$



Scheme 1. Schematic illustration of iodide detection using AgNPs and H_2O_2 in acidic medium.

$$\bullet OH+H_2O_2\rightarrow O_2^{\bullet -}+H_2O+H^{+} \quad (2)$$

Consequently, on the basis of the above experimental data, a possible anti-etching mechanism of recognition iodide by AgNPs in acidic medium was proposed (as shown in Scheme 1). In acidic medium, the interaction of AgNPs and H_2O_2 would produce powerful oxidizing species, which could continually oxidized AgNPs in the absence of iodide, leading to a significant "oxidation-etching" of AgNPs with greatly reduced absorbance. However, after adding iodide to AgNPs, the powerful oxidizing species produced by the reaction of AgNPs and H_2O_2 would be scavenged by iodide through oxidizing iodide to iodine. The oxidization of iodide protected the AgNPs from further "oxidation-etching" by the as-produced powerful oxidizing species, resulted in the increased absorbance of AgNPs with increased concentrations of iodide.

2.2.2. The mechanism of sensing iodide in neutral medium

The distinctly different optical responses of AgNPs to iodide in neutral medium from that in acidic medium indicated that iodide detection in our assay in neutral medium might follow another pathway.

As Fig. 1B shows, with the increase of the concentration of iodide, the absorption peak of AgNPs weakened, red-shifted and the bandwidth increased gradually, which were the characteristics of aggregation of metal NPs [46,47]. From Fig. S2B, it is clear that in neutral medium, after adding H_2O_2 (0.2 mM), almost no change in color and absorption of AgNPs was observed. This is because AgNPs catalyzed the decomposition of H_2O_2 through a regeneration process of AgNPs under proper circumstances [36]. In aqueous solutions with elevated pH, the generation of $\bullet$OH by the reaction of AgNPs and H_2O_2 was inhibited due to that the as-produced $\bullet$OH could be converted to superoxide (Eq. (2)) at a very fast rate ($\kappa>1.0\times10^{7}\ M^{-1}\ s^{-1}$) [36].

To make the detection mechanism for iodide in neutral medium clear, TBA was also used to verify the generation of $\bullet$OH (Fig. 5). The color and absorption of AgNPs after reaction with iodide and H_2O_2 (0.2 mM) in the absence and presence of TBA almost had no change, indicating that almost no $\bullet$OH was produced after the reaction of AgNPs and H_2O_2 in neutral medium.

The produced Ag^+ from the reaction of AgNPs and H_2O_2 (Eq. (1)) could be reduced to elementary Ag by the as-produced $O_2^{\bullet -}$ and electron charged AgNPs (AgNP^{*-}) whose formation was mediated by $O_2^{\bullet -}$, leading to the regeneration of AgNPs (Eq. (3), Eq. (4), Eq. (5)) [36]. In the presence of iodide, a nucleophilic reagent, iodide could be absorbed on the surface of AgNPs through donating its electron pairs to unoccupied orbitals of AgNPs. In addition, due to the lower K_{sp} of AgI (9.3×10^{-17}), the

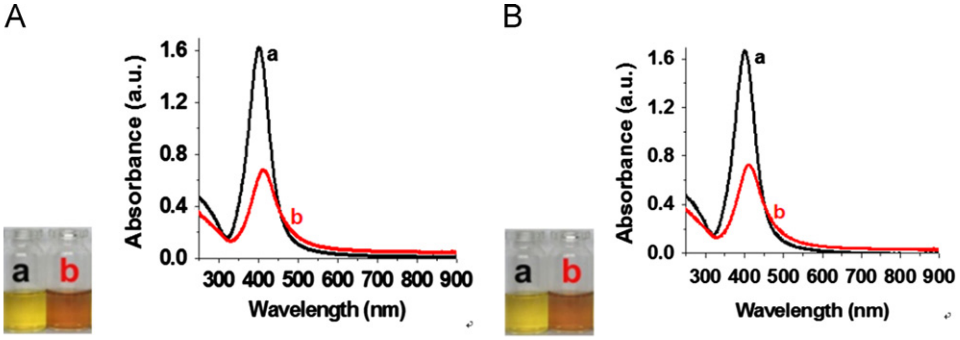


Fig. 5. The evolution of absorption profiles and the corresponding color of solutions in neutral medium: (A) AgNPs+H_2O_2 (a), AgNPs+I^-+H_2O_2 (b); (B) AgNPs+TBA+H_2O_2 (a), AgNPs+I^-+TBA+H_2O_2 (b). TBA: 0.2 mL (95%), I^-: 10 μM, H_2O_2: 0.2 mM. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

produced Ag^+ from the oxidation of AgNPs by H_2O_2 could be fast complexed by iodide, forming AgI. The formation of AgI promoted the oxidation-etching of AgNPs, which was consistent with the result that the presence of a complex agent could accelerate the oxidation-etching of AgNPs [45]. Moreover, the absorption of AgI could neutralize the negative charges of citrate molecules on the surface of AgNPs and induced aggregation of AgNPs in solution.

