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1 **A simple and sensitive sensor for silver ions based on unmodified**
2 **gold nanoparticles by using dynamic light scattering techniques**

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29 **Abstract:** A simple and sensitive assay for Ag^+ was developed with unmodified gold nano-
30 particles (AuNPs) by using dynamic light scattering (DLS) techniques. Ag^+ could induce the
31 oligonucleotide (5'-ATC ACT ATA TCA TAT ACT CAT-3') to change from a sin-
32 gle-stranded structure to a double-stranded structure and desorb from the surface of AuNPs,
33 which triggered the aggregation of AuNPs in the salt solution. The average hydrodynamic
34 diameter of aggregated AuNPs could be detected by using DLS techniques. Under the op-
35 timum conditions, the average hydrodynamic diameter of AuNPs is proportional to the
36 concentration of Ag^+ within the range of 13.3 - 100.0 nM, with a detection limit of 3.2 nM.
37 The method is easy to operate, and has low sample consumption, high sensitivity and selec-
38 tivity.

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40 **Keywords:** Dynamic light scattering; Silver ions; Sensors; Unmodified gold nanoparticles
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Graphical Abstract

A simple and sensitive sensor for silver ions based on unmodified gold nanoparticles by using dynamic light scattering techniques

Scheme 1. Schematic illustration of a sensor for Ag^+ based on unmodified gold nanoparticles by using DLS techniques

66

67 **Introduction**

68 Ag^+ was widely applied in electric industry, photographic industry, imaging, pharmacy, and
69 mirror. However, it was a heavy metal ion and its overuse in industrial production has trig-
70 gered environmental crisis¹⁻⁵. Ag^+ could inactivate sulfhydryl enzymes and combine with
71 amine, imidazole and carboxyl groups of various metabolites^{6,7}, which would result in toxic
72 effect to organisms. The content standard of Ag^+ in drinking water for U.S. Environmental
73 Protection Agency and World Health Organization was lower than $0.5 \mu\text{M}$ ⁸. Therefore, de-
74 veloping a highly sensitive and selective method to detect silver ions was needed urgently
75 for environmental protection and human health. Various methods to detect silver ions have
76 been established, such as inductively coupled plasma atomic emission spectrometry
77 (ICP-AES), electrochemistry, atomic absorption spectrometry(AAS), inductively coupled
78 plasma mass spectrometry (ICP-MS), atomic fluorescence spectrometry, and scanning elec-
79 trochemical microscopy⁹⁻¹⁵. However, most of these methods require expensive and sophis-
80 ticated instrument, skilled personnel and time-consuming sample pre-treatment.

81 Gold nanoparticles (AuNPs) have become one of the most popular materials for sensing
82 of the analytes of interest because of their ease in preparation and stability, and the extent of
83 AuNPs aggregation could be readily controlled by DNA hybridization¹⁶ and other recogni-
84 tion processes¹⁷⁻²⁰. A number of sensors based upon AuNPs were developed, including the
85 detection of DNA²¹⁻²², protein²³⁻²⁵, small molecules²⁶⁻²⁹ and metal ions³⁰⁻³³. Ono and
86 co-workers found that Ag^+ could specifically bind to cytosine-cytosine (C-C) mismatched
87 base pair³⁴. So a series of Ag^+ sensors were established based upon the specific recognition
88 ability of Ag^+ with C-C mismatched base pair in recent years³⁵⁻³⁸.

89 Dynamic light scattering (DLS) is an effective technique to analyze the size and size dis-

90 tribution of nanoparticles in liquid media and determining small change in the size of nano-
91 particles³⁹⁻⁴¹. The DLS technique has been widely used to detect proteins⁴²⁻⁴⁴, DNA^{35, 42},
92 small molecules^{45, 41, 46}, lead ions⁴⁷, and mercury ions^{48, 49} and so on because it was of high
93 sensitivity, low cost and ease of operation compared with other more sophisticated tech-
94 niques⁵⁰. To the best of our knowledge, there was no DLS sensor for silver ions. Herein, we
95 constructed a simple and sensitive sensor for Ag⁺ with label-free AuNPs by using a DLS
96 technique (**Scheme 1**).

