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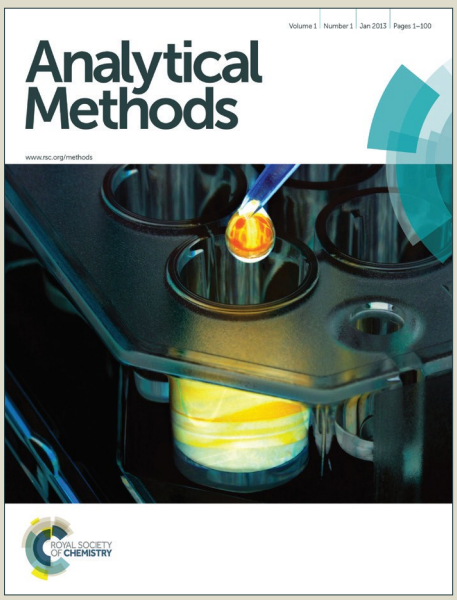

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Colorimetric determination of ammonium persulfate in water-borne adhesive for cigarette based on silver triangular nanoparticles

Yanqun Xu[a], Anyi Chen[b], Ruizhi Zhu[a], Naiding Wang[a], Zhigang Tai[b], Hongtao Feng[a]*

Abstract

In this paper, a simple method for the determination of ammonium persulfate using silver triangular nanoparticles (silver TNPs) was developed. Specifically, silver TNPs exhibited strong appreciable surface plasmon resonance (SPR) signals at 670 nm, and low concentration of ammonium persulfate could induce an SPR decrease of silver TNPs with color changed from blue to colorless. Furthermore, it was also found that the SPR decreasing intensity was proportional to the concentration of ammonium persulfate over the range of 0.10-0.70 mmol L^{-1}, with a correlation coefficient of 0.9994. The spiked recoveries were in the range of 94.4%-105.8% with RSD of 3.3%-5.6%. Finally, a method for ammonium persulfate detection by UV–vis spectrophotometric was established and successfully applied for determination of ammonium persulfate in water-borne adhesive for cigarette.

Key words: silver triangular nanoparticles, ammonium persulfate, colorimetric

1. Introduction

It is well known that the quality of cigarette materials is one of the key factors affecting the quality and grade of cigarette products. Water-borne adhesive, as one kind of cigarette materials, is frequently used for gluing of cigarette lap and cigarette filter. However, some chemicals which do harm to respiratory system and immune system would be introduced into water-borne adhesive in the process of manufacture for technical reason.[1, 2] Therefore, the detection methodology of harmful chemicals in water-borne adhesive had been widely studied.

Ammonium persulfate was often used as an initiator in the synthesis of water-borne adhesive due to its strong oxidation performance.[3] And there always have some residual ammonium persulfate in water-borne adhesive used for cigarette manufacturing, which may either cause or intensify diseases such as asthma and skin reactions to smoker.[4,5] Therefore, it is necessary to set up analysis methods to monitor ammonium persulfate in water-borne adhesive, since ammonium persulfate is an ionic compound, the determination of ammonium persulfate is equal to the determination of persulfate in water-borne adhesive. As we all known that, persulfate with strong oxidant has been widely used for water and soil decontaminants,[6] circuit board fabrication,[7] cosmetics,[8] and polymerization,[9] and a number of methods have been reported for the determination of persulfate, such as reductometric,[10, 11] spectrophotometric,[12, 13] and electrochemical methods.[14,15] Most of these reported methods were excellent performance, but suffer from some drawbacks such as time-consuming and labor intensive.

In recent years, silver nanoparticles (Ag NPs) have attracted great interests as a colorimetric probe, which can directly detect analytes by monitoring the color change using UV-vis spectroscopy or even with naked eyes. Apparently, nearly no complicated instruments are involved in the detection procedures. Furthermore, the color change is highly sensitive to the size, shape, capping agent, medium refractive index, and state of Ag NPs. Many successful examples have been reported in the determination of analytes regarding to environmental contaminations,[16-18] food safety,[19] pharmaceutical analysis.[20] Silver triangular nanoparticles (silver TNPs) as one kind of anisotropic Ag NPs has been extensively investigated, since the extraordinarily plasmonic features across visible-NIR regions. Silver TNPs exhibit intense and tunable localized surface plasmon resonance (SPR) and have been utilized to analytical chemistry with satisfactory results.[21-26]

