Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Droplet detection: Simplification and Optimization of detecting conditions towards high sensitivity quantitative determination of melamine in milk without any pretreatment

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Figure S1 shows the SEM image of prepared AgNPs. The SEM image shows that the synthesized Ag NPs are almost spherical with a narrow size distribution. The average diameter of Ag NPs is about 50 nm.

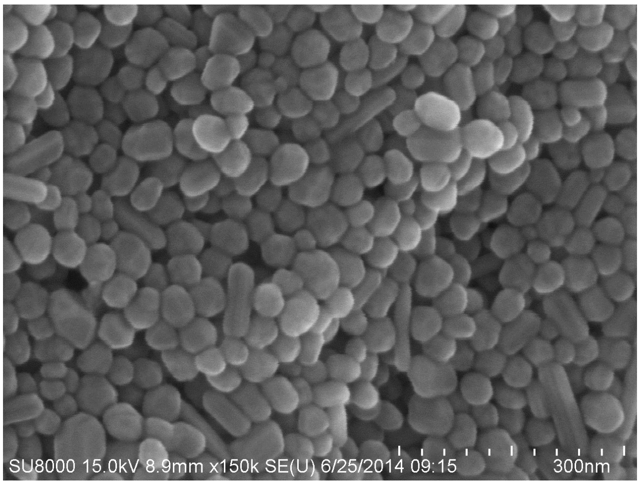

Figure S1. SEM image of colloidal silver nanoparticles.

The relationship between Raman intensity and sample height was investigated using melamine solution with different concentrations (10 ppb, 100 ppb and 1 ppm) as sample and the result was shown in Figure S2. The result shows that the optimal height value does not rely on the concentration of melamine solution, which is conducive to the quantitative detection of melamine in wide concentration range.

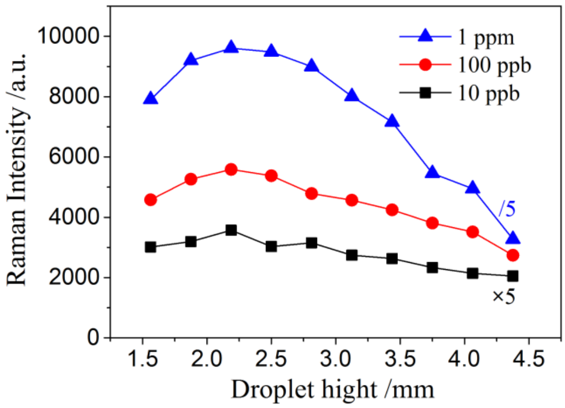

Figure S2. Raman intensity of melamine solution with different concentrations (10ppb~1ppm) under different droplet heights.

The volume radio of sample solution to Ag colloidal is critical to the SERS performance. Raman intensities at 701 cm^{-1} of melamine under different mixture ratio are shown in Figure S3. The result shows that a properly volume radio is very important for obtaining an optimized Raman enhancement. When the volume radio of sample solution to Ag colloidal is 4, the Raman intensity reaches the maximum value.

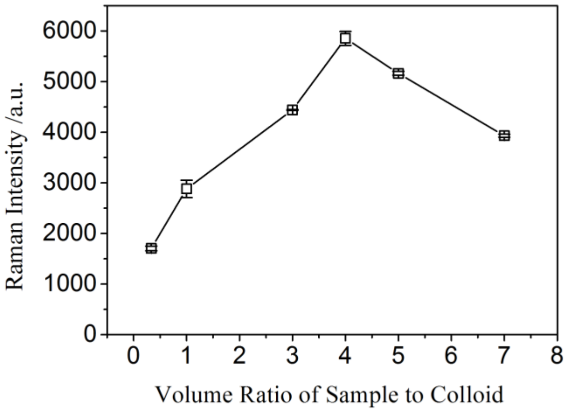

Figure S3. Effect of the volume ratio of sample to colloidal on SERS intensity of melamine solution.

It is well known that the SERS performance of metal colloidal strongly depend on the amount of Cl^- and the pH of detection solution.[1–3] However, previous study in the literature always change the volume of NaCl solution to investigate the effect of the amount of Cl^- on SERS enhancement. It is inevitably influenced by the change of solution volume. To avoid this,[4] only the concentrations of Cl^- or OH^- were changed in our experiments. Figure S4 shows the influence of the concentration of NaCl on SERS intensity of melamine solution. The optimal concentration of NaCl is 4 M for SERS measurement.

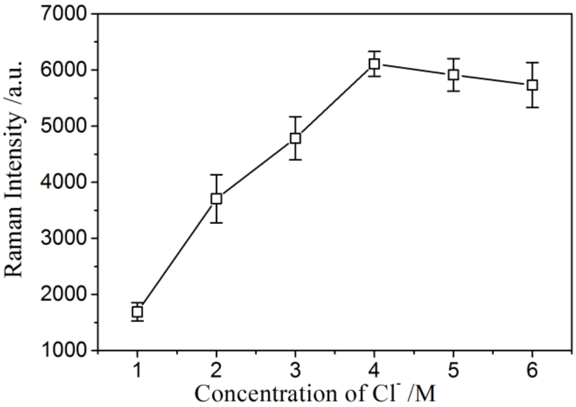

Figure S4. Effect of the concentration of NaCl on SERS intensity of melamine solution.