97 **Experimental**

98 **Reagents**

99 Oligonucleotides were synthesized by Sangon Biotech. Co. Ltd. (Shanghai, China) and were
100 used without further purification. HAuCl₄·3H₂O and AgNO₃ were obtained from Sig-
101 ma-Aldrich Co., MOPS (BioBasic Inc.), all other chemicals were analytical reagent grade.
102 Nanopure water (18.1 MΩ) was obtained from a 350 Nanopure water system (Guangzhou
103 Crystalline Resource Desalination of Sea Water and Treatment Co. Ltd.) and was used for
104 all experiments.

105 **Design of oligonucleotides**

106 The oligonucleotide 5'-ATC ACT ATA TCA TAT ACT CAT-3' (oligo-1), which was
107 self-complementary sequence except cytosine-cytosine mismatched pairs, was designed for
108 our research. As shown in **Scheme 1**, single-stranded DNA (oligo-1) could adsorb on the
109 surface of AuNPs and prevent AuNPs from aggregation in the salt solution. However, when
110 there were silver ions in the solution, oligo-1 would change from a single-stranded structure
111 to a duplex structure and desorb from the surface of AuNPs because of the formation of cy-
112 tosine-Ag⁺-cytosine bond. The change of DNA structure induced by Ag⁺ resulted in the in-
113 crease of AuNPs average diameter, which could be determined by using the sensitive DLS

114 technique. The oligonucleotide, 5'-AGA ACA ATAATA TCT TTT TTT-3' (oligo-2), was
115 designed as the control sequence.

116 **Instrumentation**

117 The absorption spectrum and the melting curve were obtained with TU-1901 UV-visible
118 absorption spectrometer by using 1 cm path length quartz cells. The size distributions of the
119 nanoparticles were determined from the Transmission electron microscope (TEM) images,
120 which were recorded with a JEM-2010HR transmission electron microscope (Japan). The
121 average hydrodynamic diameter of the nanoparticles was measured by using Zeta
122 plus/90plus Dynamic Light Scattering Instrument (Brookhaven Instrument Co. USA). The
123 DLS instrument was performed under the following conditions: temperature: 25°C, detector
124 angle: 90°, incident laser wavelength: 683 nm, and laser power: 100 mW. All sizes reported
125 here were based on the intensity average, and each reported particle size was the average of
126 three times measurements.

127 **Preparation and characterization of AuNPs**

128 AuNPs were synthesized by reducing HAuCl₄ with citrate⁵¹. The average size was 14.5±2
129 nm, which was calculated from the TEM picture that containing at least 100 particles.
130 However, it was smaller than 39.6 nm that obtained by the DLS technique. These might be
131 interpreted that DLS measured the hydrodynamic diameter while TEM provided a more
132 precise size of the hard AuNPs core⁵². The concentration of AuNPs was estimated with
133 UV-visible absorption spectrum based on an extinction coefficient of $2.7 \times 10^8 \text{ M}^{-1} \cdot \text{cm}^{-1}$ at
134 520 nm for ~13nm particles⁵¹.

135 **DLS measurement**

136 50µl prepared AuNPs and 4µl oligo-1(1.0 µM) were mixed with 46µl MOPS buffer (10mM,

137 pH 7.0), then a certain amount of Ag^+ were added into the mixture and incubated for 45mins.
138 After that, several microliter salt solutions (NaNO_3 , final 0.06M) was added and incubated
139 for another 12mins. Finally, the sample solutions were diluted with nano-pure water to
140 600 μl for the DLS measurement.