In this paper, it was found that the ammonium persulfate could oxidize the silver TNPs and decrease the SPR band of silver TNPs. Low concentration of ammonium persulfate had a good affinity to silver TNPs, and resulting in a transformation of Ag^0 to Ag^+ with solution color changing from blue to colorless. The color of silver NPs changes with the decrease of SPR band of silver TNPs, a linear relationship was obtained between the concentration of ammonium persulfate and the maximum absorbance of silver TNPs. Thus, a simple analytical method was developed to detect ammonium persulfate by using silver TNPs.

2. Experimental

2.1. Materials

All commercially available reagents were of analytical grade. Silver nitrate ($AgNO_3$, 99.8%) was purcthased from Dingguochangsheng Biological Technology Co., Ltd. (Beijing, China). Trisodium citrate dehydrate ($C_6H_5O_7Na_3 \cdot 2H_2O$, 99.0%) was purchased from Tianjin Chemical Reagent Co., Ltd. Sodium borohydride ($NaBH_4$, 96.0%) was bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Hydrogen peroxide (H_2O_2, 30wt. %) was purchased from Chuangdong Chemical Co., Ltd. (Chongqing, China). Ammonium persulfate ($(NH_4)_2S_2O_8$, 98.0%) was bought from Guanghua Chemical Reagent Co., Ltd. (Guangdong, China). The pH value of the reaction systems were controlled by Britton-Robinson (B-R) buffer solutions. Three batches of water-based adhesive for tobacco came from China Tobacco Yunnan Industrial Co. Ltd.

2.2. Instruments

Transmission electron microscope (TEM) patterns were conducted under JEM 2100 and operated at 200 kv. The specimen was prepared by dropping the solution onto the copper grids and air dried naturally. UV-vis absorption spectrum was obtained on a UV-2550 spectrophotometer (Shimadzu, Japan) equipped with a 1-cm quartz cell. Atomic absorption spectrometry (AAS) was obtained using a Z-2000 polarized Zeeman atomic absorption spectrophotometer (Hitachi, Japan). The pH value of the solution was measured by a pH meter (Lei Ci Instrument Factory, Shanghai, China). A sczl-2 magnetic stirrer (Yu Hua Instrument Inc. Gongyi, China) was used to blend the solutions in a round-bottom flask to prepare the silver TNPs. An H-1850 centrifuge was used in pretreatment of samples (Xiang Yi Instrument Inc. Hunan, China). A

SB-2000 water bath pot (Shanghai Instrument Inc. Shanghai, China) was employed to heat the silver colloids in the aging process.

2.3. Preparation of silver TNPs

Silver TNPs were synthesized following the procedure conducted by Mirikin et al with some modification.[27-30] Typically, 24.75 mL of deionized water were added to a 50 mL round-bottom flask and continuously magnetically stirred at room temperature in the presence of air. Subsequently, silver nitrate (0.1 mmol L^{-1}, 25 μL), trisodium citrate (75 mmol L^{-1}, 500 μL), hydrogen peroxide (30 wt.%, 60 μL) were successively added to the deionized water. Next, sodium borohydride (100 mmol L^{-1}, 100 μL) was rapidly injected into the above mixture. The color of colloid turned to pale yellow immediately, suggesting the reduction of silver. After 1-2 min, the colloid changed to deep-yellow, indicating the formation of small silver nanoparticles. Over the next several minutes, the color of the colloid continued to change from yellow to red. Depending on the different amount of $NaBH_4$ used, the final color of the solution ranged from red (35 μL $NaBH_4$) to blue (100 μL $NaBH_4$), as shown in Figure S1. The formation of silver TNPs was confirmed by TEM characterization, the morphology had clearly triangular corners. As shown in Figure 1, the UV-vis absorption peak wavelength of silver TNPs was about 670 nm.

