

# Analytical Methods

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: Y. Xu, A. chen, R. Zhu, N. Wang, Z. Tai and H. Feng, *Anal. Methods*, 2015, DOI: 10.1039/C5AY02707A.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

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

4     Yanqun Xu<sup>a</sup>, Anyi Chen<sup>b</sup>, Ruizhi Zhu<sup>a</sup>, Naiding Wang<sup>a</sup>, Zhigang Tai<sup>b</sup>, Hongtao  
5     Feng<sup>a\*</sup>

6     **Abstract**

7         In this paper, a simple method for the determination of ammonium persulfate  
8     using silver triangular nanoparticles (silver TNPs) was developed. Specifically, silver  
9     TNPs exhibited strong appreciable surface plasmon resonance (SPR) signals at 670  
10    nm, and low concentration of ammonium persulfate could induce an SPR decrease of  
11    silver TNPs with color changed from blue to colorless. Furthermore, it was also found  
12    that the SPR decreasing intensity was proportional to the concentration of ammonium  
13    persulfate over the range of 0.10-0.70 mmol L<sup>-1</sup>, with a correlation coefficient of  
14    0.9994. The spiked recoveries were in the range of 94.4%-105.8% with RSD of  
15    3.3%-5.6%. Finally, a method for ammonium persulfate detection by UV-vis  
16    spectrophotometric was established and successfully applied for determination of  
17    ammonium persulfate in water-borne adhesive for cigarette.

18  
19    **Key words:** silver triangular nanoparticles, ammonium persulfate, colorimetric

Analytical Methods Accepted Manuscript

## 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.<sup>1,2</sup> 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.<sup>3</sup> 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.<sup>4,5</sup> 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,<sup>6</sup> circuit board fabrication,<sup>7</sup> cosmetics,<sup>8</sup> and polymerization,<sup>9</sup> and a number of methods have been reported for the determination of persulfate, such as reductometric,<sup>10, 11</sup> spectrophotometric,<sup>12, 13</sup> and electrochemical methods.<sup>14,15</sup> 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,<sup>16-18</sup> food safety,<sup>19</sup> pharmaceutical analysis.<sup>20</sup> 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.<sup>21-26</sup>

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<sup>0</sup> to Ag<sup>+</sup> 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 ( $\text{AgNO}_3$ , 99.8%) was purchased from Dingguochangsheng Biological Technology Co., Ltd. (Beijing, China). Trisodium citrate dehydrate ( $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$ , 99.0%) was purchased from Tianjin Chemical Reagent Co., Ltd. Sodium borohydride ( $\text{NaBH}_4$ , 96.0%) was bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30wt. %) was purchased from Chuangdong Chemical Co., Ltd. (Chongqing, China). Ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , 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.<sup>27-30</sup> 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<sup>-1</sup>, 25 μL), trisodium citrate (75 mmol L<sup>-1</sup>, 500 μL), hydrogen peroxide (30 wt.%, 60 μL) were successively added to the deionized water. Next, sodium borohydride (100 mmol L<sup>-1</sup>, 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<sub>4</sub> used, the final color of the solution ranged from red (35 μL NaBH<sub>4</sub>) to blue (100 μL NaBH<sub>4</sub>), 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 ( $c = A/\epsilon \cdot b$ ), where A is the maximum absorbance of silver TNPs at the maximum wavelength,  $\epsilon$  is the molar extinction coefficient of silver TNPs, b is the optical length which is usually 1.0 cm. However, the molar extinction

( $\epsilon$ ) of silver TNPs is uncertain in each preparation. Therefore, we use “X” as the value of  $1/\epsilon$ , and thus,  $A \cdot X$  as the concentration of silver TNPs

## 2.4. General procedures

The detection of ammonium persulfate were carried out by the following procedures. First, 800  $\mu\text{L}$  of silver TNPs was added into a clear centrifugal tube (5.0 mL) with variable concentration of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . Then, the mixture solution was diluted by deionized water to a volume of 4.0 mL and heated in a water bath at 80  $^\circ\text{C}$  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,<sup>27, 31-33</sup> the SPR absorption spectrum 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  $^\circ\text{C}$ , the color of silver TNPs suspension changed from blue to

1  
2  
3  
4 130 colorless, the absorption peak of silver TNPs at 670 nm decreased with the increase of  
5  
6 131 ammonium persulfate concentration (Figure 2). TEM images of silver TNPs showed  
7  
8  
9 132 that the number of silver TNPs obviously reduced after ammonium persulfate was  
10  
11 133 added (Figure 3). This phenomenon suggested that the silver TNPs were oxidized by  
12  
13 134 ammonium persulfate.