141 Results and discussion

142 DLS and colorimetric data

143 The average hydrodynamic diameter of AuNPs under different conditions was detected by
144 DLS technique. As shown in **Fig. 1**, the average diameter of oligo-1-adsorbed AuNPs was
145 43.3nm (**Fig. 1a**), it increased to 67.6 nm (**Fig. 1b**) upon addition of 0.06 M NaNO_3 , which
146 might be due to the slightly aggregated AuNPs. However, when there was 15.0 nM Ag^+ in
147 the solution, the average diameter increased from 67.6 nm to 103.3 nm(**Fig. 1c**), which in-
148 dicated that the presence of Ag^+ resulted in the aggregation of AuNPs and the increase of
149 their average diameter in the salt solution.

150 The aggregation of AuNPs induced by Ag^+ could be verified by the change of the solu-
151 tion color and absorption spectra. As shown in **Fig. 2**, the solution of oligo-1-adsorbed
152 AuNPs without Ag^+ remained red with a absorption peak at 520 nm after the addition of
153 0.06 M NaNO_3 (**Fig. 2a**), while it changed to purple in the presence of 5.0 μM Ag^+ (**Fig. 2b**),
154 and changed to blue in the presence of 7.0 μM Ag^+ (**Fig. 2c**), accompanied with a dramatic
155 decrease of the absorption peak (520 nm) and the appearance of a new absorption band
156 around 650nm, which implied that the aggregation of AuNPs occurred in the presence of
157 silver ions. The similar aggregation of AuNPs induced by Ag^+ was demonstrated by TEM
158 images in good accordance with the DLS results.

159 To explore the mechanism of Ag^+ induced aggregation of AuNPs, the melting curve of
160 oligo-1 was studied. As displayed in **Fig. 3**, there was no obvious melting temperature which

could be found from the melting curve of oligo-1 in the absence of Ag^+ (**Fig. 3a**). However, a melting temperature of 28°C could be observed from the melting curve after the addition of Ag^+ (**Fig. 3b**), which revealed that the addition of silver ions could induce the self-complementary oligo-1 to change from a single-stranded structure to a stable double-stranded structure through the formation of C- Ag^+ -C bond, and lead to the occurrence of AuNPs aggregations.

Optimization of the experimental conditions

The concentration of NaNO_3 could affect the aggregation of AuNPs, so influence of the NaNO_3 concentration on the average diameter of AuNPs was investigated. As shown in **Fig. 4a**, the diameter change of AuNPs in the absence and presence of Ag^+ was non-significant when the NaNO_3 concentration was lower than 10 mM, and the size difference became obvious when the NaNO_3 concentration reached 10 mM. Although there was a more obvious diameter change at 11.7 mM NaNO_3 concentration, the average diameter without Ag^+ increased dramatically, which indicated that the aggregation of AuNPs took place. The aggregation of AuNPs in the absence of Ag^+ was unfavorable to the next detection of larger diameter induced by the addition of Ag^+ and would cause large experimental errors. So 10.0mM NaNO_3 was chosen for our research.

Oligo-1 could absorb on the surface of AuNPs and prevent the aggregation of AuNPs in the salt solution. So the effect of the oligo-1 concentration on the average diameter of AuNPs was studied. As shown in **Fig. 4b**, in the absence of Ag^+ , the average diameter of AuNPs reached a platform within the concentration range of 6.7-10.0 nM, while the average diameter increased apparently with the gradual decrease of oligo-1 concentration, and the lower oligo-1 concentration could not protect AuNPs from aggregation. The diameter change with and without Ag^+ is obvious in the solution containing 6.7 nM oligo-1. Therefore 6.7 nM oligo-1 was applied for our research.

The value of pH could affect the DNA hybridization relative to the aggregation of AuNPs. The effect of pH on the average diameter of AuNPs was demonstrated in **Fig. 4c**. There was a distinct size difference between with and without Ag^+ in the pH range of 7.0-8.0, and a diameter platform appeared. However, the average diameter of AuNPs without Ag^+ clearly increased when pH value was less than 7.0, which was likely caused by stabilizing the duplex formation because of protonation of the cytosine bases in acidic solution³⁴. When the value of pH was less than 7.0, oligo-1 cannot protect AuNPs well from aggregation. Hence, pH 7.0 was selected for this work.

