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Theory and Experiment for Quantitative Detection of Melamine by Surface-Enhanced Raman Spectroscopy

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Abstract

Melamine is harmful to human health. Excessive use will seriously endanger human health. Therefore, it is necessary to detect the content of melamine in food. In this study, melamine was taken as the research object, and the Raman peaks of melamine were analyzed by density functional theory and compared with the actual samples. After that, melamine was detected by surface-enhanced Raman spectroscopy using gold nanoparticles and silver nanoparticles as substrates respectively. The experimental results showed that the Raman signal of silver nanoparticles as substrates was better than that of gold nanoparticles, Therefore, The method has the advantages of simple operation and short process time, and provides a method for detecting melamine.

Keywords: melamine; gold nanoparticles; silver nanoparticles; surface-enhanced Raman spectroscopy; density functional theory;

1. INTRODUCTION

Melamine is a triazine nitrogen-containing heterocyclic organic compound, which is a post-processing product of urea[1].It is a white monoclinic crystal. Melamine is difficult to be metabolized and excreted in the human body, which belongs to inert metabolism[2],Due to its higher nitrogen content, it reaches 66.7%[3],Therefore, some unscrupulous enterprises illegally add melamine to dairy products to increase the nitrogen content to pass the Kjeldahl method. Poor, long-term excessive intake of melamine can seriously damage kidney function, leading to renal failure, which may be life-threatening in severe cases[4],Therefore, it is necessary to find a method to detect melamine in dairy products.

Up to now, the commonly used detection method is Gas Chromatography/Mass Spectrometry[5],High Performan ce Liquid Chromatography/Mass Spectrometry[6],Enzyme-linked immunosorbent assay[7],capillary electrophoresis[8], Chemiluminescence method[9],and localized surface plasmon resonance[10],etc.Although these methods have high accuracy for melamine, these methods have high detection cost, complicated detection process, and require prof essional researchers to operate. Therefore, this paper establishes a simple, fast and accurate trace detection meth od.

Raman spectroscopy is a molecular vibrational spectrum based on the Raman scattering effect, and the molecul ar structure can be analyzed based on the spectral information[11]. Because the signal is weak, it has not been widely used. However, when the sample is in close contact with the rough surfaces of precious metals gold an d silver, the Raman signal of the sample molecule is immediately enhanced, and can be enhanced to 5 to 6 o rders of magnitude[12]. This phenomenon is called for surface-enhanced Raman spectroscopy (SERS).SERS detec tion requires a small amount of samples, and can perform non-destructive testing on samples, and can perform qualitative and quantitative analysis and calculation of substances.

In this study, a fast and sensitive biosensor was constructed based on the melamine quantitative detection biose nsor based on surface-enhanced Raman spectroscopy. Through using gold nanoparticles and silver nanoparticles as a substrate, increase the SERS signal of melamine.By comparing the SERS signal intensities of the two sub

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strates, it is shown that the silver nanoparticles have a stronger SERS signal intensity than the melamine increa sed when the gold nanoparticles are used as the substrate.

2. Materials and Test Methods

2.1Materials and Instruments

Tetrachloroauric acid tetrahydrate ($HAuCl_4•4H_2O$), silver nitrate ($AgNO_3$), L-ascorbic acid (AA), hydroxylamine hydrochloride ($HONH_2HCl$), sodium hydroxide (NaOH) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). The configuration of the melamine solution in the test should be noted. Take 0.126g of melamine powder from the analytical balance and completely melt it with 0.5mL of absolute ethanol, add water to make up to 10mL as the mother solution, and seal and refrigerate. The concentration of the melamine solution after constant volume was 12.6 $mg·mL^{-1}$, and the melamine solution used in the test was diluted with water to the use concentration with mother liquor. Ultrapure water is used in practically all solution preparations. The glassware used in this study was cleaned with aqua regia [$HCl:HNO_3$=3:1(v/v)], and rinsed with ultrapure water several times before the experiment.

2.2Synthesis of Gold Nanoparticles

Place the conical beaker containing 100mL, 0.01% chloroauric acid solution on the magnetic heating stirrer, stir gently, set the heating temperature to 120°C, after the solution boils, adjust the stirrer to vigorous stirring mode, and at the same time quickly Add 1 mL of 1% trisodium citrate solution. After 10s, the solution turns gray, black, blue, and finally turns purple. After the solution turns purple-red, continue to heat and stir for ten minutes, after that, stop heating and continue stirring until the temperature drops to room temperature, stop stirring, and save the solution to the refrigerator.

2.3Synthesis of Silver Nanoparticles

Dissolve 0.0168g of silver nitrate in a conical beaker of 90ml of deionized water, place the beaker on a magnetic stirrer, accelerate stirring, then dissolve 0.0208g of hydroxylamine hydrochloride in 5mL of water as solution 1, and then take 0.018g of hydroxide Sodium is dissolved in 4.5mL of water as solution 2. Mix solutions 1 and 2 well and pour them into the silver nitrate solution quickly. The color of the solution turns yellow-green and finally turns gray. After continuous stirring for ten minutes, put it in the refrigerator for further use.

