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Selective determination of melamine in milk samples using 3-mercapto-1-propanesulfonate-modified gold nanoparticles as colorimetric probe

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ABSTRACT

A novel and sensitive colorimetric method for determination of melamine in milk samples was developed by a 3-mercapto-1-propanesulfonate-modified gold nanoparticles (MPS-GNPs) probe. Melamine molecule has multiple $-NH_2$ groups. These functional groups can interact with MPS to form strong hydrogen bonding and induce the aggregation of the MPS-GNPs, resulting in a dramatic color change from red to blue. Therefore, the concentration of melamine in milk samples can be quantitatively detected by the naked eyes or a UV-vis spectrometer. Moreover, investigations have revealed that the sensitivity of the detection could be clearly improved by adding NaCl to the modified GNPs solution, which leads to a more rapid color change in the NaCl-optimized GNPs system. It is worth noting that the absorption ratio (A_{650}/A_{520}) of the modified GNPs in the NaCl-optimized system exhibited a linear correlation with melamine concentration and the limit of detection is 8 nM, well below the safety limit (1 ppm for infant formula in China).

1. Introduction

Melamine is a kind of triazine analogue with three amino groups, which is frequently used as an industrial chemical in the production of multipurpose melamine-formaldehyde resins. Because of its high nitrogen content (66% by mass) [1], melamine has been illegally added into milk products by unethical producers to obtain an incorrectly high readout of apparent protein content since the protein levels are estimated by the conventional standard Kjeldahl or Dumas tests. High concentration of melamine is proved to be greatly toxic to human, which can result in the formation of insoluble melamine cyanurate crystalsin [2] in kidneys, thus causing renal failure [3]. It has been reported that high concentration of melamine were deliberately adulterated into milk and various dairy products, resulting in serious renal failure and death of infants in September 2008. In recent years, the intentional adulteration of melamine used in pet foods and human foods has attracted increasing concerns [3]. It is therefore worth investigating the concentration detection and determination of melamine in foods. Thus, detection and determination of melamine has become necessary and urgent. Traditionally, different types of conventional analysis technology have been developed, such as liquid chromatography–tandem mass spectrometry [4], extractive electrospray ionization mass spectrometry [5], time-of-flight mass spectrometry [6], surface-desorption ionization atmospheric pressure chemical mass spectrometry [7]. However, to the best of our knowledge, those methods need complicated preconcentration, time-consuming steps and high-cost instruments, which limit their widely application. Recently electrochemical methods [8] and capillary electrophoresis [9] have been developed to detect melamine in milk, but most of these methods require complicated instruments and professional staff, limiting their application in marketplaces and rural areas. Hence, exploring an accurate, rapid and convenient analytical method to detect melamine still remains a challenge for chemists.

With the developments of nanotechnology, novel methods of colorimetric assay have been exploited. Gold nanoparticles (GNPs) have been extensively used as colorimetric probe for sensing and biosensing owing to their unique size-dependent and interparticle-distance dependent optical properties and the accompanying color change of solution. Up to now, GNPs-based colorimetric methods have been reported on the detection of DNA [10], bacteria [11], metal ions [12], cancerous cells [13] and so on. Recently, Lu's group [14] and Kuang's group [15] have respectively developed 1-(2-mercaptoethyl)-1,3,5-triazinane-2,4,6-trione (MTT)-stabilized GNPs and 18-crown-6-thiol-modified GNPs as colorimetric probe for melamine detection in milk based on hydrogen-bonding recognition between modifiers and melamine. In addition, Zhang's group [16], Wang's group [17] and Chen's group [18] have proposed a simple colorimetric method using unmodified GNPs to detect

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the concentration of melamine in milk. Although these methods exhibited high selectivity for melamine, the complex synthesis of modifiers or time-consuming sample pretreatments limited their potential application. Therefore, the development of on-site, real-time and low-cost melamine sensing has become increasingly attractive.

Inspired by these works, we developed a novel and sensitive 3-mercapto-1-propanesulfonate-modified gold nanoparticles (MPS-GNPs) probe for determination of melamine in milk. 3-Mercapto-1-propanesulfonate (MPS) molecule binded with melamine via hydrogen bonding between the sulfo group of MPS and the amine groups of melamine. Furthermore MPS can be easily conjugated to GNPs through –SH group. Thus, the MPS-GNPs can be cross linked in the presence of certain amount of melamine, accompanying clear color change (from red to blue). Moreover, the GNPs system has a better sensitivity for detection of melamine by adding NaCl to the modified GNPs solution. It is worth noting that the absorption ratio (A_{650}/A_{520}) of the modified GNPs in the NaCl-optimized system exhibited a linear correlation with melamine concentration and the limit of detection is 8 nM, well below the safety limit (1 ppm for infant formula in China). Further more, the detection with the proposed method can be finished within minutes. Therefore, NaCl-optimized MPS-GNPs system as a novel, on-site, real-time and low-cost melamine sensing, would have a wide range of practical applications.

