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Short Communication

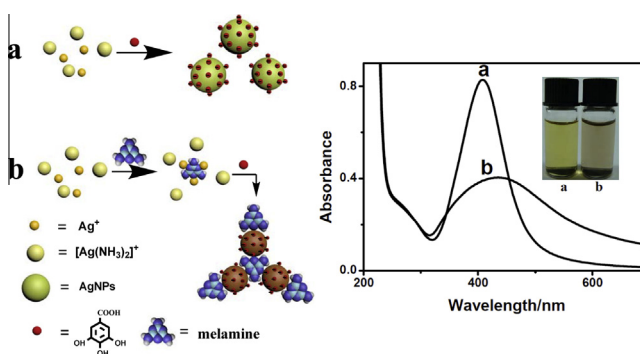
## One-step, room temperature, colorimetric melamine sensing using an in-situ formation of silver nanoparticles through modified Tollens process

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## HIGHLIGHTS

- We developed a one-step, RT, and colorimetric method for melamine detection.
- The assay is based on the absorption ratio change of the in-situ formed AgNPs.
- The formed AgNPs are characterized by TEM and UV–vis, respectively.
- The possible mechanism for the aggregation of the formed AgNPs was discussed.
- The method was applied successfully to the determination of melamine in milk samples.

## GRAPHICAL ABSTRACT



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## ABSTRACT

We have developed a rapid, sensitive, one-step, and selective colorimetric detection method for melamine (MEL) in milk powder based upon an in-situ formation of silver nanoparticles (AgNPs) through modified Tollens process at room temperature. The triazine ring N atoms of MEL molecule were strategically designed to complex the  $\text{Ag}^+$  through electron donor–acceptor interaction. During the AgNPs formation procedure, the MEL molecule, which has been covalently bonded with the  $\text{Ag}^+$  ions, was adsorbed to the surface of as-prepared AgNPs, resulting in the aggregation of the adjacent AgNPs with detectable decreases of absorption signal. The concentration of MEL can be determined with the naked eye or a UV–vis spectrometer at which the yellow-to-brown color change associated with aggregate enhancement takes place. This method enables rapid (less than 30 min) and sensitive (limit of detection, LOD, 10 nM) detection, and it was also able to discriminate MEL from sixteen other milk relevant coexisting compounds. This assay does not utilize organic cosolvents, enzymatic reactions, light-sensitive dye molecules, lengthy protocols, or sophisticated instrumentation thereby overcoming some of the limitations of conventional methods.

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## Introduction

Melamine (MEL; 1,3,5-triazine-2,4,6-triamine) is an important organic compound, which is mainly used in producing MEL–formaldehyde resins or as raw material in other chemical industry.

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Due to the high non-protein nitrogen content (66% by mass) of MEL, it is unethically used by milk manufacturers in adulterating milk to make it appear more protein-rich based on the Kjeldahl method for protein analysis in milk products. However, excessive ingestion of MEL can induce renal failure and even death in human beings and animals. A safety limit of MEL has been officially regulated (2.5 ppm in the USA and EU; 1 ppm for infant formula in China) [1]. Consequently, it is important to develop a reliable and highly sensitive method that can detect MEL in milk products on-site and real-time. Up to now, a variety of methods for detecting MEL, such as immunoassay [2–4], GC–MS [5,6], HPLC [7], SERS [8–10], chemiluminescence [11,12], fluorescence [13–16], Rayleigh Light Scattering [17,18], surface plasmon resonance [19], capillary electrophoresis [20] and electrochemical method [21] have been reported. Although each of these methods can detect MEL selectively with high sensitivity, most of them are costly, require sophisticated instrumentation and highly trained operators, and time-consuming, which makes rapid and on-site sensing of MEL difficult and limits the scope of their routine applications. On the contrary the colorimetric detection technology for MEL allows detection up to micro/submicromolar levels and that too without involving any expensive instrumentation [22–24]. Therefore, the development of colorimetric sensors for MEL has emerged as a mounting area of significant importance.

In the recent past, coinage metal (Cu, Ag, and Au) nanoparticles-based colorimetric sensors have drawn intense attention. Among them, gold nanoparticles (AuNPs) are the ideal color indicating probes for detection of MEL, which exhibit high extinction coefficients, strongly distance-dependent optical properties, and colors arising from AuNPs at nanomolar concentrations allow them to be easily monitored by the naked eye without the aid of any advanced instruments [25]. In this regard, a number of assays have been developed for MEL based on the label-free or labeled AuNPs [22,26–32]. Lu et al. designed a kind of thiol-functionalized cyanuric acid derivative (MTT)-stabilized AuNPs as a colorimetric sensor for detecting MEL in milk products based on the hydrogen-bonding interaction between MTT and MEL [22]. Additionally, silver nanoparticles (AgNPs) have been paid more attention owing to their plasmon absorbance superior to AuNPs and their easy readout (often with the naked eye) and high sensitivity [33–35].