14 135 To verify the silver ion production, the mixture of the (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>-silver TNPs was  
15  
16 136 centrifuged at 18500 rpm for 10 minutes on the centrifuge, and the atomic absorption  
17  
18 137 value of the top pellucid liquid was measured under the conditions of 328.1 nm, 2.0  
19  
20 138 mA lamp current, 0.4 nm spectral pass band, air/acetylene flow rate of 15 L min<sup>-1</sup>/2 L  
21  
22 139 min<sup>-1</sup>. The result showed that with the increase of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentration, the  
23  
24 140 absorption value improved correspondingly (Table S1). The results demonstrated that  
25  
26 141 silver TNPs converted to silver ion after reacted with ammonium persulfate.

27  
28  
29 142 **3.2. The selection of analysis probe**

30  
31 143 Ag NPs used in this paper was prepared by conventional thermal route with slight  
32  
33 144 modification.<sup>29, 30</sup> Ag NPs with different colors were obtained by changing the amount  
34  
35 145 of NaBH<sub>4</sub> or H<sub>2</sub>O<sub>2</sub> during the preparation. As shown in Figure S1, the maximum  
36  
37 146 absorption wavelength of Ag NPs was shifted with the color changed. Ag NPs with  
38  
39 147 different colors were studied for ammonium persulfate detection. After reacting with  
40  
41 148 ammonium persulfate, a sequence of UV-vis spectrograms were obtained, the results  
42  
43 149 showed that Ag NPs with different colors had the similar changing rule in the  
44  
45 150 presence of ammonium persulfate (see supporting information, Figure S2, Figure S3,  
46  
47  
48  
49  
50  
51 151 Fig S4). The colormetric method proposed by our group was based on comparing the  
52  
53  
54  
55  
56  
57  
58  
59  
60



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  $\text{Ag}^+$ , with the concentration of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  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.<sup>34</sup> Therefore, the pH influence on the system of silver TNPs/ $(\text{NH}_4)_2\text{S}_2\text{O}_8$  was investigated. As Figure 4 showed that the value of maximum absorbance of silver TNPs/ $(\text{NH}_4)_2\text{S}_2\text{O}_8$  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/ $(\text{NH}_4)_2\text{S}_2\text{O}_8$  system has been investigated in the range of 20–90 °C using a water bath, and the result was shown in Figure 5.  $\Delta$  (maximum absorbance) represented the extent of reaction

174 between silver TNPs and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , which was calculated as  $\Delta$  (maximum  
175 absorbance) =  $A_{\text{max before}} - A_{\text{max after}}$ , where  $A_{\text{max before}}$  is the maximum absorbance of  
176 silver TNPs before reacted with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , and  $A_{\text{max after}}$  is the maximum absorbance  
177 of silver TNPs after reacted with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . As can be seen, with the temperature  
178 increased the value of  $\Delta$  (maximum absorbance) became smaller, indicating  
179  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  was reacted more and more completely. According to the control test,  
180 silver TNPs became unstable at a high temperature (90 °C), which might lead to  
181 erroneous results. Therefore, 80 °C was selected as optimum temperature of reaction  
182 in the following experiments.

### 183 3.5. Effect of reaction time

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

### 192 3.6. Effects of coexistence substances

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

butanal, crotonaldehyde, glyoxal, orthoboric acid, sodium bicarbonate,  $\text{Pb}^{2+}$ ,  $\text{As}^{3+}$ , 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  $\text{mmol L}^{-1}$ , and the regression coefficient ( $R^2$ ) was 0.9989. The detection limit of ammonium persulfate in this sensing method was 0.01 mM ( $3\sigma$ ), 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  $\text{mmol L}^{-1}$  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  $\text{mmol L}^{-1}$  (1.84  $\text{mg g}^{-1}$ ). 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 property 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<sup>-1</sup>. 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**

This work was financially supported by the Starting Research Project of Importing Talented Teachers in Kunming University of Science and Technology (KKS201226105) and the Analysis and Testing Foundation of Kunming University of Science and Technology (No. 20150653).