3. Density functional theory of melamine

3.1Theoretical calculation method

Based on the B3LYP/ 6-31g (d, p) group, the molecular model of melamine was constructed by using the software Gaussion09 and Gauss View5.0 using DFT method, and the structure optimization and calculation were carried out, and the Raman spectra of melamine were obtained.The theoretical spectrum of melamine is compared with the actual Raman spectrum of melamine powder.

3.2Molecular model of melamine

The melamine sample used in the experiment was purchased from Shenggong Bioengineering (Shanghai) Co., Ltd., the molecular formula is $C_3H_6N_6$, and the molecular,The amount is 126.12 $g·mol^{-1}$. The molecular structure of melamine is shown in Figure 1.

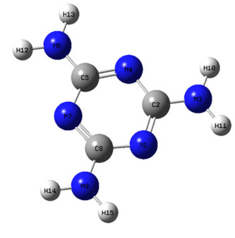

Figure 1 Molecular structure of melamine

3.3Comparison of theoretical Raman peaks of melamine and Raman peaks of melamine powder

The comparison of the simulated spectra of melamine powder and a single molecule measured in the experiment is shown in Figure 2. The 500-1000cm^{-1} area containing rich Raman information was intercepted. It can be seen that the peak position and relative intensity of the Raman spectrum are good match.There is a strong peak at 688cm^{-1} in the spectrum, which is attributed to the ring breathing vibration of the ring composed of C-N. There are also several more obvious peaks of moderate intensity, respectively at 984cm^{-1}, this vibration mode is in-plane vibration, and the moderate intensity peak at 984cm^{-1} is attributed to the C-N-C scissor vibration in the ring.In addition, there are several peaks with weaker intensity values, such as 584cm^{-1}. 584cm^{-1} is assigned to the out-of-plane bending vibration of N-H. The calculated Raman peak is at 688cm^{-1}, and the experimental Raman peak is at 672cm^{-1}.The difference is due to the fact that only the individual molecule of melamine is considered in the calculation process, ignoring the results of the interaction between the molecules. Therefore, there are several gaps in Raman shifts.Overall The calculated Raman frequency shift is in good agreement with the experimental Raman frequency shift.

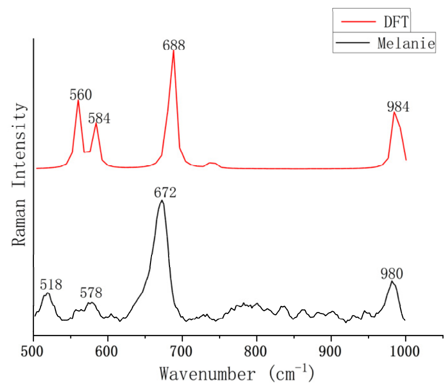

Figure 2 DFT peak and powder Raman peak of melamine

4. Experimental results

Under the condition of 120℃, 0.5mL, 1% trisodium citrate solution was used to reduce 50mL, 0.01% chloroauric acid solution to prepare gold nanoparticle sol with particle size of 60nm, and silver nanoparticles with particle size of 50nm prepared by hydroxylamine hydrochloride method For the nanoparticle sol, 10μL of melamine solution of 1 mg·mL^{-1} was mixed with 60 nm gold sol, 10μL of the mixture was dropped on a clean silicon wafer, dried at room temperature, and its SERS spectrum was detected; the results are shown in Figure 3. When gold nanoparticles are used as the substrate, the fluorescence is strong and the Raman signal is weak. When silver nanoparticles are used as the substrate, the signal of the Raman peak is significantly enhanced. It shows that silver nanoparticles have better SERS signal than gold nanoparticles as substrates.

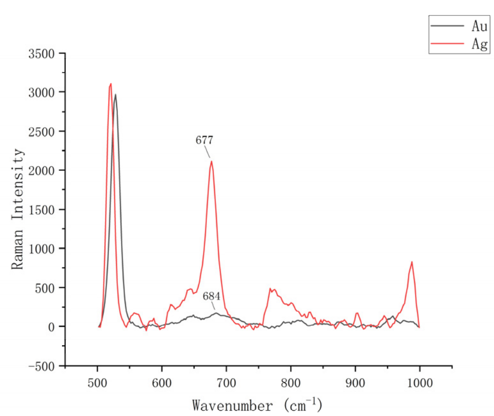

Figure 3 Silver nanoparticles and gold nanoparticles as substrates

5. Conclusion

Based on density functional theory, the structure of melamine molecule was optimized, and a stable molecular structure was obtained. The Raman spectrum of melamine was calculated, and the Raman spectrum of melamine was verified by experiments. The results were compared with peaks and assigned vibrations. It shows that the theoretical calculation and experimental results are in good agreement. Using gold nanoparticles and silver nanoparticles as reinforcement substrates, the results show that the enhancement effect of silver nanoparticles is significantly better than that of gold nanoparticles.

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