From the cyclic voltammograms results of the AgNPs after reaction with iodide and H_2O_2 (Fig. 6), we could find another three new peaks including two oxidation peaks and one reduction peak, besides the oxidation peak (at about 0.2 V) of elementary Ag. By comparing with Fig. S5 and Fig. S6, we could find that the oxidative peak at about −0.15 V was attributed to the oxidation of iodide to iodine. Then, iodine could be further oxidized with an anodic peak at around 1.3 V by electron transferring. In addition to these oxidation peaks, a cathodic signal at −0.2 V was found, which might be ascribed to the reduction of Ag^+. These results could be rationalized by considering that in neutral medium the reaction of AgNPs and iodide in the presence of H_2O_2 (0.2 mM) mainly produced AgI not iodine on the surface of AgNPs. To confirm these results, the mixture of AgNPs and AgI (produced by mixing Ag^+ (0.1 mM) and iodide (0.1 mM), $[Ag^+][\text{iodide}] > K_{sp}$ (9.3×10^{-17})), were studied by cyclic voltammograms measurements. The cyclic voltammograms results (Fig. S7) were similar to that of the products when iodide and H_2O_2 were sequentially added to AgNPs in neutral medium (Fig. 6).

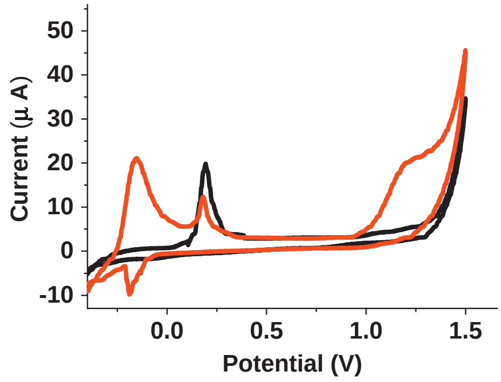


Fig. 6. Cyclic voltammograms of AgNPs after reaction with 0.2 mM H_2O_2 in the absence (black curve) and presence (red curve) of 10 μM iodide in neutral condition. The scan rate was 100 mV s^{-1}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$AgNP + O_2^{\bullet -} \rightarrow AgNP^{*-} + O_2 \quad (3)$$

$$Ag^+ + O_2^{\bullet -} \rightarrow AgNP + O_2 \quad (4)$$

$$Ag^+ + AgNP^{*-} \rightarrow AgNP + AgNP \quad (5)$$

Additional analysis of the zeta potential, hydrodynamic diameter and the resonance light scattering intensity of AgNPs further manifested the mechanism of the aggregation of AgNPs after reaction with iodide and H_2O_2 in neutral medium (Fig. 7A). With the increase of the concentration of iodide in the presence of H_2O_2, the negative charges of AgNPs decreased from −35.6 to −0.67 mV, which should be ascribed to the detachment of negative citrates from the surface of AgNPs. As a result of the loss of negative charges, aggregated AgNPs formed, accompanied by the increase of hydrodynamic diameter of AgNPs from 83.7 to 490.6 nm. Meanwhile, the resonance light scattering intensity, which was dependent on the size of AgNPs, also increased with the increase of the concentration of iodide (Fig. 7A). Besides, TEM

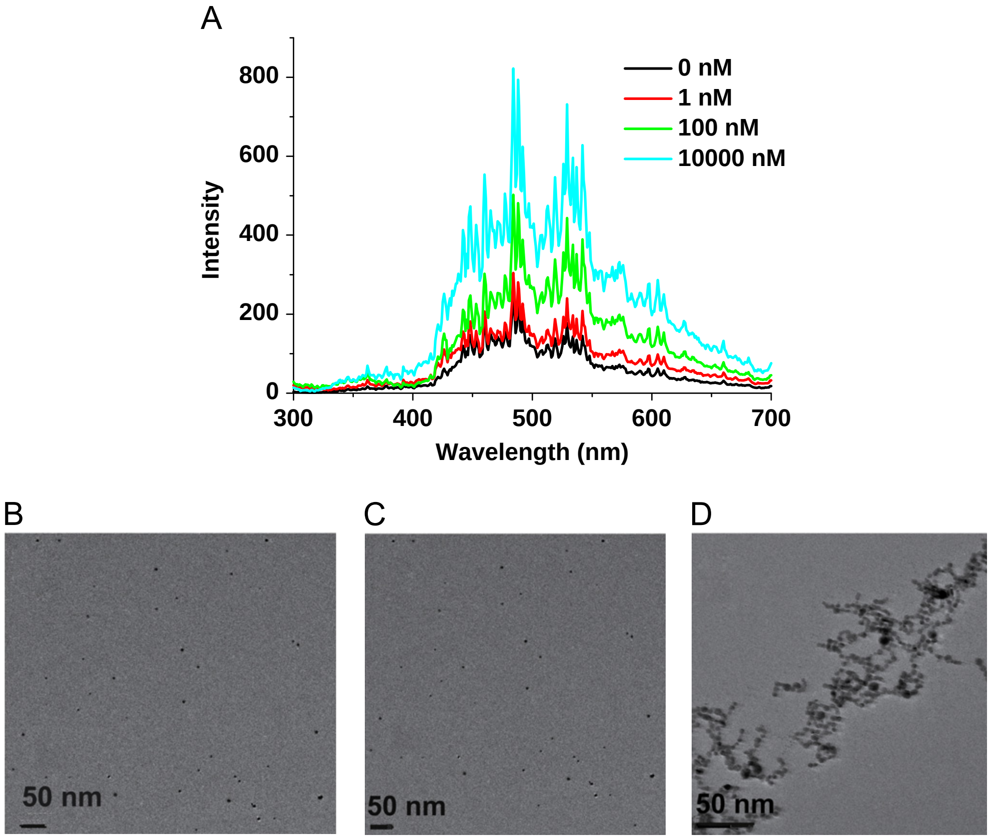
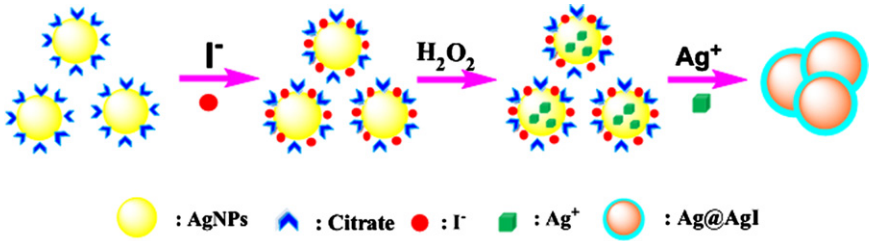