The average diameter was influenced by the absorption and desorption of oligo-1 on the surface of AuNPs. So the effect of incubation time was investigated. As displayed in **Fig. 4d**, in the absence of Ag^+ , the absorption of oligo-1 on the surface of AuNPs was close to a balance in 40 minutes. The desorption of oligo-1 induced by the addition of Ag^+ reached equilibrium in 45 minutes. Therefore, 45 minutes was used for incubation time throughout the research.

Sensitivity and selectivity

Under the optimum conditions, the relation between the average diameter of AuNPs and the concentration of Ag^+ was investigated. As demonstrated in **Fig. 5**, the average hydrodynamic diameter of AuNPs in the solution was linear with the concentration of Ag^+ in the range of 13.3-100.0 nM, and the linear regression equation was $\Delta D = 61.2 + 1.54C$ (C : nM, $r = 0.9932$), with a detection limit of 3.2 nM ($C_{\text{DL}} = 3\sigma/\text{slope}$). To investigate the selectivity of the method, the average diameter in the presence of different metal ions was studied. The different metal ions (K^+ , Ni^{2+} , Co^{2+} , Zn^{2+} , Mg^{2+} , Ba^{2+} , Sr^{2+} , Ca^{2+} , Al^{3+} , Cu^{2+} , Cd^{2+} , Pb^{2+} and Hg^{2+}) were used to examine the selectivity. As displayed in **Fig. 6**, compared with that of blank solution, the average diameter after the addition of 50 nM Ag^+ increased obviously, while little change could be observed upon the addition of 500 nM other metal ions (10

times Ag^+ concentration). In addition, a control experiment was conducted by replacing the oligo-1 with oligo-2 (control sequence), the average diameter in the presence of 50 nM Ag^+ was almost the same as that of blank. These results revealed that the method was of good selectivity.

Conclusion

Hence, a simple and sensitive method for detecting Ag^+ was established with unmodified AuNPs by using DLS techniques. Silver ions could specifically bind with cytosine bases and form C- Ag^+ -C bond, which induced the oligonucleotide to change from a single-stranded structure to a double-stranded structure and desorb from the surface of AuNPs. The addition of silver ions would lead to the assembly of AuNPs and the increase of their average diameter in the salt solution, which could be measured by the DLS technique. Under the optimum conditions, the average hydrodynamic diameter of AuNPs had a linear relation with the concentration of Ag^+ within the range of 13.3-100.0 nM, with a detection limit of 3.2 nM. The method has several advantages such as low sample consumption, simple operation, high sensitivity and selectivity. In addition, the method can be also applied to the detection of other metal ions or small molecules which can cause a similar conformational change of DNA.