2. Experimental

2.1. Materials

Sodium citrate and sodium chloride were purchased from Tianjin Kaitong Chemicals Company (Tianjin, China). $HAuCl_4{\cdot}4H_2O$ was obtained from Shanghai Chemical Reagent Company (Shanghai, China). Sodium 3-mercapto-1-propanesulfonate (MPS) was supplied by Shanghai Crystal Pure Chemicals Company. Melamine and trichloroacetic acid were obtained from Chengdu Kelong Chemical Factory. The milk and the infant formula were purchased from the local supermarket. All solvents and reagents used in the experiments were of analytical grade and double-distilled water was used throughout.

2.2. Apparatus

DMF-101B Collector constant temperature heating magnetic stirrer was supplied by Gongyi Yuhua Instrument Company (Henan, China). Absorption spectra were recorded using Shimazu 2450 UV–vis 400 – 800 nm with quartz cells of path length 1 mm. The photographs were taken with FinePix F200EXP digital camera. The pH measurement was carried out on model PHS-3CT digital ion analyzer (Shanghai Instruments, Shanghai, China). Transmission electron microscopy (TEM) observations were obtained using the 100CX II (JEM; Japan) transmission electron microscope.

2.3. Preparation of the GNPs

Typically, all glassware used in the procedure was dipped in aqua regia (HCl/HNO_3, volume ratio 3:1) for 30 min, rinsed thoroughly with double-distilled water and then dried in vacuum dryer at 60 °C. Colloidal GNPs of 13 nm in diameter were synthesized by the citrate reduction method [19,20]. 100 mL of $HAuCl_4$ (1 mM) solution was heated to reflux with vigorous stirring, and then 10 mL of 38.8 mM sodium citrate was quickly added into. The color of the solution changed from pale yellow to wine red within 1 min. The solution was heated under reflux for another 20 min. Then the heating source was removed and the solution was continuously stirred until it had cooled to room temperature (23–25 °C). The resultant gold colloids were stored in 4 °C. The transmission electron microscopy (TEM) was utilized to characterize the size and the shape of the GNPs. The TEM data showed the GNPs with a nearly uniform particle size of 13 nm. The MPS-GNPs were prepared by ligand-exchange reaction between MPS and the citrate-capped GNPs. 10 μL MPS solution (1 mM) was added to the solution of citrate-capped GNPs (10 mL) and stirred for 5 h at room temperature, and then the MPS-GNPs were obtained [14].

2.4. Detection of melamine

The MPS-GNPs solution containing a suitable amount of NaCl was used as a stock liquid for detecting melamine. Different amount of melamine was added into the above stock liquid. After 1 min, the color change was observed by the naked eyes and the absorbance spectra were recorded with UV-vis spectrometer.

2.5. Detection of melamine in milk samples

Milk samples were pretreated according to previous report [21]. Briefly, 4 mL of milk samples spiked with different concentrations of melamine were mixed with 1.2 mL of 300 g/L trichloroacetic acid. After being shaked for 1 min, the mixture was centrifugated at 3500 rpm for 5 min. The supernatant was adjusted to pH 7 with NaOH solution before being centrifugated for another 5 min. The final supernatant was used for detection.