Fig. 7. The resonance light scattering spectra of the AgNPs with different concentrations of iodide (0 nM, 1 nM, 100 nM, 10000 nM) in the presence of 0.2 mM H_2O_2 in neutral medium (A). The HRTEM images of AgNPs (B) and AgNPs before (C) and after (D) adding iodide (10 μM) in the presence of 0.2 mM H_2O_2 in neutral medium.



Scheme 2. Schematic depiction of the colorimetric detection of iodide based on AgNPs and H_2O_2 in neutral medium.

images also provided more information about the size and morphology of AgNPs (Fig. 7B, C, D). After adding H_2O_2 (0.2 mM), AgNPs were still dispersed (Fig. 7B, C). However, the dispersed AgNPs aggregated after adding iodide and H_2O_2 (0.2 mM) (Fig. 7D), which were in good accordance with the results of dynamic light scattering (DLS) and resonance light scattering analysis. All of these results indicated that AgNPs aggregated after interacted with iodide in the presence of H_2O_2.

The proposed mechanism for iodide detection in neutral medium by forming AgI, which deposited on the surface of AgNPs and induced aggregation of AgNPs (as depicted in Scheme 2).

Taking into account of the following obtained results, the mechanism of detecting iodide by AgNPs in alkaline medium was similar to that in neutral medium. From Fig. S8 we could find that powerful oxidizing species was not produced in alkaline medium after the reaction of AgNPs and H_2O_2. Moreover, with the increase of the concentration of iodide in the presence of H_2O_2, the absorbance of AgNPs red-shifted and weakened gradually (Fig. 1C), which were characteristics of the aggregation of AgNPs. In addition, negative charges on the surface of AgNPs decreased from -35.6 to -12.67 mV, and the hydrodynamic diameter (from 80.23 to 206.3 nm) and the resonance light scattering intensity increased with the increase of the concentration of iodide in the presence of H_2O_2 (Fig. S9A), indicating that AgNPs aggregated due to the lack of sufficient charges on their surface. TEM images also provided further evidence for the aggregation of AgNPs induced by iodide in the presence of H_2O_2 in alkaline medium (Fig. S9B, C, D). All these results were fully in accordance with the detection mechanism of iodide by AgNPs in neutral medium. Due to that the redox potential of H_2O_2 decreased with the solution pH [48], the oxidation-etching ability of H_2O_2 for AgNPs was reduced, leading to the much lower sensitivity for iodide detection in alkaline medium than that in neutral medium.

3. Conclusions

In summary, we have presented an innovative and ultrasensitive colorimetric sensor for iodide based on the pH-dependent interaction of AgNPs and H_2O_2. In acidic medium, AgNPs reacted with H_2O_2 to produce Ag^+ and powerful oxidizing species. Powerful oxidizing species could etch AgNPs seriously. While, iodide acting as an antioxidant could protect AgNPs from oxidation-etching by powerful oxidizing species. In neutral and alkaline medium, the reaction of AgNPs and H_2O_2 mainly produce Ag^+. The existence of iodide could complex with Ag^+, forming AgI, which induced aggregation of AgNPs. Due to the different responses of iodide to these different products of H_2O_2 and AgNPs in solutions with different pH, iodide could be detected via two different mechanisms with acceptable selectivity and outstanding sensitivity. Furthermore, this method provided an innovative sensing platform for the detection of iodide with simplicity and speediness.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.12.029.

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