238 **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

239

240

241

**Table 2.** Results for the determination of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in water-based adhesive for cigarette

Sample No.	Added (mmol L <sup>-1</sup> )	Found(mmol L <sup>-1</sup> )	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

244

245 **Notes and references**

246 <sup>a</sup> Research & Development Center, China Tobacco Yunnan Industrial Co., Ltd,  
247 Kunming, 650231, China. *Email:369546858@qq.com*

248 <sup>b</sup> Faculty of Science and Life Technology, Kunming University of Science and  
249 Technology, Kunming, 650500, China.

- 250 1. M. Sopori, *Nature Reviews Immunology*, 2002, **2**, 372-377.
- 251 2. A. Spira, J. Beane, V. Shah, G. Liu, F. Schembri, X. Yang, J. Palma and J. S. Brody, *Proceedings of*  
252 *the National Academy of Sciences of the United States of America*, 2004, **101**, 10143-10148.
- 253 3. J. M. Liddle, N. T. Mooney, G. Smith and W. C. Wright, *Journal*, 1992.
- 254 4. X. Muñoz, M.-J. Cruz, R. Orriols, C. Bravo, M. Espuga and F. Morell, *CHEST Journal*, 2003, **123**,  
255 2124-2129.
- 256 5. A. A. Fisher and A. Dooms-Goossens, *Archives of dermatology*, 1976, **112**, 1407-1409.
- 257 6. P. F. Killian, C. J. Bruell, C. Liang and M. C. Marley, *Soil & Sediment Contamination*, 2007, **16**,  
258 523-537.
- 259 7. J. Branson, J. Naber and G. Edelen, *Education, IEEE Transactions on*, 2000, **43**, 257-261.
- 260 8. T. Mensing, W. Marek, M. Raulf-Heimsoth and X. Baur, *European Respiratory Journal*, 1998,  
261 **12**, 1371-1374.
- 262 9. H.-R. Lin, *European Polymer Journal*, 2001, **37**, 1507-1510.
- 263 10. N. Wahba, M. El Asmar and M. El Sadr, *Analytical Chemistry*, 1959, **31**, 1870-1871.
- 264 11. N. Wahba, M. F. El Asmar and M. M. El Sadr, *Analytical Chemistry*, 1959, **31**, 1870-1871.
- 265 12. C. Liang, C.-F. Huang, N. Mohanty and R. M. Kurakalva, *Chemosphere*, 2008, **73**, 1540-1543.
- 266 13. K.-C. Huang, R. A. Couttenye and G. E. Hoag, *Chemosphere*, 2002, **49**, 413-420.
- 267 14. D. Amin, *Analytst*, 1981, **106**, 1217-1221.
- 268 15. M. Roushani and Z. Abdi, *Sensors and Actuators B: Chemical*, 2014, **201**, 503-510.
- 269 16. V. N. Mehta, A. K. Mungara and S. K. Kailasa, *Analytical Methods*, 2013, **5**, 1818-1822.
- 270 17. G. M. Patel, J. V. Rohit, R. K. Singhal and S. K. Kailasa, *Sensors and Actuators B: Chemical*, 2015,  
271 **206**, 684-691.
- 272 18. J. V. Rohit, J. N. Solanki and S. K. Kailasa, *Sensors and Actuators B: Chemical*, 2014, **200**,  
273 219-226.
- 274 19. J. V. Rohit and S. K. Kailasa, *Analytical Methods*, 2014, **6**, 5934-5941.
- 275 20. S. K. Laliwala, V. N. Mehta, J. V. Rohit and S. K. Kailasa, *Sensors and Actuators B: Chemical*,  
276 2014, **197**, 254-263.
- 277 21. X. Yang, J. Ling, J. Peng, Q. Cao, Z. Ding and L. Bian, *Analytica Chimica Acta*, 2013, **798**, 74-81.
- 278 22. X. Hou, S. Chen, J. Tang, Y. Xiong and Y. Long, *Analytica Chimica Acta*, 2014, **825**, 57-62.
- 279 23. C. Gao, Z. Lu, Y. Liu, Q. Zhang, M. Chi, Q. Cheng and Y. Yin, *Angewandte Chemie International*  
280 *Edition*, 2012, **51**, 5629-5633.
- 281 24. J. N. Anker, W. P. Hall, O. Lyandres, N. C. Shah, J. Zhao and R. P. Van Duyne, *Nature materials*,  
282 2008, **7**, 442-453.
- 283 25. X. Jiang, Q. Zeng and A. Yu, *Langmuir*, 2007, **23**, 2218-2223.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