Figure S5 shows the influence of the concentration of NaOH on SERS intensity of melamine solution. The peak areas at 701 cm^{-1} increase with the increase of concentration of NaOH solution, and the increase of the peak intensity is not significant when the concentration of NaOH is larger than 1 M. In contrast to previous studies, both the concentration-dependent curves of Cl$^-$ or OH$^-$ have single peak for SERS measurements obtained from silver colloidal, we find in our study that once the concentrations of Cl$^-$ or OH$^-$ are exceed a certain threshold, the SERS enhancement would maintain at a steady value without obvious fluctuation.

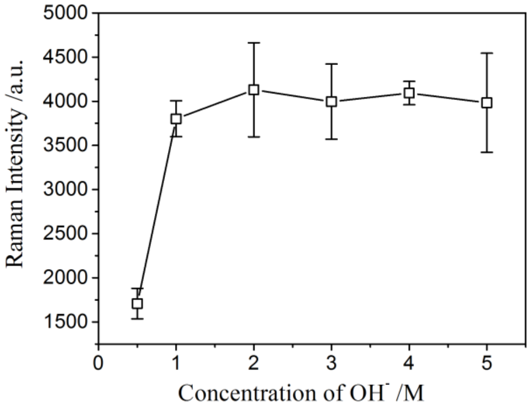

Figure S5. Effect of the concentration of NaOH on SERS intensity of melamine.

To evaluate the applicability of proposed method for detecting melamine in other kinds of milk, a characterization in the variation of the 701/929 intensity ratio for three types of milk (pasteurized milk, skimmed milk, sweet milk) has been conducted. The ingredient of pasteurized milk is raw milk; the ingredients of skimmed milk are raw milk, food flavors, food additives such as glycerin monostearate, glycerol distearates, sucrose fatty acid ester, microcrystalline cellulose, sodium carboxymethylcellulose, sodium tripolyphosphate and food flavors; the ingredients of sweet milk are raw milk, softened water, white sugar, food flavors, food additives such as monoglycerides, diacylglycerol, alginate, carrageenan, xanthan gum, and nisin. Table S1 presents nutrient reference values (NRV) of three kinds of milk.

Table S1. Nutrient reference values of three kinds of milk.

Nutrient content	Nutrient Reference Values (NRV)%		
	Pasteurized milk	Skimmed milk	Sweet milk
Energy	3	2	3
Protein	5	5	4
Fat	6	0	5
Carbohydrate	2	2	2
Sodium (Na)	3	3	3

SERS spectra of three kinds of milk were shown in Figure S6(a), it is worth noting that the absolute Raman intensity of skimmed milk is stronger than that of pasteurized milk and sweet milk. This is mainly because skimmed milk has little fat and thus has a minor hindering effect for SERS enhancement. I_{701}/I_{929} peak ratios of three kinds of blank milk were shown in Figure S6(b), the 701/929 intensity ratio for three types of milk are almost at the same level.

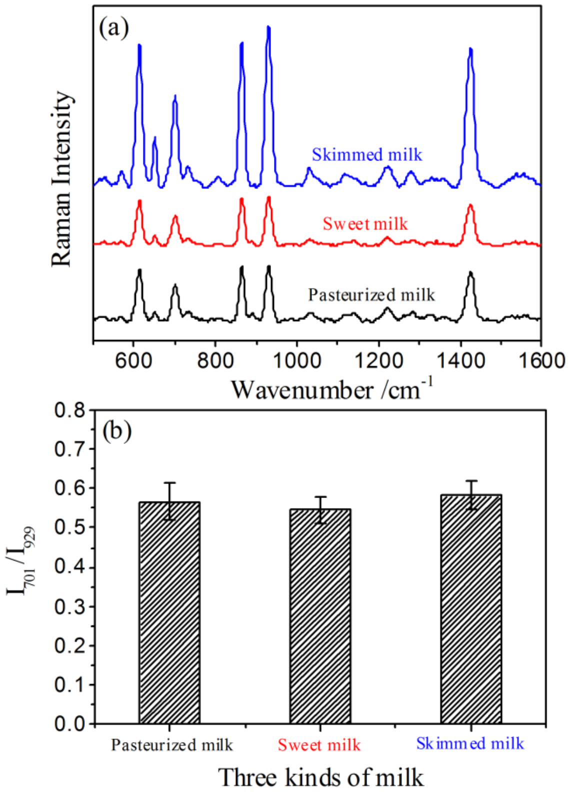

Figure S6. (a) SERS spectra of three kinds of blank milk sample; (b) I_{701}/I_{929} peak ratios of three kinds of blank milk.

Reference:

1. A. M. Michaels and L. Brus, *J. Phys. Chem. B*, 2000, **104**, 11965–11971.

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3. P. Cao, J. Yao, B. Ren, R. Gu, and Z. Tian, *J. Phys. Chem. B*, 2002, **106**, 7283–7285.

4. P. Ma, F. Liang, Y. Sun, Y. Jin, Y. Chen, X. Wang, H. Zhang, D. Gao, and D. Song, *Microchim. Acta*, 2013, **180**, 1173–1180.