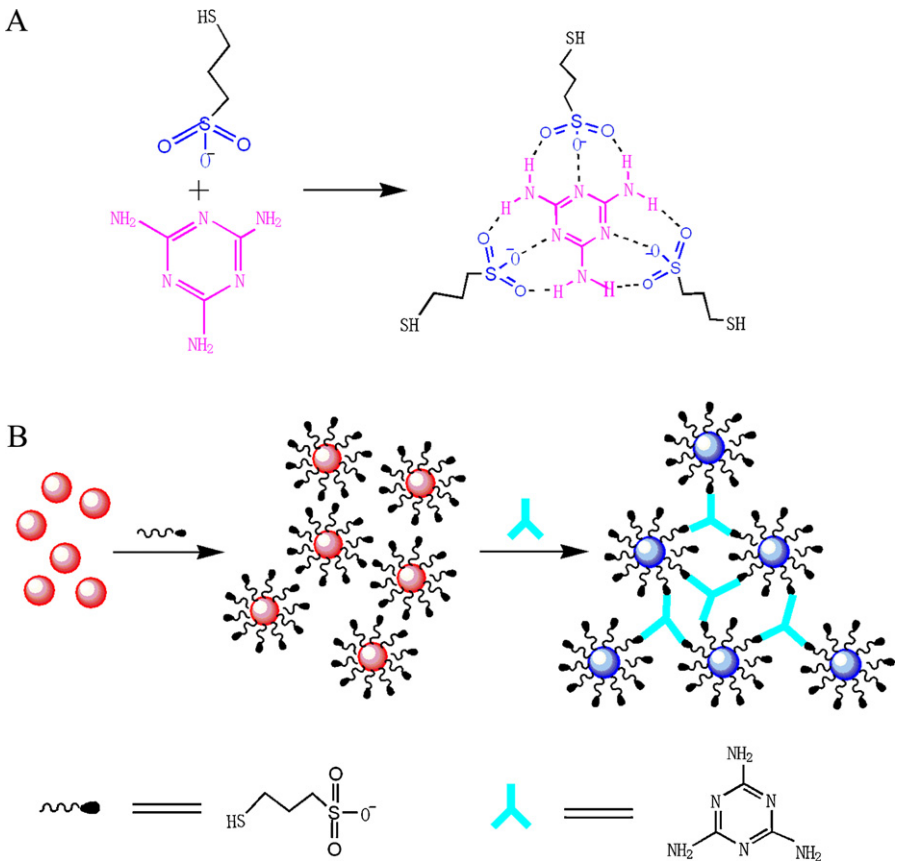
As far as infant formula, it was pretreated according to previous report [22]. To a centrifuge tube was added 1.0 g of dry powder (spiked with different concentrations of melamine) and 2.0 mL water, being shaked for 1 min, and then 2.0 mL of 300 g/L trichloroacetic acid was added into. After being ultrasonically treated for 10 min, the mixture was centrifuged at 3500 rpm for 5 min to separate the deposit. The supernatant was then transferred into another centrifuge tube and adjusted to pH 7 with NaOH solution. The solution was centrifuged at 3500 rpm for 5 min to remove the deposit again and the final supernatant was used for detection.

To detect melamine, 50 μL of the extraction was added to 400 μL GNPs stock liquid, then the solution was reacted for 5 min at room temperature. Finally absorption spectra of the solution were recorded by UV-vis spectrophotometer. The absorption ratio (A_{650}/A_{520}) was utilized to quantify the concentration of melamine.

3. Results and discussion

3.1. Detection principle

It is known that the melamine and MPS can form a stable complex, exhibiting three complementary NH···O and N···O hydrogen bonds (as shown in Scheme 1A). It is considered that such triple hydrogen bonding is particularly useful for controlling molecular self-assembly [23]. In addition, the experimental result showed that the MPS-GNPs were well dispersed in distilled water, and the strong surface plasmon resonance of the uniform colloid was at 520 nm (Fig. S1 in supporting information). So we deduce that the hydrogen bonds between melamine and MPS can cross-link the neighboring MPS-GNPs and induce the aggregation of GNPs (as shown in Scheme 1B). The changes of the optical properties can be directly showed by the color change. The solution color changed from wine red to blue correspondingly (as shown in Fig. 1A). On the other hand, melamine caused a red shift and broadened the surface plasma band of MPS-stabilized GNPs in UV–visible spectrum (Fig. 1B). The characteristic plasma resonance-absorption peak of the monodisperse functional GNPs is at 520 nm. But the intensity of the peak at 520 nm will become weaker and shift to 650 nm when melamine concentration is increased, indicating the aggregation of GNPs.



Scheme 1. (A) Hydrogen-bonding recognition between melamine and MPS. (B) Schematic representation of the MPS-stabilized GNPs colorimetric mechanism for melamine detection.