284 26. L. Tang, C. Dong and J. Ren, *Talanta*, 2010, **81**, 1560-1567.  
285 27. R. Jin, Y. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz and J. G. Zheng, *Science*, 2001, **294**,  
286 1901-1903.  
287 28. R. Jin, Y. C. Cao, E. Hao, G. S. Métraux, G. C. Schatz and C. A. Mirkin, *Nature*, 2003, **425**,  
288 487-490.  
289 29. Q. Zhang, N. Li, J. Goebel, Z. Lu and Y. Yin, *Journal of the American Chemical Society*, 2011, **133**,  
290 18931-18939.  
291 30. G. S. Métraux and C. A. Mirkin, *Advanced Materials*, 2005, **17**, 412-415.  
292 31. A. Brioude and M. P. Pileni, *The Journal of Physical Chemistry B*, 2005, **109**, 23371-23377.  
293 32. N. Okada, Y. Hamanaka, A. Nakamura, I. Pastoriza Santos and L. M. Liz Marzán, *The Journal of*  
294 *Physical Chemistry B*, 2004, **108**, 8751-8755.  
295 33. C. Xue and C. A. Mirkin, *Angewandte Chemie International Edition*, 2007, **46**, 2036-2038.  
296 34. Y. Chen, C. Wang, Z. Ma and Z. Su, *Nanotechnology*, 2007, **18**, 325602.  
297 35. M. F. de Oliveira, R. J. Mortimer and N. R. Stradiotto, *Microchemical Journal*, 2000, **64**,  
298 155-159.  
299 36. L. Zhao, S. Yang, L. Wang, C. Shi, M. Huo and Y. Li, *Journal of Environmental Sciences*, 2015, **31**,  
300 235-239.  
301 37. M. F. D. Oliveira, A. A. Saczk, J. A. G. Neto, P. S. Roldan and N. R. Stradiotto, *Sensors*, 2003, **3**,  
302 371-380.  
303  
304  
305  
306  
307  
308  
309

Analytical Methods Accepted Manuscript



## 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  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .

**Fig. 3.** TEM images of silver TNPs before and after reaction with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .

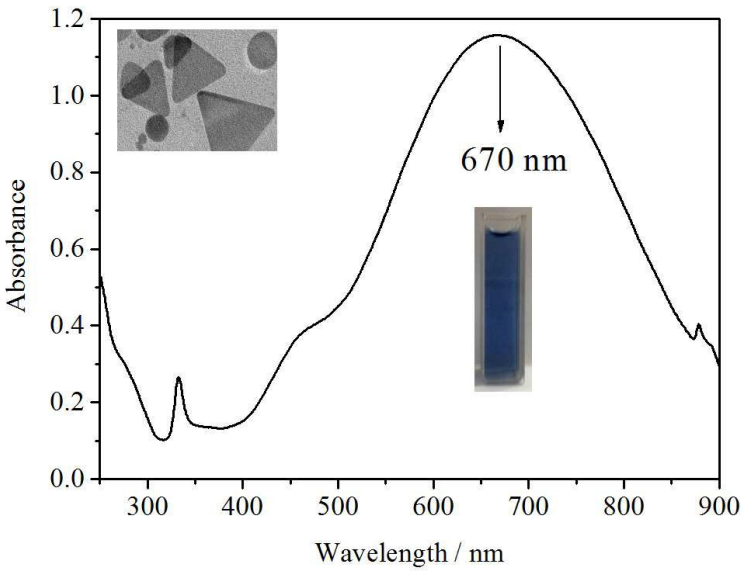
**Fig. 4.** Effects of pH on silver TNPs and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  interaction.

**Fig. 5.** Effect of reaction temperature on silver TNPs and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  interaction.