The concentration of the silver TNPs solution was defined by its UV–vis absorption using the Beer–Lambert Law ($c = A/\varepsilon \cdot b$), where A is the maximum absorbance of silver TNPs at the maximum wavelength, ε is the molar extinction coefficient of silver TNPs, b is the optical length which is usually 1.0 cm. However, the molar extinction

(ε) of silver TNPs is uncertain in each preparation. Therefore, we use "X" as the value of 1/ε, and thus, A·X as the concentration of silver TNPs

2.4. General procedures

The detection of ammonium persulfate were carried out by the following procedures. First, 800 μL of silver TNPs was added into a clear centrifugal tube (5.0 mL) with variable concentration of $(NH_4)_2S_2O_8$. Then, the mixture solution was diluted by deionized water to a volume of 4.0 mL and heated in a water bath at 80 ^oC for 30 min. The blank tests were carried out under the same conditions. Subsequently, the resulting mixture was used for UV-vis spectral analysis. For sample detection, 0.5000 g of water-based adhesive for tobacco was firstly dissolved in 25 mL deionized water and extracted for 15 minutes on an oscillator. The extract solution was centrifuged at 18500 rpm for 10 minutes, and the supernatant was diluted 1.5 fold and used for spectrophotometric detection after reacted with silver TNPs.

3. Results and discussion

3.1. Features of silver TNPs after interacted with ammonium persulfate

TEM, UV-vis spectrophotometer and AAS were used to study the mechanism of reaction between silver TNPs and ammonium persulfate. Compared the spectrum with reported reference,[27, 31-33] the SPR absorption spetrum of silver TNPs prepared here showed a weak transversal out-of-plane quadrupole band (334 nm), out-of-plane dipole band (430 nm) and a very intense in-plane dipole band (670 nm) (shown as Figure 1). After addition of ammonium persulfate in silver TNPs solution and heated for 30 min at 80 ^oC, the color of silver TNPs suspension changed from blue to

colorless, the absorption peak of silver TNPs at 670 nm decreased with the increase of ammonium persulfate concentration (Figure 2). TEM images of silver TNPs showed that the number of silver TNPs obviously reduced after ammonium persulfate was added (Figure 3). This phenomenon suggested that the silver TNPs were oxidized by ammonium persulfate.

To verify the silver ion production, the mixture of the $(NH_4)_2S_2O_8$-silver TNPs was centrifuged at 18500 rpm for 10 minutes on the centrifuge, and the atomic absorption value of the top pellucid liquid was measured under the conditions of 328.1 nm, 2.0 mA lamp current, 0.4 nm spectral pass band, air/acetylene flow rate of 15 L min^{-1}/2 L min^{-1}. The result showed that with the increase of $(NH_4)_2S_2O_8$ concentration, the absorption value improved correspondingly (Table S1). The results demonstrated that silver TNPs converted to silver ion after reacted with ammonium persulfate.

3.2. The selection of analysis probe

Ag NPs used in this paper was prepared by conventional thermal route with slight modification.[29, 30] Ag NPs with different colors were obtained by changing the amount of $NaBH_4$ or H_2O_2 during the preparation. As shown in Figure S1, the maximum absorption wavelength of Ag NPs was shifted with the color changed. Ag NPs with different colors were studied for ammonium persulfate detection. After reacting with ammonium persulfate, a sequence of UV-vis spectrograms were obtained, the results showed that Ag NPs with different colors had the similar changing rule in the presence of ammonium persulfate (see supporting information, Figure S2, Figure S3, Fig S4). The colormetric method proposed by our group was based on comparing the

gradual spectrum changes in the presence of the analyte, and finding the relationship between maximum absorbance and concentration of ammonium persulfate. The value of maximum absorbance can be used for describing the transformation process of silver TNPs to Ag^+, with the concentration of $(NH_4)_2S_2O_8$ increased, the value of maximum absorbance decreased. Compared with red and purple silver colloid, blue silver colloid with higher value of maximum absorbance has wider linear range and higher sensitivity, thus the blue silver colloid was selected as the analysis probe.

3.3. Effect of pH

The pH of the test solution was one of the prime factors affecting the stability of silver TNPs. Chen had found that the acidity affected the change of the shape and size of silver TNPs.[34] Therefore, the pH influence on the system of silver TNPs/$(NH_4)_2S_2O_8$ was investigated. As Figure 4 showed that the value of maximum absorbance of silver TNPs/$(NH_4)_2S_2O_8$ system changed with the pH value. The value of maximum absorbance achieved relative high and get stable in the range of 6.80-7.24. However, when the pH continues to increase, silver TNPs are unstable and aggregate together (Supporting information, Figure. S5). Therefore, the pH 6.80 was selected as optimum value.