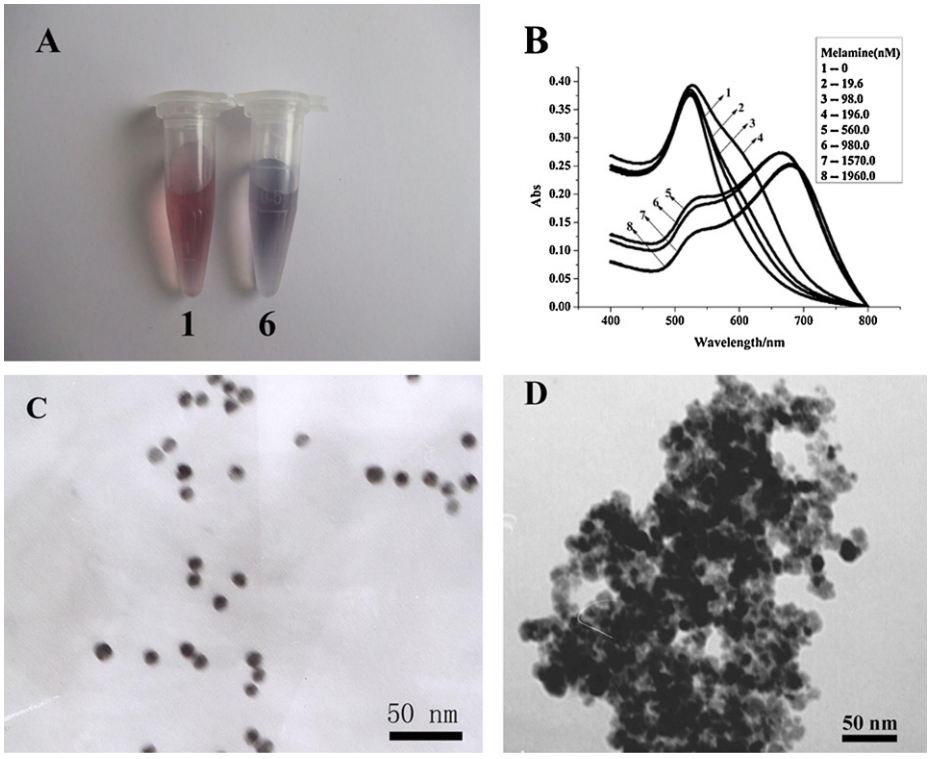


Fig. 1. (A) Visual color change of the MPS-stabilized GNPs upon addition of melamine (from left to right: 0, 980.0 nM). (B) UV–vis absorption spectra formed in the presence of different concentrations of melamine in pH 7.0 buffer. (C and D) The corresponding TEM images (0 and 980.0 nM, respectively).

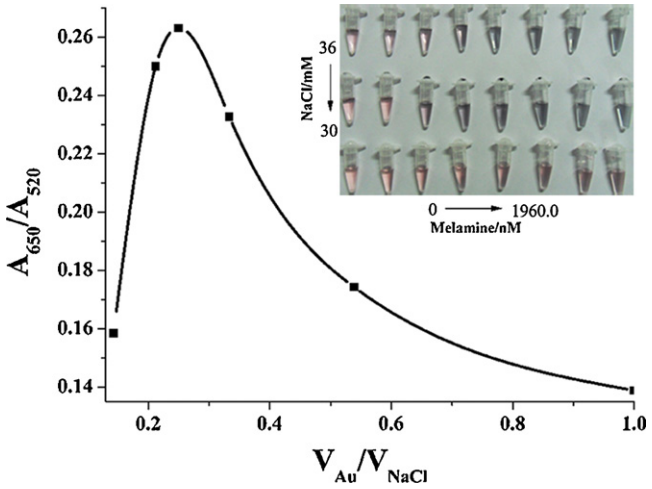


Fig. 2. Effect of media volume ratio (V_{Au}/V_{NaCl}) on the absorption ratio (A_{650}/A_{520}) (final concentration of melamine: 200.0 nM). The insert are photographs of 100 μL GNPs solution mixed with 10 μL melamine solution and 400 μL NaCl solution. The final concentrations of melamine (from left to right) are 0, 19.8, 98.0, 196.0, 589.0, 980.0, 1570.0 and 1960.0 (nM) and the concentrations of NaCl (from up to down) are 36, 34, 30 (mM), respectively.