However, in these strategies, firstly metal nanoparticles are required to be synthesized under demanding reaction conditions, and then they are modified and used for sensing of MEL. The process of metal nanoparticles synthesis and MEL detection are separate, so it needs two or three steps to realize the detection of MEL, which is complicated and make the rapid and on-site detection of MEL in raw milk samples difficult. In this regard, it is necessary to establish a simple, rapid and one-step method for sensing of MEL. Zhao's group explored the formation process of AuNPs as MEL colorimetric probes for the sensitive detection of MEL in real sample [36,37]. However, the low-cost and low-toxic determination has not been realized. Ma et al. recently reported that one-step visual detection of MEL in raw milk during the synthesis process of silver/dopamine nanoparticles [38], but the reaction reagents are expensive such as dopamine. Importantly, the manipulation process was laborious and time-consuming following their use. Furthermore, its signal induction mechanism has not been elucidated clearly.

In this paper, we have designed a new rapid and one-step method for direct determination of MEL through the well-known Ag-mirror reaction. The detection of MEL has been achieved within 30 min at room temperature through monitoring MEL induced aggregation of the forming AgNPs. That is, the MEL determination and the AgNPs formation were realized in one step. As well known, it is a usual phenomenon that nanoparticles adsorb the parent ions on its surface, after the AgNPs forming, the  $\text{Ag}^+$  would remain

adsorbed on the surface of as-prepared AgNPs. When MEL was added to the abovementioned solution, due to strong electron donor–acceptor interaction of the triazine ring N atoms of MEL with  $\text{Ag}^+$ , the MEL molecule bonded with the  $\text{Ag}^+$  ions would adsorb to the surface of as-prepared AgNPs, resulting in the aggregation of the adjacent AgNPs with the significant absorbance change (as shown in Scheme S1, Supporting Information). According to the Beer–Lambert law, there is a linear correlation between the MEL concentration and the absorbance of AgNPs. It can be used for rapidly and sensitively detecting MEL in milk sample in one step and the results were satisfactory. Additionally, for further improving the detection performance, the detailed mechanism underlying this special phenomenon was investigated.

## Experimental

### Chemicals and materials

All the reagents were of analytical reagent grade unless specified; distilled water was used throughout the experiments. All glassware used was cleaned in aqua regia (HCl:HNO<sub>3</sub>, 3:1), rinsed thoroughly with triply distilled water, and oven dried prior to use.

MEL was purchased from Sigma (St. Louis, USA). Gallic acid (GA) was commercially purchased from Tianjin Yongda Reagent Development Center (Tianjin, China). Silver nitrate was supplied by Tianjin Kermel Chemical Reagent (Tianjin, China). Liquid milk and milk powder were purchased from local supermarket.

### Instrumentation

The absorption spectra were recorded on a UV-1800 spectrophotometer (Shimadzu, Kyoto, Japan) with 1 cm path length cells. Fluorescence measurements were carried out at room temperature using a Hitachi 4600 spectrofluorimeter (Hitachi, Tokyo, Japan). An excitation wavelength ( $\lambda_{\text{ex}}$ ) of 240 nm was used, and fluorescence intensities were recorded at 368 nm. Photographs for color changes were taken with a Panasonic DMC-FX 30 digital camera. A vortex mixer, MVS-1 (Jinbeide, Beijing, China), was employed to blend the solution.

All electrochemical experiments were performed with a CHI 650D electrochemical workstation (Chenhua, Shanghai, China). A bare glassy carbon disk electrode (2 mm in diameter) and a platinum wire (1 mm in diameter) were used as the working and counter electrodes, respectively. The reference electrode was a mercurous sulfate electrode (MSE) and all of the potential values are reported with respect to this electrode unless otherwise stated. A glassy carbon electrode was polished carefully to a mirrorlike surface with 0.3–0.05  $\mu\text{m}$  of alumina aqueous slurry and then successively washed in an ultrasonic cleaner with water and ethanol.

The TEM sample was imaged using an H-7500 electron microscope (Hitachi, Japan) operating at 80 kV accelerating voltage at 200 k magnification. A typical sample for TEM was prepared by drying naturally a drop of solution containing silver nanoparticles at room temperature on a carbon-coated copper grid.

### Colorimetric detection of MEL

The  $[\text{Ag}(\text{NH}_3)_2]^+$  solution was prepared according to our previously published methods [39]: firstly, 95 mL of 1 mM AgNO<sub>3</sub> solutions were mixed with 3.8 mL of 10 mM NaOH, and then 3 mL of 0.25 M NH<sub>3</sub>·H<sub>2</sub>O solution were added into the mixture at room temperature. (*Caution! The solution is dangerous to form the explosive silver azide. It should be discarded quickly after using up.*)

Volumes of 2.5 mL of the as-prepared solution, and different concentrations of MEL were mixed in advance, and the mixture

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