3.4. Effect of reaction temperature

The temperature of reaction was an important parameter, which has an influence on reaction rate. The effect of reaction temperature on silver TNPs/$(NH_4)_2S_2O_8$ system has been investigated in the range of 20–90 ^oC using a water bath, and the result was shown in Figure 5. Δ (maximum absorbance) represented the extent of reaction

between silver TNPs and $(NH_4)_2S_2O_8$, which was calculated as Δ (maximum absorbance) = $A_{max\ before}$ - $A_{max\ after}$, where $A_{max\ before}$ is the maximum absorbance of silver TNPs before reacted with $(NH_4)_2S_2O_8$, and $A_{max\ after}$ is the maximum absorbance of silver TNPs after reacted with $(NH_4)_2S_2O_8$, As can be seen, with the temperature increased the value of Δ (maximum absorbance) became smaller, indicating $(NH_4)_2S_2O_8$ was reacted more and more completely. According to the control test, silver TNPs became unstable at a high temperature (90 ^oC), which might lead to erroneous results. Therefore, 80 ^oC was selected as optimum temperature of reaction in the following experiments.

3.5. Effect of reaction time

The effect of reaction time was carried out under the optimum conditions in the range of 10 to 60 min. Four different concentrations of ammonium persulfate were used for the tests and the results were shown as Figure 6. With the reaction time increased, the value of maximum absorbance of silver TNPs reacted with low concentration of ammonium persulfate got stable quickly (within 20 min), while the high concentration of ammonium persulfate would take a longer time. For accurate determination of ammonium persulfate in real samples, 30 minutes was selected for the optimum reaction time.

3.6. Effects of coexistence substances

The effects of coexistence substances were carried under the optimum conditions, a number of substances which might exist in water-based adhesive and dissolve in water, were investigated in this study (including formaldehyde, acetaldehyde, acetone,

butanal, crotonaldehyde, glyoxal, orthoboric acid, sodium bicarbonate, Pb^{2+}, As^{3+}, ammonium persulfate). The results were shown as Figure 7, the higher concentration of coexistence substances did not affect the determination of ammonium persulfate, which suggested this method had a good selectivity.

3.7. Analytical performance

The linearity of the method was tested under the optimum experimental conditions, the calibration curve (Figure 8) was obtained with a good linearity in the range from 0.10 to 0.70 mmol L^{-1}, and the regression coefficient (R^2) was 0.9989. The detection limit of ammonium persulfate in this sensing method was 0.01 mM (3σ), which was comparable to some reported persulfate assays. We compared this method with some commonly used methods, the results (Table 1) indicated that the proposed method was a good platform for the detection of ammonium persulfate.

In order to study the validity of the proposed method, three batches of water-based adhesive before and after spiking were used for the determination of ammonium persulfate. The results were list in Table 1, As can be seen, the mean recoveries were in the range from 94.4 to 105.8% at 0.2, 0.4, and 0.6 mmol L^{-1} spiked levels, and the relative standard deviations (RSDs) were in the range from 3.3% to 5.6%, the average content of ammonium persulfate in the water-based adhesive for cigarette is 0.109 mmol L^{-1} (1.84 mg g^{-1}). These parameters indicated that the present method with high sensitivity and reliability could be used for the determination of ammonium persulfate in water-based adhesive.

3.8. Repeatability and reproducibility

Five batches of silver TNPs (with maximum absorption wavelength in range from 549 to 607 nm),which prepared at different days using same reagents, were used for ammonium persulfate detection. As shown in Table S2, the detection values were very close to the defined concentrations. Thus, the colorimetric method proposed here have outstanding advantages of good precision and reproducibility.

4. Conclusions

In this contribution, a simple method for ammonium persulfate detection was established according to the oxidation properity of ammonium persulfate. The maximum absorbance of silver TNPs damped clearly with increasing the concentrations of ammonium persulfate over the range of 0.10-0.70 mmol L^{-1}. Good recoveries were obtained in the range of 94.4%-105.8% with RSD lower than 5.6%. The proposed method for ammonium persulfate detection by UV–vis spectrophotometric observation has been applied to analysis of ammonium persulfate in water based adhesive for cigarette with satisfactory results.