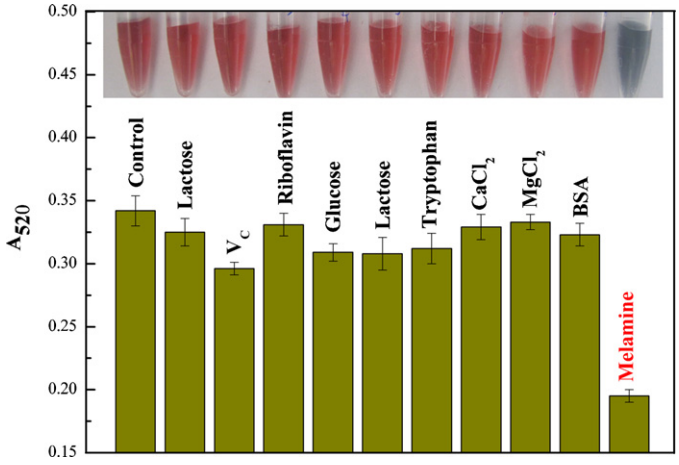


Fig. 3. UV–vis spectra of the MPS-GNPs in the presence of melamine or other interferences (the final concentrations of melamine and other interferences were 728.0 nM) and the corresponding photographs insert in figure (from left to right: control, lactose, Vitamin C (V_C), riboflavin, glucose, lactose, tryptophan, $CaCl_2$, $MgCl_2$, bull serum albumin (BSA), melamine).

To further demonstrate the degree of the GNPs aggregation, the modified GNPs solutions with and without melamine were observed by TEM (Fig. 1 C and D). With the absence of melamine, the modified GNPs are well dispersed (Fig. 1C). However, with the presence of melamine (980.0 nM), the GNPs are aggregated for the reaction of $-SO_3H$ groups on the GNPs surface with $-NH_2$ groups of melamine (Fig. 1D). These results further conforms the above proposition we presented.

Therefore, MPS-GNPs could be a colorimetric sensor for detection of melamine in milk products.

3.2. Optimization of assay conditions

The performance of the proposed method is strongly affected by the assay conditions such as media pH, concentration of NaCl electrolyte and volume ratio of V_{Au}/V_{NaCl}.

3.2.1. Impact of pH

Media pH not only influences the interaction between modified GNPs and melamine, but also affects the stability of GNPs. The effect of pH on the response of the GNPs solution was carried out at a pH range from 4.0 to 12. The results in the experiments (Fig. S2 in supporting information) showed that the absorption ratio (A_{650}/A_{520}) at pH 7.0 shows the sharp peak, while in the section of high pH value (pH > 7.0) and low pH value (pH < 7.0), the absorption ratio (A_{650}/A_{520}) decrease gradually. This is probably due to the fact that when meeting strong acidic media or basic media, melamine can be hydrolysed as a result of yielding ammeline, ammelide and cyanuric acid [8]. However, the hydrolysates could not induce the aggregation of MPS-stabilized GNPs. Therefore, pH of media was selected as 7.0.

3.2.2. Impact of NaCl

As pointed out earlier, the formation of GNPs influences the colorimetric signal which is associated with the interaction between melamine and the MPS-GNPs. Therefore it is speculated that the sensitivity and sensing range of the colorimetric signal are related to the resistance of GNPs to aggregate. NaCl is well-known to destabilize the GNPs [24], thus, it can greatly influence the color of GNPs solution in the experiment. The NaCl solution was beforehand migrated into the solution of modified GNPs and the mixture was used for melamine detection. As was expected, a different sensitivity and sensing range were obtained for the GNPs including different volumes of NaCl. As shown in Fig. 2, visually apparent color changes from red to blue occurred in melamine concentrations between 98.0 and 1960.0 nM with NaCl at 34 mM, whereas a color change occurred only when melamine reached 589.0 nM with NaCl at 30 mM and a color change occurred without melamine in GNPs solution with NaCl at 36 mM. It was indicated that the proposed colorimetric assay exhibited high sensitivity to detect melamine when the addition of NaCl was 34 mM.

In addition, the formation of GNPs aggregation is also influenced by the volume ratio (V_{Au}/V_{NaCl}). As indicated in Fig. 2, the mutation point of the absorption ratio (A_{650}/A_{520}) is at 0.25 of the media volume ratio. The measurements of extinct ratios further demonstrate that NaCl is capable of improving the sensitivity of the proposed method. Therefore, the 34 mM NaCl and 0.25 of the media volume ratio were employed for further assay.

Table 1
Concentration of melamine in milk and infant formula samples as measured by the MPS-stabilized GNPs colorimetric probes.

	Melamine added (nM)	Recovered (nM) ±SD[a]	Recovery (%)	CV (%)
Milk				
1	20.0	20.9 ± 0.537	104.5	2.7
2	30.0	29.4 ± 0.473	98.0	1.6
3	300	311 ± 9.965	103.7	3.3
4	350	349.8 ± 13.004	99.9	3.7
Powder				
1	40.7	38.1 ± 2.420	93.6	5.9
2	353.6	359.2 ± 13.833	101.6	3.9

[a] Average value of three determinations ± standard deviation.