Acknowledgments

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References

- (1) Barriada, J. L.; Tappin, A. D.; Evans, E. H.; Achterberg, E. P., *Trac-Trends Anal. Chem.* **2007**, *26* (8), 809.
- (2) Chen, C.; Liu, H.; Zhang, B.; Wang, Y.; Cai, K.; Tan, Y.; Gao, C.; Liu, H.; Tan, C.; Jiang, Y., *Tetrahedron* **2016**, *72* (27–28), 3980.
- (3) Yang, Y.; Zhang, S.; Kang, M.; He, L.; Zhao, J.; Zhang, H.; Zhang, Z., *Anal. Biochem.* **2015**, *490*, 7.
- (4) Su, J.; Huang, S.; He, S.; Zeng, X., *Chem. Res. Chinese U* **2016**, *32* (1), 20.
- (5) Zhao, J.; Fan, Q.; Zhu, S.; Duan, A.; Yin, Y.; Li, G., *Biosens. Bioelectron.* **2013**, *39* (1), 183.
- (6) Liu, L.; Zhang, D.; Zhang, G.; Xiang, J.; Zhu, D., *Org. Lett.* **2008**, *10* (11), 2271.
- (7) AshaRani, P. V.; Low Kah Mun, G.; Hande, M. P.; Valiyaveetil, S., *Acs Nano* **2009**, *3* (2), 279.
- (8) Hu, M.; Fan, J.; Cao, J.; Song, K.; Zhang, H.; Sun, S.; Peng, X., *Analyst* **2012**, *137* (9), 2107.
- (9) Liu, J. F.; Chao, J. B.; Liu, R.; Tan, Z. Q.; Yin, Y. G.; Wu, Y.; Jiang, G. B., *Anal. Chem.* **2009**, *81* (15), 6496.
- (10) Wu, J.; Chumbimuni-Torres, K. Y.; Galik, M.; Thammakhet, C.; Haake, D. A.; Wang, J., *Anal. Chem.* **2009**, *81* (24), 10007.
- (11) Iyoshi, S.; Taki, M.; Yamamoto, Y., *Inorg. Chem.* **2008**, *47* (10), 3946.
- (12) Yan, G.; Wang, Y.; He, X.; Wang, K.; Su, J.; Chen, Z.; Qing, Z., *Talanta* **2012**, *94*, 178.
- (13) Hadioui, M.; Leclerc, S.; Wilkinson, K. J., *Talanta* **2013**, *105*, 15.
- (14) Szigeti, Z.; Malon, A.; Vigassy, T.; Csokai, V.; Grün, A.; Wygladacz, K.; Ye, N.; Xu, C.; Chebny, V. J.; Bitter, I.; Rathore, R.; Bakker, E.; Pretsch, E., *Anal. Chim. Acta* **2006**, *572* (1), 1.
- (15) Yang, H.; Liu, X.; Fei, R.; Hu, Y., *Talanta* **2013**, *116*, 548.

- (16) Li, H.; Rothberg, L., *Proc. Natl. Acad. Sci. U S A* **2004**, *101* (39), 14036.
- (17) Xin, A.; Dong, Q.; Xiong, C.; Ling, L., *Chem. Commun. (Camb)* **2009**, (13), 1658.
- (18) Jans, H.; Huo, Q., *Chem. Soc. Rev.* **2012**, *41* (7), 2849.
- (19) Yuan, Z.; Hu, C.-C.; Chang, H.-T.; Lu, C., *Analyst* **2016**, *141* (5), 1611.
- (20) Zhou, W.; Gao, X.; Liu, D.; Chen, X., *Chem. Rev.* **2015**, *115* (19), 10575.
- (21) Koo, K. M.; Sina, A. A. I.; Carrascosa, L. G.; Shiddiky, M. J. A.; Trau, M., *Anal. Methods-Uk* **2015**, *7* (17), 7042.
- (22) Wang, G.; Akiyama, Y.; Takarada, T.; Maeda, M., *Chem-Eur. J.* **2016**, *22* (1), 258.
- (23) Huang, X.; Xu, Z.; Mao, Y.; Ji, Y.; Xu, H.; Xiong, Y.; Li, Y., *Biosens. Bioelectron.* **2015**, *66*, 184.
- (24) Chen, P.; Chung, M. T.; McHugh, W.; Nidetz, R.; Li, Y.; Fu, J.; Cornell, T. T.; Shanley, T. P.; Kurabayashi, K., *Acs Nano* **2015**, *9* (4), 4173.
- (25) Sun, S.; Shen, H.; Liu, C.; Li, Z., *Analyst* **2015**, *140* (16), 5685.
- (26) Hu, J.; Ni, P.; Dai, H.; Sun, Y.; Wang, Y.; Jiang, S.; Li, Z., *Analyst* **2015**, *140* (10), 3581.
- (27) Peng, J.; Wang, Y.; Liu, L.; Kuang, H.; Li, A.; Xu, C., *RSC Adv.* **2016**, *6* (10), 7798.
- (28) Yu, Y. Y.; Zhang, L.; Sun, X. Y.; Li, C. L.; Qiu, Y.; Sun, H.P.; Tang, D. Q.; Liu, Y. W.; Yin, X. X., *Chem. Commun.* **2015**, *51* (42), 8880.
- (29) Chen, G.; Tong, H.; Gao, T.; Chen, Y.; Li, G., *Anal. Chim. Acta* **2014**, *849*, 1.
- (30) Chansuvarn, W.; Tuntulani, T.; Imyim, A., *Trac-Trends Anal. Chem.* **2015**, *65*, 83.
- (31) Chen, G. H.; Chen, W. Y.; Yen, Y. C.; Wang, C.-W.; Chang, H.-T.; Chen, C.-F., *Anal. Chem.* **2014**, *86* (14), 6843.
- (32) Sener, G.; Uzun, L.; Denizli, A., *Anal. Chem.* **2014**, *86* (1), 514.
- (33) Miao, P.; Liu, L.; Li, Y.; Li, G., *Electrochem. Commun.* **2009**, *11* (10), 1904.
- (34) Ono, A.; Cao, S.; Togashi, H.; Tashiro, M.; Fujimoto, T.; Machinami, T.; Oda, S.;