Acknowledge

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Table 1. Comparison of analytical features for some reported persulfate assays

Method	Probe	Linear range (mM)	Detection limit (mM)	Ref
Voltammetric	electrode modified with a Prussian blue film	0.05-3	Not given	[35]
Spectrophotometric	Methylene Blue	0-1.5	0.0028	[36]
Flow injection amperometric	Prussian Blue film-modified electrode	0.1-1.0	0.09	[37]
Colorimetric	Silver TNPs	0.1-0.7	0.01	This article

Table 2. Results for the determination of $(NH_4)_2S_2O_8$ in water-based adhesive for cigarette

Sample No.	Added (mmol L^{-1})	Found(mmol L^{-1})	Recovery(%)	RSD (%) (n=3)
1	0	0.122		
	0.2	0.304	94.4	5.6
	0.4	0.515	98.7	3.8
	0.6	0.719	96.7	5.1
2	0	0.086		
	0.2	0.291	105.8	3.7
	0.4	0.472	97.1	4.6
	0.6	0.663	96.6	3.8
3	0	0.102		
	0.2	0.297	98.3	3.5
	0.4	0.491	97.8	3.3
	0.6	0.688	98.0	4.8

Notes and references

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Figures

Fig. 1. Characteristic absorption spectrum, TEM image and color of silver TNPs.
Fig. 2. UV-vis spectra of silver TNPs before and after reaction with $(NH_4)_2S_2O_8$.
Fig. 3. TEM images of silver TNPs before and after reaction with $(NH_4)_2S_2O_8$.
Fig. 4. Effects of pH on silver TNPs and $(NH_4)_2S_2O_8$ interaction.
Fig. 5. Effect of reaction temperature on silver TNPs and $(NH_4)_2S_2O_8$ interaction.
Fig. 6. Effect of reaction time on silver TNPs and $(NH_4)_2S_2O_8$ interaction.
Fig. 7. Effect of coexistence substances.
Fig. 8. (A) UV-vis spectra of silver TNPs by the addition of $(NH_4)_2S_2O_8$ concentration range from 0 to 1.0 mmol L^{-1}. (B) The linear for detection of $(NH_4)_2S_2O_8$.

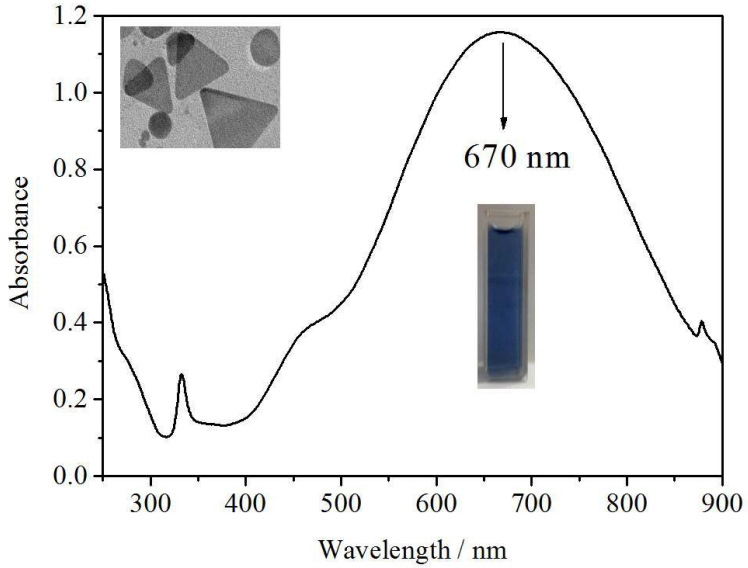

Figure 1. Characteristic absorption spectrum, TEM image and color of silver TNPs.