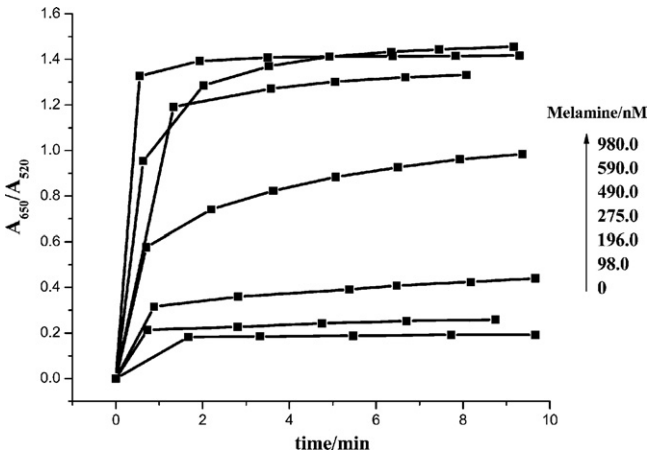


Fig. 4. Plot of A_{650}/A_{520} versus time at different melamine concentration.

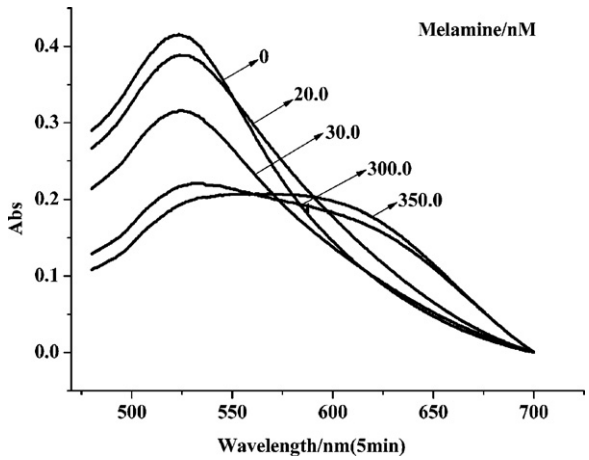


Fig. 6. UV–vis spectra at different concentrations of melamine in milk. Spectra were recorded after mixing MPS-GNPs and the treated milk sample for 5 min.

3.3. The interference experiment

To examine the specificity of the proposed colorimetric probe for detection of melamine, the interferences of the common ions in milk were investigated under identical conditions. Fig. 3 shows visual color change and UV–vis absorption spectra of the modified GNPs formed in the presence of melamine and other potential interferences. It is clearly observed that only melamine induced a dramatic color change from wine red to blue and the others did not induce the GNPs aggregation. At the same time, Fig. 3 displayed that only melamine exhibited a dramatic decrease in the absorbance intensity at 520 nm, and the interferences had a negligible value. Above results indicated that this proposed colorimetric method was appropriate for the selective recognition of melamine. For making a higher sensitivity, the milk samples should be pretreated to reduce the possible interferences.

3.4. Aggregation kinetics of the modified GNPs with melamine

Because of the fast response of the probe, it can be used for on-site and real-time detection of melamine in milk. The aggregation kinetics of the proposed assay was examined with different melamine concentration by measuring the extinction ratio of A_{650}/A_{520} at room temperature, as shown in Fig. 4. These curves indicated that the higher the concentration of melamine was, the faster the extinction ratio rose within 1 min. At the concentration of melamine as 490.0 nM, the extinct ratio exhibited a rapid increase during the first 1.5 min and then remained constant, revealing that the aggregation of the modified GNPs induced by hydrogen bonding was promptly completed in the initial stage. Thus, the proposed method was enabled to sensitive and rapid detection of melamine in milk samples.

3.5. The detection of melamine under the optimized conditions

To evaluate the sensitivity of melamine dependent on the colorimetric assay under the optimized detection conditions, the color change of MPS-GNPs solution was recorded by digital camera, the surface plasma resonance peak shift of GNPs was monitored by UV-vis spectroscopy, and the extinction ratio was compared at various concentrations of melamine. As shown in Fig. 5A, the absorbance of MPS-GNPs solution at 650 nm increased progressively and the absorbance around 520 nm decreased obviously, on the addition of melamine from 98.0 nM to 589.0 nM. At the same time, on the addition of melamine from 0 to 589.0 nM, the color of the GNPs mixture solution changed from red to deep-red and then to blue within 1 min gradually. When the concentration of melamine is 98.0 nM, a clear color change from wine-red to purple could be easily differentiated by naked eyes (shown in inset of Fig. 5A). The absorbance ratios (A_{650}/A_{520}) were utilized for the quantitative determination of the melamine and the data were shown in Fig. 5B. The calibration curve for melamine detection represented excellent linearity with an R of 0.984 in the range from 10 to 150 nM and an R of 0.994 in the range from 150 to 600 nM. The detection limit was calculated to be 8 nM ($S/N = 3$) by using UV-vis spectrometer, which was well below the safety limit (2.5 ppm in the USA and EU; 1 ppm for infant formula in China).