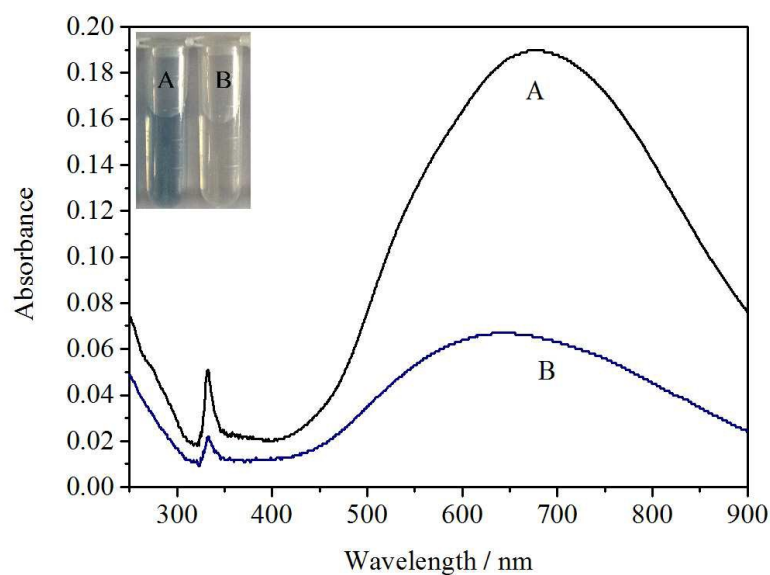
**Fig. 6.** Effect of reaction time on silver TNPs and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  interaction.

**Fig. 7.** Effect of coexistence substances.

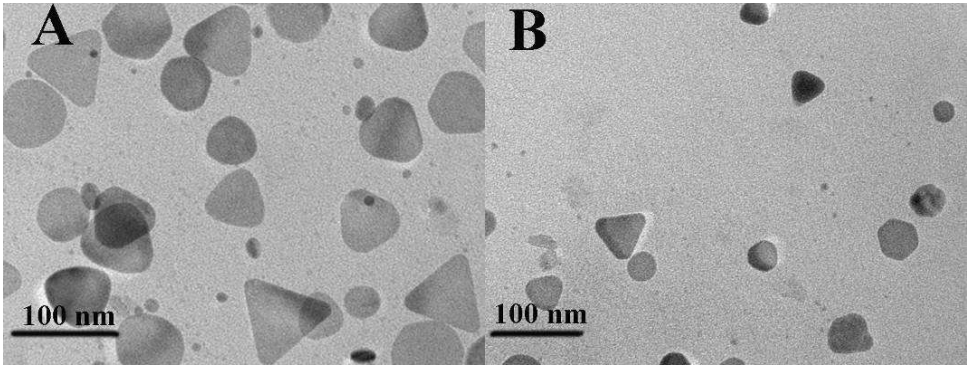
**Fig. 8.** (A) UV-vis spectra of silver TNPs by the addition of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  concentration range from 0 to 1.0 mmol L<sup>-1</sup>. (B) The linear for detection of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .



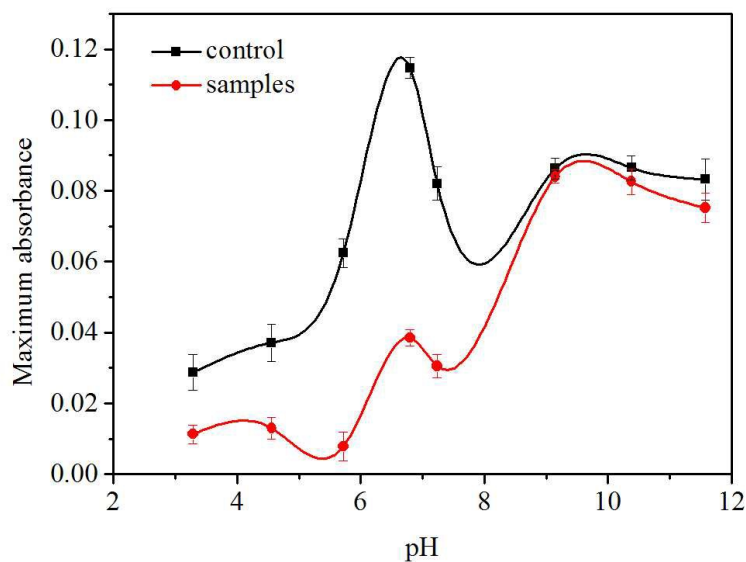
**Figure 1.** Characteristic absorption spectrum, TEM image and color of silver TNPs.