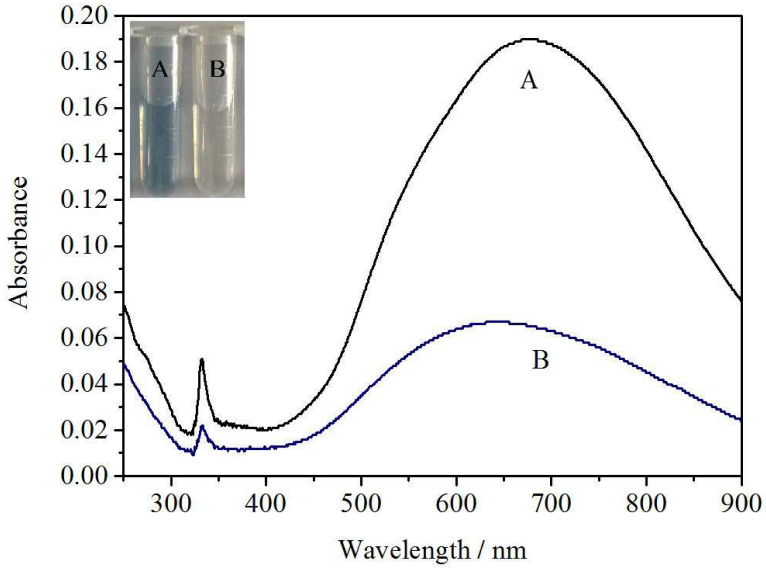

Figure 2. UV-vis spectra of silver TNPs before (A) and after (B) reaction with $(NH_4)_2S_2O_8$ (1. 0 mmol L^{-1}), pH 6.80, reaction for 30 min at 80 ^oC

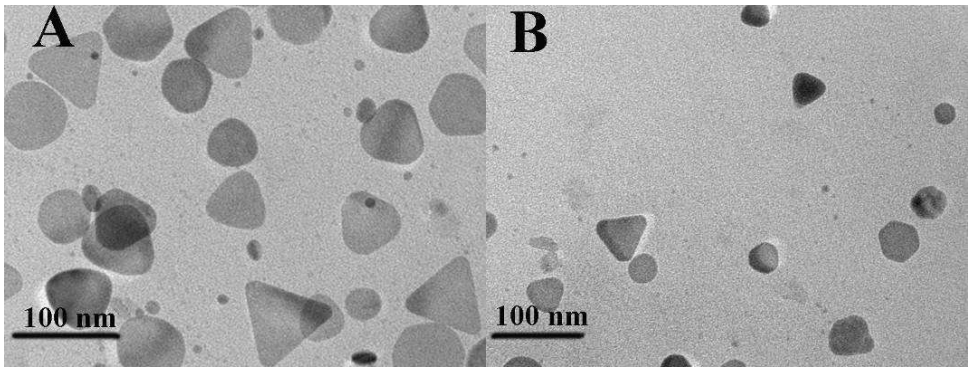

Figure 3. TEM images of silver TNPs before (A) and after (B) reaction with $(NH_4)_2S_2O_8$ (0.60 mmol L^{-1}).

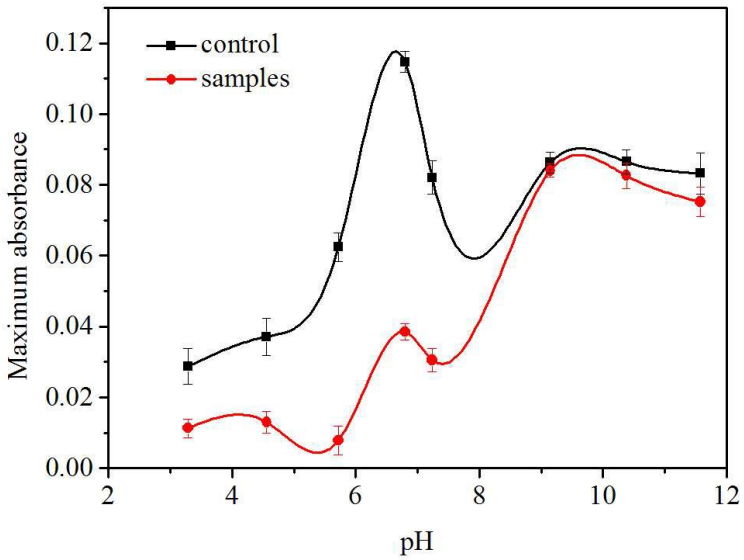

Figure 4. Effects of pH on silver TNPs and $(NH_4)_2S_2O_8$ interaction. Condition: concentration of silver TNPs, 0.286X mol L^{-1}; $(NH_4)_2S_2O_8$, 0.60 mmol L^{-1}; B-R buffer, 0.02 mol L^{-1}