In order to confirm the efficiency of the proposed method, the control experiment based on the utilization of non-modified

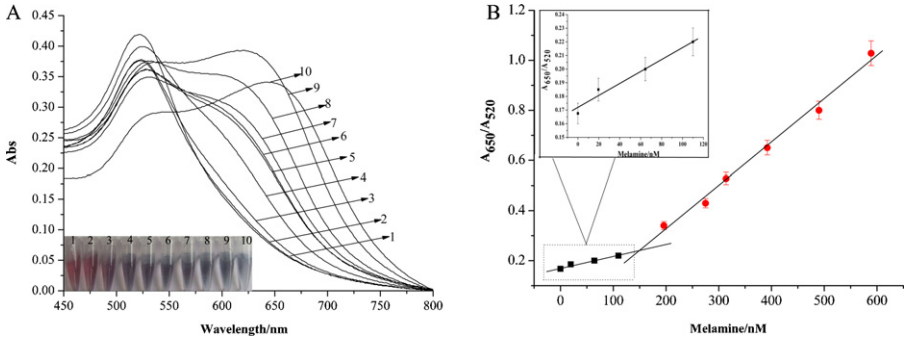


Fig. 5. (A) The extinction spectra of the MPS-stabilized GNPs formed upon treatment with different concentrations of melamine in pH 7.0 buffer. (from left to right: 1–10. The final concentrations of melamine are 0, 19.6, 98.0, 196.0, 235.0, 275.0, 314.0, 392.0, 490.0, and 589.0 nM, respectively). The insert are the corresponding photographs. (B) The linear relationship between the extinction ratio with the concentration of melamine, respectively.

GNPs (without MPS) for melamine detection had been did (see supporting information). Fig. S3 showed that a significant color change occurred between 185 and 350 nM for GNPs with MPS whereas a color change occurred between 270 and 350 nM for GNPs without MPS. It displayed that the MPS modified GNPs was sensitive to melamine. This is because that the hydrogen bonding between the sulfo groups of MPS and the amine groups of melamine is stronger than that between the carboxyl groups of sodium citrate and the amine groups. Moreover the stability of the modified GNPs has been enhanced.

3.6. The detection of melamine in real samples

In order to demonstrate whether the MPS-stabilized GNPs can be used for the direct detection of melamine in milk samples and infant formula samples, different concentration of melamine were doped into the real samples, and then the samples were extracted according to the procedure described in Section 2.5. Finally, the UV–visible absorption spectra of GNPs with the spiked samples were obtained and the concentration of melamine was quantified based on the absorption ratio (A_{650}/A_{520}) (Fig. 6 and Table 1). As shown in Fig. 6, the intensity of the characteristic plasma resonance peak at 520 nm of the individual functional GNPs became weaker and appeared red-shifted upon increasing the spiked concentration of melamine. At last, a new resonance-absorption peak appeared at about 650 nm, clearly indicating the aggregation of GNPs. When the concentration of melamine was 300 nM, the color of the GNPs solution changed from wine-red to blue within 5 min, suggesting that the proposed method could be used to detect as low as 300 nM of melamine in milk by naked eye observation. Analytical results in Table 1 showed that the recoveries vary from 98.0% to 104.5% in the spiked melamine milk samples with the variation coefficient of 1.6–3.7%, and the percentage recovery of melamine in powder samples ranged from 93.6% to 101.6%. Due to a higher content of protein, fat, mineral salts and carbohydrate in infant formula than liquid milk, it exhibited lower detection sensitivity in infant formula. Although the sensitivity of our method was lower than that of liquid chromatography–tandem mass spectrometry [4], extractive electrospray ionization mass spectrometry [5], our method still reveals obvious advantage such as without complicated preconcentration and expensive apparatus, short analysis time and low cost etc.

As mentioned above, the safety limit of melamine in infant formula is legally regulated at 1 ppm, by Chinese government. Therefore, the proposed method was able to be utilized for detection of melamine in milk product with naked eyes observation within 30 min and would be effective in the prevention of melamine in remote rural regions.

4. Conclusion

In summary, a simple, rapid, selective and cost-effective colorimetric assay using MPS modified GNPs to detect melamine was developed. Due to the multiple strong hydrogen-binding sites to the surface of modified GNPs, melamine can directly induce the aggregation of the GNPs as a molecular linker, resulting in an obvious color change from wine-red to blue. The modified-GNPs probe has a good sensitivity for detection of melamine, the absorption ratio linearly increased with the increasing concentration of melamine. With the help of UV-vis spectrometer, the detection limit of the proposed method is 8 nM, which is far lower than that of traditional methods. Thus this colorimetric assay is promising for on-site and real-time detecting melamine adulterant in milk products.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.06.017.

References

[1] D. Kimbrough, A. Jensen, J. Chem. Educ. 87 (2010) 496–499.
[2] H. Ji, X. Xu, Langmuir 26 (2010) 4620–4622.
[3] C. Brown, K. Jeong, R. Poppenga, B. Puschner, D. Miller, A. Ellis, K. Kang, S. Sum, A. Cistola, S. Brown, J. Vet. Diagn. Invest. 19 (2007) 525–531.
[4] M. Filigenzi, B. Puschner, L. Aston, R. Poppenga, J. Agric. Food Chem. 56 (2008) 7593–7599.
[5] H. Chen, A. Venter, R. Cooks, Chem. Commun. 2006 (2006) 2042–2044.
[6] L. Vaclavik, J. Rosmus, B. Popping, J. Hajslova, J. Chromatogr. A 1217 (2010) 4204–4211.
[7] S. Yang, J. Ding, J. Zheng, B. Hu, J. Li, H. Chen, Z. Zhou, X. Qiao, Anal. Chem. 81 (2009) 2426–2436.
[8] Q. Cao, H. Zhao, L. Zeng, J. Wang, R. Wang, X. Qiu, Y. He, Talanta 80 (2009) 484–488.
[9] C. Chang, S. Chu, W. Tseng, J. Chromatogr. A 1217 (2010) 7800–7806.
[10] J. Liu, Y. Lu, J. Am. Chem. Soc. 125 (2003) 6642–6643.
[11] A. Singh, D. Senapati, S. Wang, J. Griffin, A. Neely, P. Candice, K. Naylor, B. Varisli, J. Kalluri, P. Ray, ACS Nano 3 (2009) 1906–1912.
[12] X. Xu, J. Wang, K. Jiao, X. Yang, Biosens. Bioelectron. 24 (2009) 3153–3158.
[13] C. Medley, J. Smith, Z. Tang, Y. Wu, S. Bamrungsap, W. Tan, Anal. Chem. 80 (2008) 1067–1072.
[14] K. Ai, Y. Liu, L. Lu, J. Am. Chem. Soc. 131 (2009) 9496–9497.
[15] H. Kuang, W. Chen, W. Yan, L. Xu, Y. Zhu, L. Liu, H. Chu, C. Peng, L. Wang, N. Kotov, Biosens. Bioelectron. 26 (2011) 2032–2037.
[16] H. Chi, B. Liu, G. Guan, Z. Zhang, M. Han, Analyst 135 (2010) 1070–1075.
[17] Q. Cao, H. Zhao, Y. He, X. Li, L. Zeng, N. Ding, J. Wang, J. Yang, G. Wang, Biosens. Bioelectron. 25 (2010) 2680–2685.
[18] L. Guo, J. Zhong, J. Wu, F. Fu, G. Chen, X. Zheng, S. Lin, Talanta 82 (2010) 1654–1658.
[19] W. Haiss, N. Thanh, J. Aveyard, D. Fernig, Anal. Chem. 79 (2007) 4215–4221.
[20] J. Liu, Y. Lu, Nat. Protoc. 1 (2006) 246–252.
[21] L. Li, B. Li, D. Cheng, L. Mao, Food Chem. 122 (2010) 895–900.
[22] H. Huang, L. Li, G. Zhou, Z. Liu, Q. Ma, Y. Feng, G. Zeng, P. Tinnefeld, Z. He, Talanta (2010), doi:10.1016/j.talanta.2011.05.006.
[23] J. Liu, Y. Lu, J. Am. Chem. Soc. 126 (2004) 12298–12305.
[24] K. Sato, K. Hosokawa, M. Maeda, J. Am. Chem. Soc. 125 (2003) 8102–8103.