- 284 Miyake, Y.; Okamoto, I.; Tanaka, Y., *Chem. Commun.* **2008**, (39), 4825.
- 285 (35)Zhao, C.; Qu, K. G.; Song, Y. J.; Xu, C.; Ren, J. S.; Qu, X. G., *Chem-Eur. J.* **2010**, 16
- 286 (27), 8147.
- 287 (36)Xie, W. Y.; Huang, W. T.; Li, N. B.; Luo, H. Q., *Chem. Commun.* **2012**, 48 (1), 82.
- 288 (37)Zhou, X. H.; Kong, D. M.; Shen, H. X., *Anal. Chem.* **2010**, 82 (3), 789.
- 289 (38)Pu, W. D.; Zhao, Z.; Wu, L. P.; Liu, Y.; Zhao, H. W., *J. Nanosci. Nanotechno.* **2015**, 15
- 290 (8), 5524.
- 291 (39)Zhang, Y.; Fei, W. W.; Jia, N. Q., *Nanoscale Res. Lett.* **2012**, 7.
- 292 (40)Miao, X. M.; Ling, L. S.; Shuai, X. T., *Biosens. Bioelectron.* **2013**, 41, 880.
- 293 (41)Liu, X.; Dai, Q.; Austin, L.; Coutts, J.; Knowles, G.; Zou, J.; Chen, H.; Huo, Q., *J. Am.*
- 294 *Chem. Soc.* **2008**, 130 (9), 2780.
- 295 (42)Li, C.; Ma, J. H.; Fan, Q. X.; Tao, Y. Q.; Li, G. X., *Chem. Commun.* **2016**, 52 (50),
- 296 7850.
- 297 (43)Seow, N.; Tan, Y. N.; Yung, L. Y. L.; Su, X., *Scientific Reports* **2015**, 5, 18293.
- 298 (44)Lai, Y. H.; Koo, S.; Oh, S. H.; Driskell, E. A.; Driskell, J. D., *Anal. Methods-Uk* **2015**,
- 299 7 (17), 7249.
- 300 (45)Dasary, S. S. R.; Senapati, D.; Singh, A. K.; Anjaneyulu, Y.; Yu, H. T.; Ray, P. C., *Acs*
- 301 *Appl. Mater. Inter.* **2010**, 2 (12), 3455.
- 302 (46)Ma, H. X.; Wu, B. N.; Huang, C. S.; Jia, N. Q., *Anal. Methods-Uk* **2014**, 6 (1), 67.
- 303 (47)Beqa, L.; Singh, A. K.; Khan, S. A.; Senapati, D.; Arumugam, S. R.; Ray, P. C., *Acs*
- 304 *Appl. Mater. Inter.* **2011**, 3 (3), 668.
- 305 (48)Xiong, C.; Ling, L. S., *Talanta* **2012**, 89, 317.
- 306 (49)Fu, C. Y.; Ma, H. X.; Huang, C. S.; Jia, N. Q., *Anal. Methods-Uk* **2015**, 7 (18), 7455.
- 307 (50)Zheng, T.; Bott, S.; Huo, Q., *Acs. Appl. Mater. Inter.* **2016**, 8 (33), 21585.
- 308 (51)Jin, R.; Wu, G.; Li, Z.; Mirkin, C. A.; Schatz, G. C., *J. Am. Chem. Soc.* **2003**, 125 (6),

309 1643.