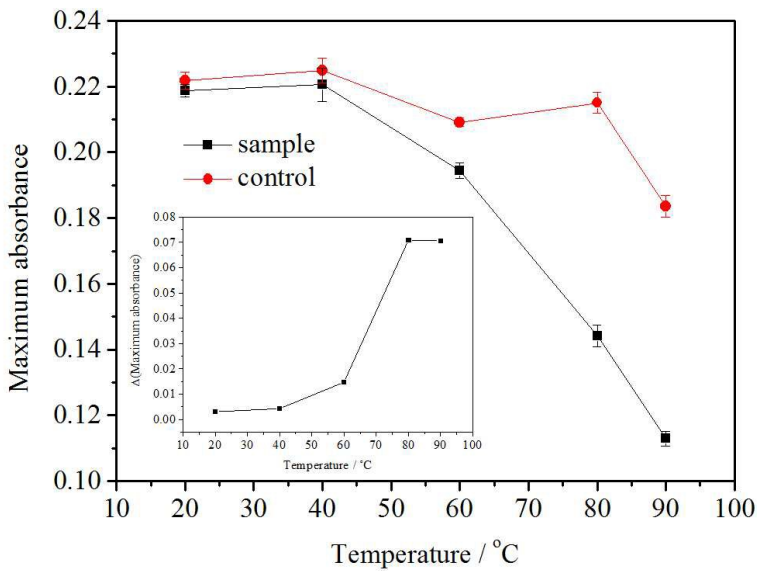
**Figure 2.** UV-vis spectra of silver TNPs before (A) and after (B) reaction with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (1.0 mmol L<sup>-1</sup>), pH 6.80, reaction for 30 min at 80 °C



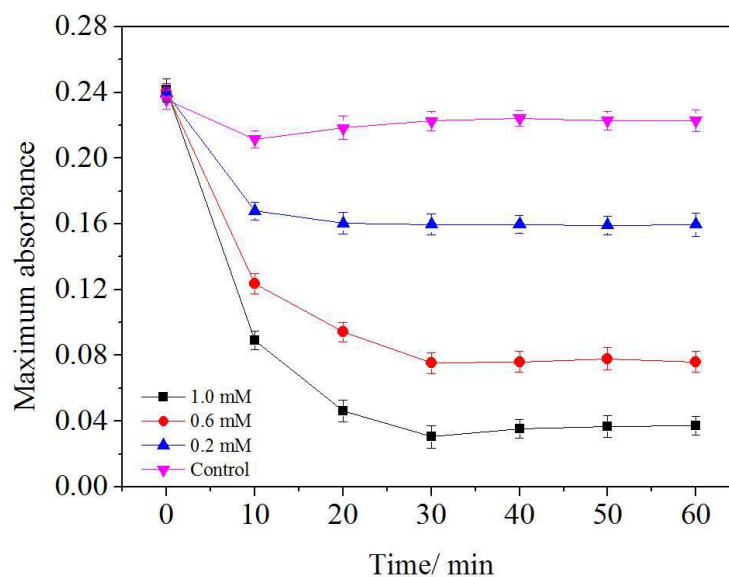
**Figure 3.** TEM images of silver TNPs before (A) and after (B) reaction with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  ( $0.60 \text{ mmol L}^{-1}$ ).



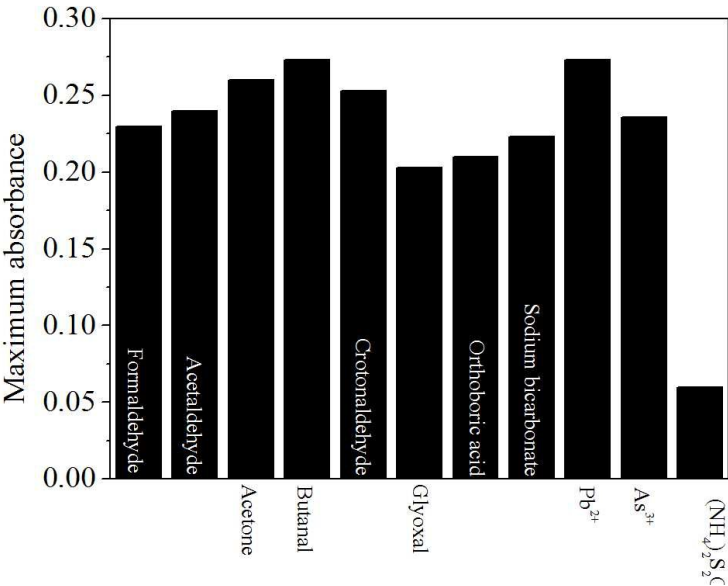
**Figure 4.** Effects of pH on silver TNPs and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  interaction. Condition: concentration of silver TNPs,  $0.286 \times 10^{-3} \text{ mol L}^{-1}$ ;  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $0.60 \text{ mmol L}^{-1}$ ; B-R buffer,  $0.02 \text{ mol L}^{-1}$