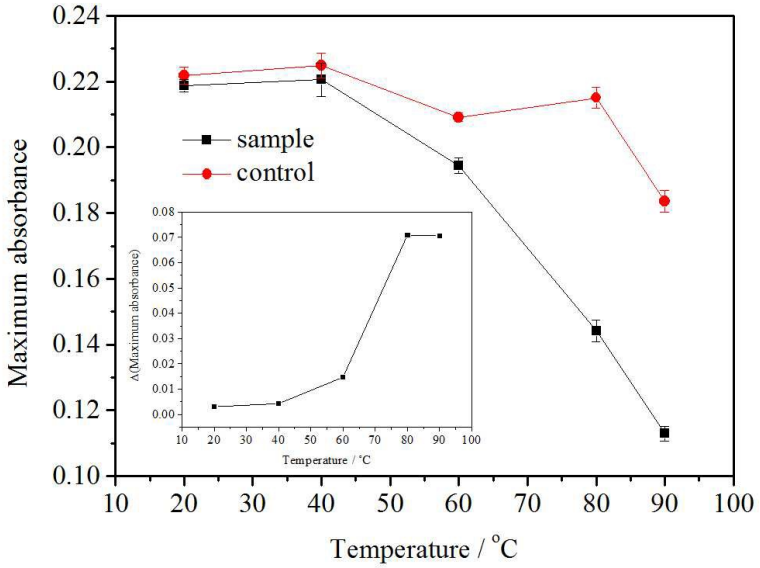

Figure 5. Effect of reaction temperature on silver TNPs and $(NH_4)_2S_2O_8$ interaction. Condition: concentration of silver TNPs, 0.286X mol L^{-1}; $(NH_4)_2S_2O_8$, 0.60 mmol L^{-1}

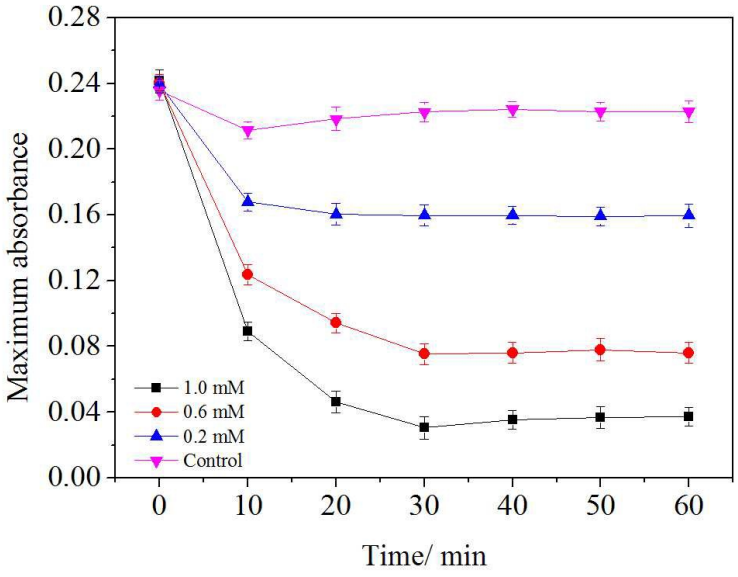

Figure 6. Effect of reaction time on silver TNPs and $(NH_4)_2S_2O_8$ interaction. Four different concentrations of $(NH_4)_2S_2O_8$ (0, 0.2, 0.6, and 1.0 mmol L^{-1}) were used for interacting with silver TNPs, concentration of silver TNPs, 0.286X mol L^{-1}

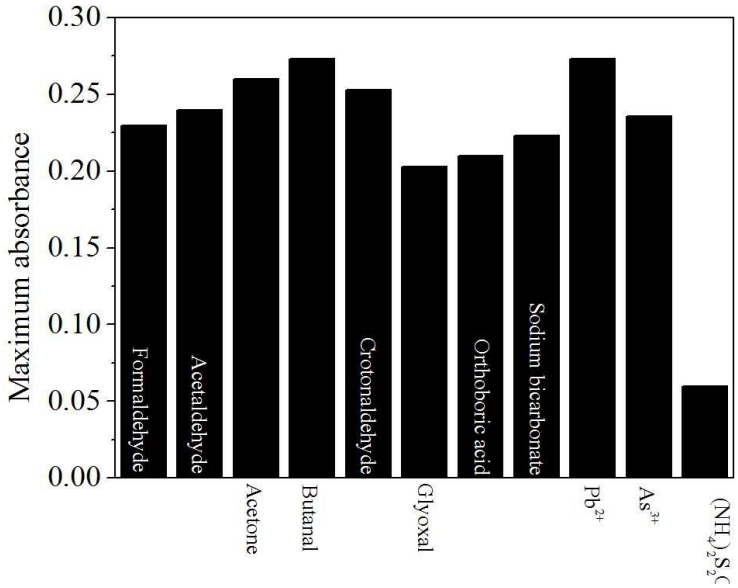

Figure 7. Effect of coexistence substances. Experimental condition: concentration of silver TNPs, 0.286X mol L^{-1}; $(NH_4)_2S_2O_8$, 0.60 mmol L^{-1}; others, 12 mmol L^{-1}

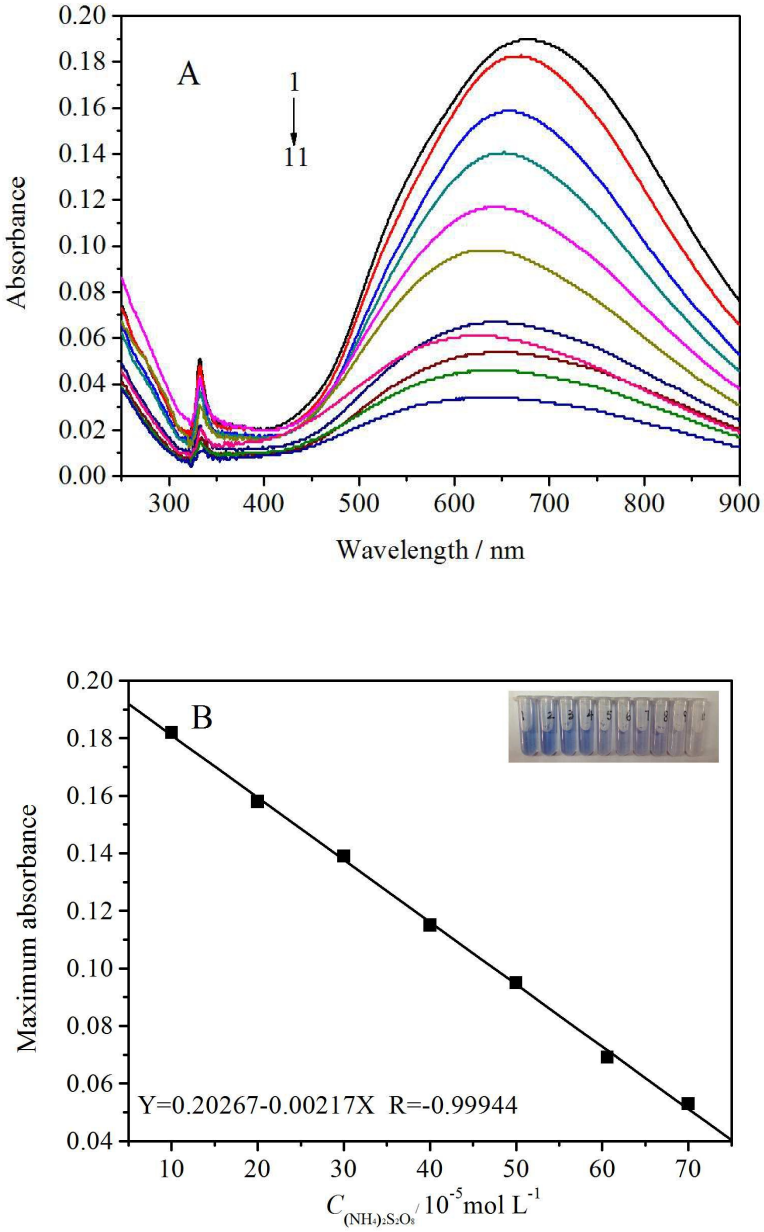

Figure 8. (A) UV-vis spectra of silver TNPs by the addition of $(NH_4)_2S_2O_8$ concentration range from 0 to 1.0 mmol L^{-1} (No. 1 - 11). (B) The linear for detection of $(NH_4)_2S_2O_8$.