310 (52)Miao, X. M.; Xiong, C.; Wang, W. W.; Ling, L. S.; Shuai, X. T., *Chem-Eur. J.* **2011**, *17*

311 (40), 11230.

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316 **Scheme 1.** Schematic illustration of a DLS sensor for silver ions with unmodified gold nanoparticles

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318 **Fig. 1.** The size distribution of AuNPs under different conditions

319 (a) 0.96 nM AuNPs + 10 mM MOPS buffer (pH 7.0) + 6.7 nM oligo-1; (b) a + 10.0 mM NaNO₃; (c) a +

320 15.0 nM Ag⁺ + 10.0 mM NaNO₃.

Fig. 2. The TEM images and the change of the solution color and absorption spectra in the absence and presence of Ag⁺

(a) 4.6 nM AuNPs + 80 nM oligo-1 + 0.06 M NaNO₃; (b) a + 5.0 μM Ag⁺; (c) a + 7.0 μM Ag⁺

Fig. 3. The melting curve of 2.8 μM oligo-1 in the absence (curve a) and presence (curve b) of 9.0 μM Ag⁺. The experiments were conducted in the MOPS buffer solution (10mM, pH 7.0) containing 0.1 M NaNO₃.

Fig. 4. The influence of experimental conditions on the average diameter of AuNPs

(a) The effect of the NaNO₃ concentration on the average diameter of AuNPs. AuNPs: 0.96 nM, oligo-1:

6.7 nM, pH: 7.0, Ag⁺: 15 nM;

(b) The effect of the concentration of oligo-1 on the average diameter of AuNPs. AuNPs: 0.96 nM, pH:

7.0, Ag⁺: 15 nM, NaNO₃: 10 mM;

(c) The effect of pH on the average diameter of AuNPs. AuNPs: 0.96 nM, oligo-1: 6.7 nM, Ag⁺: 15 nM,

NaNO₃: 10 mM;

(d) The effect of incubate time on the average diameter of AuNPs. AuNPs: 0.96 nM, oligo-1: 6.7 nM,

pH: 7.0, Ag⁺: 15 nM, NaNO₃: 10 mM.

Fig. 5. Plots of diameters of AuNPs versus different Ag^+ concentrations

The inset demonstrated the calibration curve for Ag^+ . The experiments were conducted under the conditions: 0.96 nM AuNPs, 6.7 nM oligo-1, 10 mM $NaNO_3$, pH 7.0 MOPS buffer and different Ag^+ concentrations.

Fig. 6. The selectivity of this method Experimental conditions: 0.96 nM AuNPs, 6.7 nM oligo-1, 10 mM $NaNO_3$, pH 7.0 MOPS buffer, 50 nM Ag^+ or 500 nM other metal ions for the ion selectivity. The control

348 experiment was conducted with 6.7 nM oligo-2 and 50 nM Ag^+ .

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Scheme 1 Schematic illustration of a DLS sensor for silver ions with unmodified gold nanoparticles

Fig. 1 The size distribution of AuNPs under different conditions

Fig. 2 The TEM images and the change of the solution color and absorption spectra in the absence and presence of Ag^+

Fig. 3 The melting curve of 2.8 μM oligo-1 in the absence (curve a) and presence (curve b) of 9.0 μM Ag^+

296x209mm (300 x 300 DPI)

Fig. 4 The influence of experimental conditions on the average diameter of AuNPs

Fig. 5 Plots of diameters of AuNPs versus different Ag^+ concentrations

Fig. 6 The selectivity of this method