**Figure 5.** Effect of reaction temperature on silver TNPs and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  interaction.  
Condition: concentration of silver TNPs,  $0.286 \times 10^{-3} \text{ mol L}^{-1}$ ;  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $0.60 \text{ mmol L}^{-1}$

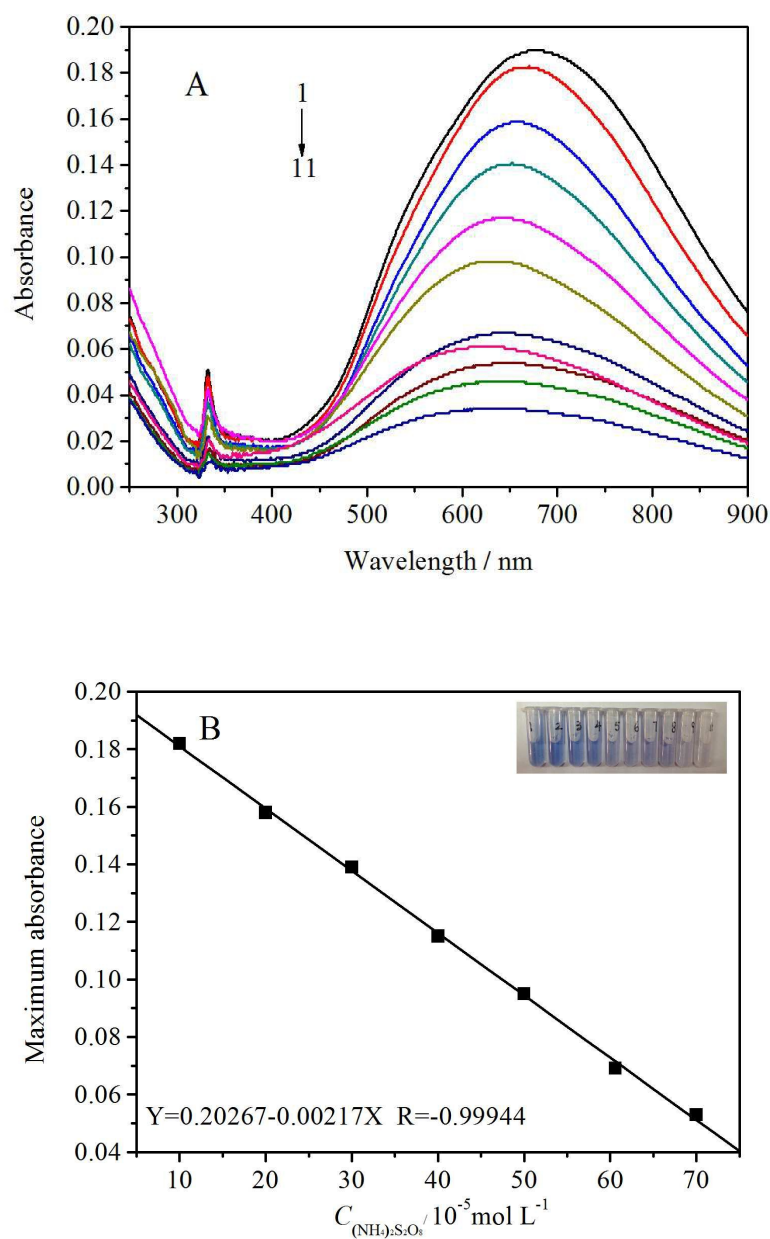


**Figure 6.** Effect of reaction time on silver TNPs and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  interaction. Four different concentrations of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (0, 0.2, 0.6, and 1.0 mmol  $\text{L}^{-1}$ ) were used for interacting with silver TNPs, concentration of silver TNPs, 0.286X mol  $\text{L}^{-1}$



**Figure 7.** Effect of coexistence substances. Experimental condition: concentration of silver TNPs, 0.286X mol L<sup>-1</sup>; (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 0.60 mmol L<sup>-1</sup>; others, 12 mmol L<sup>-1</sup>





**Figure 8.** (A) UV-vis spectra of silver TNPs by the addition of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  concentration range from 0 to  $1.0 \text{ mmol L}^{-1}$  (No. 1 - 11). (B) The linear for detection of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ .