Hindawi
Journal of Spectroscopy
Volume 2020, Article ID 4212787, 7 pages
https://doi.org/10.1155/2020/4212787

*Research Article*

# Using PDMS Plasma Cavity SERS Substrate for the Detection of Aspartame

**Lvming Chen,[1,2] Chaoqun Ma,[1,2] Lei Li,[1,2] Chun Zhu,[1,2] Jiao Gu,[1,2] Hui Gao,[1,2] Zhuowei Zhu,[1,2] Chenxu Du,[1,2] Tingyu Wang,[1,2] Jianwen Xu,[1,2] and Guoqing Chen [1,2]**

[1]*School of Science, Jiangnan University, Wuxi 241000, China*
[2]*Jiangsu Provincial Research Center of Light Industrial Optoelectronic Engineering and Technology, Wuxi 214000, China*

Correspondence should be addressed to Guoqing Chen; jncgq@jiangnan.edu.cn

Received 4 July 2019; Revised 16 October 2019; Accepted 25 October 2019; Published 20 January 2020

Academic Editor: Alessandra Durazzo



Surface-enhanced Raman spectroscopy (SERS) was used to simply and sensitively detect the artificial sweetener aspartame added to purified water. In this paper, a cavity formed spontaneously by silver ion droplets, and liquid polydimethylsiloxane (PDMS) is used as an SERS substrate to integrate plasma nanoparticles into optical devices. Firstly, Raman spectral characteristics of aspartame powder and aspartame aqueous solution were analyzed. Secondly, the effect of aspartame content in purified water on SERS intensity was investigated by using the prepared PDMS plasma cavity to test the samples. Thirdly, the SERS calibration curve was established by using the characteristic peak intensity of aspartame, and a good linearity relationship between the concentration of aspartame added in purified water and the characteristic peak intensity of 1588(±5) cm-1 was obtained. The linear regression equation and correlation coefficient ($r$) were $y = 11412.73874\ x + 107.36722$ and 0.99593, respectively. The average recovery of aspartame in purified water was 101–106%, and the relative standard deviation (RSD) was 0.121–0.496%. The experimental results show that using this method can detect aspartame in purified water correctly, which is expected to be used in the identification and detection of sweeteners in purified water.

## 1. Introduction

Aspartame (N-l-$\alpha$-aspartyl-l-phenylalanine methyl ester) is a low-calorie artificial sweetener, 150–200 times sweeter than sugar approximately [1]. It is widely used in many foods and beverages, especially soft drinks [2]. Aspartame is currently permitted as a food and beverage sweetener for use in more than 100 countries [3]. The acceptable limit of aspartame, which a person can safely consume every day over a lifetime without risk, is estimated to be 50 mg/kg of body weight; soft drinks contain aspartame at the maximum permitted level of 600 mg/L [4, 5]. Therefore, in order to improve the taste of pure water, some manufacturers will add a small amount of aspartame in their products. Foods supplemented with aspartame should be marked as "aspartame (containing phenylalanine)" because aspartame contains phenylalanine, and patients with phenylketonuria (PKU) cannot metabolize amphetamine, which may endanger intelligence and nerves and also potentially threaten pregnant women. In addition, aspartame will cause its intolerance in patients having symptoms such as headache, convulsions, nausea, and allergy [6]. So, some methods are needed to detect the content of aspartame added to food.

There are various methods to detect and quantify aspartame in food products, such as high-pressure liquid chromatography [7], capillary electrophoresis [8, 9], voltammetric and amperometric methods [10, 11], enzymatic systems [12, 13], and spectrophotometry [14, 15]. However, most of these methods are time-consuming or highly expensive; some of them require intensive sample pretreatment, and the experimental process is more complicated.

Surface-enhanced Raman spectroscopy (SERS) has become a mature and powerful analytical technique because it combines the fingerprint recognition ability of Raman spectroscopy and the plasma-enhanced sensitivity, making it effective in ultrasensitive detection. Wen Yang et al.

fabricated the Gr-AgNPs-C.w. SERS substrate with good flexibility and repeatability [16]. Lu et al. designed the AuNPs/WS2@AuNPs hybrid SERS substrate [17, 18].

Polydimethylsiloxane (PDMS) is widely used in biological detection, optical devices, and other fields because of its stable chemical properties, nontoxicity, excellent mechanical flexibility, and low cost. At the same time, PDMS is an important SERS substrate material. Its good plasticity and flexibility make SERS sensors easy to integrate into surfaces of different shapes and sizes [19, 20]. Singh et al. [21] fabricated PDMS silver nanorod arrays as active 3D SERS substrates. The disposable and flexible substrates studied by Singh et al. can withstand up to 30% tensile strain [22]. At the same time, PDMS is also suitable for the preparation of large area flexible active substrates, including the transfer printing technology [19] and shadow mask method [23].

In this paper, a plasma cavity prepared by silver nitrate and PDMS was reported. The plasma cavity combined with SERS was used to detect the content of aspartame added in purified water. Firstly, the theoretical Raman spectra of aspartame molecule were calculated, and the Raman spectra and SERS spectra of aspartame and purified water and purified water added with aspartame were analyzed. Secondly, the effect of aspartame addition on SERS intensity (characteristic peak height) in purified water was studied. Finally, the linear regression equation between the concentration of aspartame and $1588 \pm 5\ cm^{-1}$ SERS intensity in purified water was established.

## 2. Materials and Methods

*2.1. Materials and Reagents.* The Sylgard-184 polydimethylsiloxane elastomer base and the Sylgard 184 polydimethylsiloxane elastomer curing agent were bought from Dow Corning Corporation (Michigan, USA). And, aspartame was purchased from Dr. Ehrenstorfer Company, Germany, with a purity of 97.7%. The later operation was not purified and used directly. Silver nitrate is provided by Sinopharm Chemical Reagent Co., Ltd. Purified water, which is Yibao brand pure drinking water, was purchased from supermarkets.

*2.2. Instruments.* The experimental equipment is Renishaw in-Via series of confocal Raman spectrometers. The excitation source is 532 nm frequency-doubled Nd:YAG laser.

*2.3. Experimental Methods*

*2.3.1. Preparation of Plasma Cavity Based on PDMS.* substrate was prepared according to Inhee Choi's [24] method and optimized (as shown in Figure 1(a)). Firstly, the elastomer base and curing agent of Sylgard-184 were weighed and mixed in a beaker according to the mass ratio of 10 : 1. The mixture is stirred vigorously in a beaker for about 20 minutes, then shaken by ultrasound for 10 minutes, and then placed in a vacuum to remove bubbles in the mixture. Thereafter, the prepared PDMS was cast and fixed in a Petri dish (35 mm in diameter and 17 mm in height).

Then, silver nitrate solution with a concentration of 50 $\mu$g/mL was prepared, and 100 $\mu$L solution was absorbed by a pipette gun and slowly dripped onto the surface of the prepared liquid PDMS. As the surface tension of water is higher than that of liquid PDMS (about 72.8 mN/m, about 22–25 mN/m), silver nitrate solution forms a silver nitrate solution sphere at the moment of dropping into liquid PDMS. At the same time, silver ions diffuse into the liquid PDMS and react with the residual Si-H group, and silver ions gradually reduce to silver nanoparticles [25]. Finally, the Petri dish was cured at 23°C [24] for 72 hours, and silver ions gradually accumulated on the surface of the cavity with the solidification process of PDMS and formed a plasma cavity (as shown in Figure 1(b)).

For the concentration of silver nitrate solution, we did a comparative experiment. We prepared 500 $\mu$g/L, 50 $\mu$g/L, 5 $\mu$g/L, 0.5 $\mu$g/L, and 0.05 $\mu$g/L of silver nitrate solution. Because of the different density, the position of the cavity formed by silver nitrate in PDMS is different (as shown in Figure 1(c)). When the concentration is too high, the formed cavity sinks to the bottom of PDMS, and there is no opening above, which is not easy to use. Therefore, we chose to use 50 $\mu$g/L of silver nitrate to prepare the PDMS cavity.

*2.3.2. Sample Testing.* After curing, rinse with deionized water and blow-dry with nitrogen three times. To avoid oxidation of nanosilver and affecting the SERS effect, the cavity should not be dried for a long time. In the measurement, the pure water solution with aspartame was injected into the cavity for 3 minutes, then rinsed, and dried. The SERS spectrum of aspartame adsorbed by the plasma cavity was detected by an in-Via confocal Raman spectrometer. The parameters of the confocal Raman spectrometer are as follows: laser source, 532 nm; power, 12.5 mw; objective lens, 50x long focus; and exposure time, 20 s. The beam is focused at the bottom of the cavity through the 50x objective lens of the microscope and is splitted into the CCD from the filter through the diffraction grating of 1800 lines per millimeter.

*2.4. Computational Detail.* The geometric optimization and normal mode calculations of aspartame were performed with the Gaussian09 program. The hybrid B3LYP method was performed with the 6-31++G (d, p) basis set. The stable theoretical structure of aspartame is presented in Figure 2.

## 3. Results and Discussion

*3.1. Raman Spectra of Aspartame Molecule.* Comparison of the computational and experimental spectra of aspartame in aqueous solution is shown in Figure 3. It can be seen that the experimental results are close to the theoretical results.

*3.2. SERS Spectral Characteristics of Samples.* The spectrum of SERS of PDMS plasma cavity, purified water, saturated solution of aspartame (10000 mg/L at room temperature,

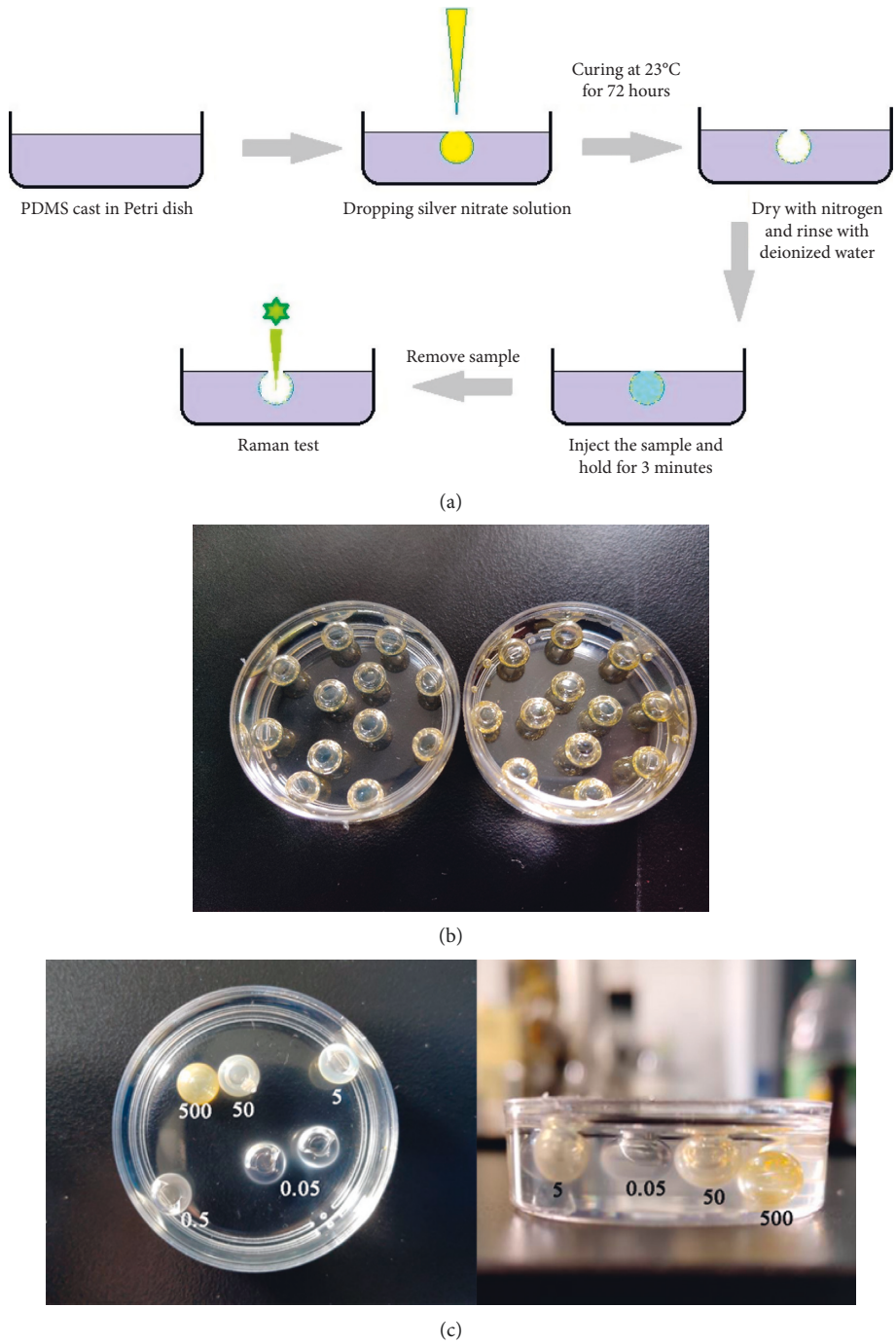


Figure 1: (a) Process of base fabrication; (b) PDMS plasma cavity is fabricated; (c) a schematic diagram of the position of the cavity formed by different concentrations of silver nitrate.

taken as a supernatant), aspartame powder, and aspartame aqueous solution are shown in Figure 4, and the main characteristic peaks of aspartame can be clearly observed. And, 958, 1005, 1032, 1207, 1588, and 1604 $cm^{-1}$ can still be observed in the saturated solution of aspartame. Among them, the characteristic peaks at 1588(±5) and 1604(±5) $cm^{-1}$ can be enhanced by the PDMS plasma cavity. According to the molecular structure of aspartame, the characteristic peaks at 1588 $cm^{-1}$ are attributed to NH, CH, $CH_2$ bending vibration, and NH in-plane bending vibration; the characteristic peaks at 1605 $cm^{-1}$ are attributed to C=C stretching vibration, $COO^-$ asymmetric stretching vibration, and $NH_3^+$ bending vibration. Therefore, the SERS characteristic peak at 1588(±5) $cm^{-1}$ can be selected as the SERS characteristic peak for the detection of aspartame in purified water. In conclusion, it is feasible to detect aspartame added in purified water by SERS.

*3.3. Effect of Adsorption Time on SERS Intensity.* The purified water solution of aspartame with a concentration of 0.3 mg/L

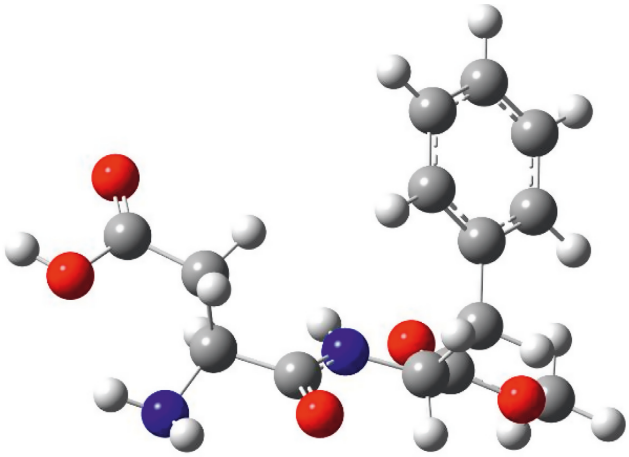

Figure 2: Theoretical structure of aspartame.

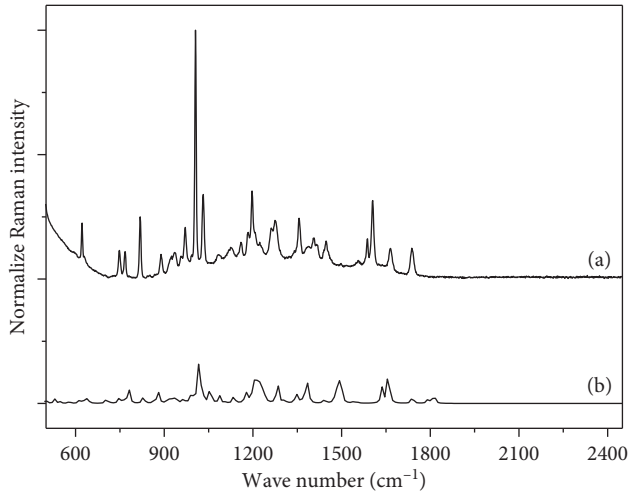


Figure 3: Comparing the Raman spectrum calculated by the aspartame gauss with the experimental data. (a) Experimental result and (b) computational results. Aspartame powder: laser wavelength, 532 nm; power, 1.25 mW; objective lens, 50x.

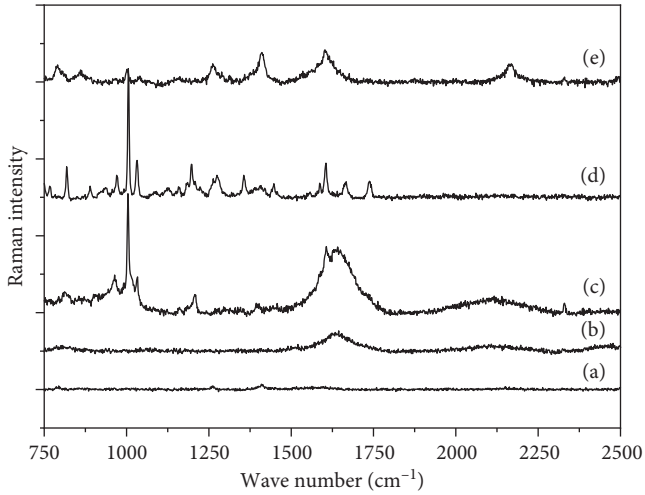


Figure 4: Raman spectra of (a) PDMS plasma cavity, (b) purified water, (c) aspartame saturated solution, (d) aspartame powder, and (e) SERS spectra of aspartame aqueous solution with a concentration of 0.3 mg/L.

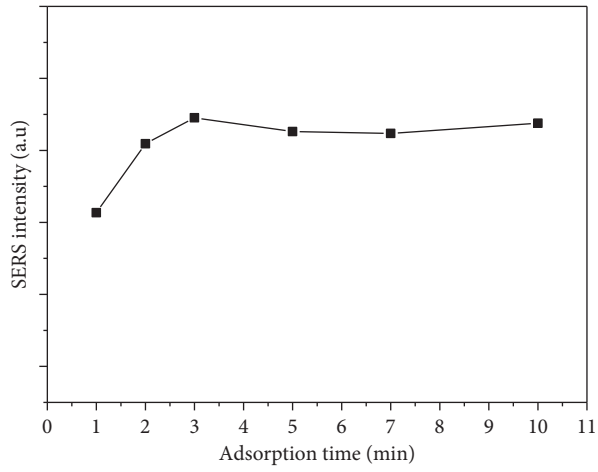


Figure 5: The effect of adsorption time on SERS intensity.

was tested by the PDMS plasma cavity. The adsorption time of the tested sample in the PDMS plasma cavity was set to 1 min, 3 min, 5 min, 7 min, 10 min, and 15 min, respectively. The relationship between characteristic peak intensity and adsorption time is shown in Figure 5. It can be seen that the intensity of the characteristic peak gradually increases with adsorption time and tends to be stable at 3 minutes. It shows that the SERS enhancement effect produced by the combination of the nanosilver substrate on the surface of the PDMS plasma cavity with aspartame in pure water is the best when the adsorption time is 3 minutes, so the optimal adsorption time is 3 minutes.

*3.4. SERS Calibration Curve and Predicted Results.* The stability of Raman light source is tested by using the corrected silicon substrate of a Raman spectrometer. The laser power is 1.25 mW, and the exposure time is 1 s. The relationship between the measured intensity and time is shown in Figure 6. From the results, it can be seen that the laser has good stability and can be quantified by using SERS characteristic peak intensity.

Figure 7 shows the SERS curve of water solution with different concentrations of aspartame added by the PDMS plasma cavity. It can be seen that the characteristic peak intensity of SERS increases with the increasing concentration of aspartame added in purified water.

Therefore, the relationship between the concentration of aspartame in aqueous solution and the characteristic peak intensity at 1588(±5) cm$^{-1}$ was established, as shown in Figure 8. It can be seen that the intensity of the characteristic peak first increases with the increase of the concentration, then decreases, and tends to be stable after reaching a certain concentration. The reason is that when the concentration of

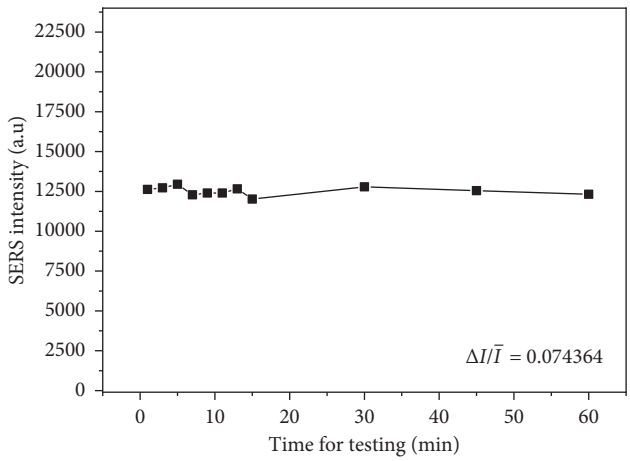


Figure 6: Stability of light source.

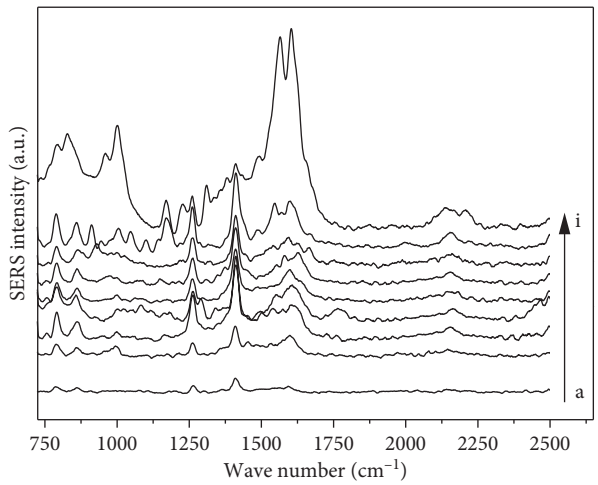


Figure 7: SERS measurement of aspartame solution by the plasma cavity. Lines a to i denote concentrations of 0, 0.004, 0.006, 0.008, 0.01, 0.02, 0.2, 2, and 20 mg/L, respectively.

aspartame in purified water reaches a certain value, the nanosilver particles in PDMS plasma chamber cannot continue to adsorb more aspartame molecules, and some of them fall off.

In the subsequent study, the concentration range of 0.005–0.05 mg/L was tested, samples at each concentration were tested three times, and the relationship curve between the concentration of aspartame aqueous solution and the intensity of characteristic peak was established. As shown in Figure 9, it was found that the relationship between concentration and intensity in this area was linear, and the linear regression equation was $y = 11412.73874x + 107.36722$.

The concentration of aspartame in purified water was predicted by using the SERS calibration curve obtained above, and the predicted result is shown in Table 1. The average recovery of aspartame in purified water is 101–106%, and the relative standard deviation (RSD) is 0.121~0.496%, which shows that the method has a good prediction effect and satisfactory reproducibility. The detection limit of aspartame in purified water can reach

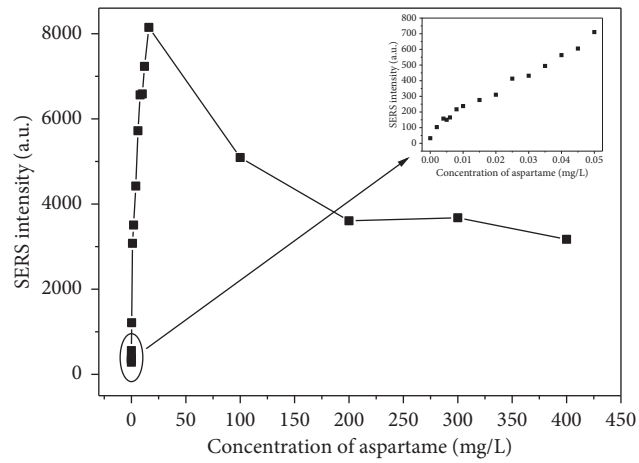


Figure 8: The relationship between the concentration of aspartame and the intensity of SERS characteristic peak.

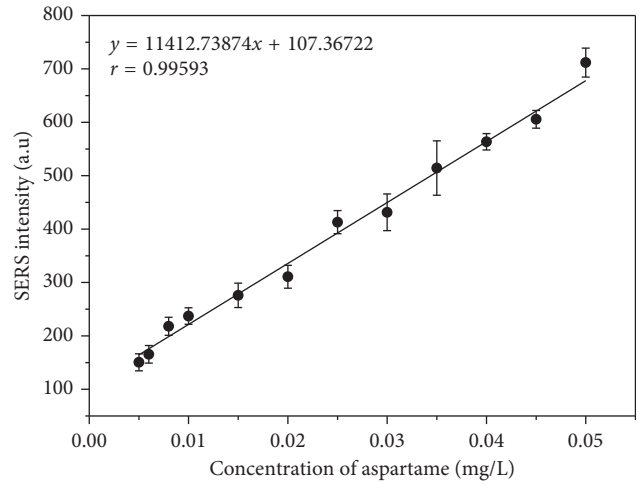


Figure 9: Curve of relationship between concentration (0.005–0.05 mg/L) of aspartame aqueous solution and characteristic peak intensity. The error bars represent the standard deviation of measurements for 12 concentrations in three separate sample runs ($n = 36$).

0.002 mg/L. The experimental results show that the method adopted in this paper is simpler and faster than other conventional detection methods, and it can provide important technical support for the detection of aspartame in purified water.

## 4. Conclusion

A simple and sensitive method using the PDMS plasma cavity as a SERS enhancement substrate was developed for the detection of aspartame added in purified water. The characteristic peaks of aspartame were calculated and measured. The effects of sample addition and adsorption time on the intensity of the characteristic peaks of aspartame were analyzed. A good linearity relationship between the concentration of aspartame added in purified water and peak intensity $I_{1588}$ at 1588(±5) cm$^{-1}$ was obtained. The linear

Table 1: Predicted results of aspartame in purified water ($n = 3$).

| Spiked (mg/L) | Detected (mg/L) | Recovery (%) | Relative standard deviation (%) |
|---|---|---|---|
| 0.0125 | 0.01277 | 102.16 | 0.121 |
| 0.0275 | 0.0292 | 106.18 | 0.496 |
| 0.0425 | 0.0428 | 100.74 | 0.372 |

regression equation and correlation coefficient (r) were $y = 11412.73874x + 107.36722$ and 0.99593, respectively. The pretreatment method proposed in this paper is simple and rapid. The detection limit of aspartame added in purified water can reach 0.002 mg/L. Therefore, the method proposed in this paper was a good detection scheme for rapid detection of aspartame added in purified water.

## Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

## Acknowledgments

This work was supported by the National Natural Science Foundation of China (61378037), National First-class Discipline Program of Food Science and Technology (JUFSTR20180302), and National Key Research and Development Program of China (2018YFC1604204 and 2018YFD0400402).

## References

[1] S.-F. Chou, "Amperometric biosensor for the determination of the artificial sweetener aspartame with an immobilized bienzyme system," *The Analyst*, vol. 121, no. 1, pp. 71–73, 1996.

[2] W. S. Tsang, M. A. Clarke, and F. W. Parrish, "Determination of aspartame and its breakdown products in soft drinks by reverse-phase chromatography with UV detection," *Journal of Agricultural and Food Chemistry*, vol. 33, no. 4, pp. 734–738, 1985.

[3] Y. Zhu, Y. Guo, M. Ye, and F. S. James, "Separation and simultaneous determination of four artificial sweeteners in food and beverages by ion chromatography," *Journal of Chromatography A*, vol. 1085, no. 1, pp. 143–146, 2005.

[4] M. Kroger, K. Meister, and R. Kava, "Low-calorie sweeteners and other sugar substitutes: a review of the safety issues," *Comprehensive Reviews in Food Science and Food Safety*, vol. 5, no. 2, pp. 35–47, 2006.

[5] EFSA Panel on Food Additives and Nutrient Sources Added to Food (ANS), "EFSA scientific opinion on the re-evaluation of aspartame (E 951) as a food additive," *EFSA Jorunal*, vol. 11, no. 12, p. 263, 2013.

[6] B. A. Magnuson, G. A. Burdock, J. Doull et al., "Aspartame: a safety evaluation based on current use levels, regulations, and toxicological and epidemiological studies," *Critical Reviews in Toxicology*, vol. 37, no. 8, pp. 629–727, 2007.

[7] M. Grembecka, P. Baran, A. Błażewicz, Z. Fijałek, and P. Szefer, "Simultaneous determination of aspartame, acesulfame-K, saccharin, citric acid and sodium benzoate in various food products using HPLC-CAD-UV/DAD," *European Food Research and Technology*, vol. 238, no. 3, pp. 357–365, 2014.

[8] A. B. Bergamo, J. A. Fracassi da Silva, and D. P. de Jesus, "Simultaneous determination of aspartame, cyclamate, saccharin and acesulfame-K in soft drinks and tabletop sweetener formulations by capillary electrophoresis with capacitively coupled contactless conductivity detection," *Food Chemistry*, vol. 124, no. 4, pp. 1714–1717, 2011.

[9] M. A. Cantarelli, R. G. Pellerano, E. J. Marchevsky, and J. M. Camiña, "Simultaneous determination of saccharin and aspartame in commercial noncaloric sweeteners using the PLS-2 multivariate calibration method and validation by capillary electrophoresis," *Journal of Agricultural and Food Chemistry*, vol. 56, no. 20, pp. 9345–9349, 2008.

[10] R. A. Medeiros, A. E. D. Carvalho, R. C. Rocha-Filho, and O. Fatibello-Filho, "Simultaneous square-wave voltammetric determination of aspartame and cyclamate using a boron-doped diamond electrode," *Talanta*, vol. 76, no. 3, pp. 685–689, 2008.

[11] F. Qu, Z.-H. Qi, K.-N. Liu, and S.-F. Mou, "Determination of aspartame by ion chromatography with electrochemical integrated amperometric detection," *Journal of Chromatography A*, vol. 850, no. 1-2, pp. 277–281, 1999.

[12] D. Xiao and M. M. F. Choi, "Aspartame optical biosensor with bienzyme-immobilized eggshell membrane and oxygen-sensitive optode membrane," *Analytical Chemistry*, vol. 74, no. 4, pp. 863–870, 2002.

[13] R. M. Peña, J. L. F. C. Lima, and M. L. M. F. S. Saraiva, "Sequential injection analysis-based flow system for the enzymatic determination of aspartame," *Analytica Chimica Acta*, vol. 514, no. 1, pp. 37–43, 2004.

[14] S. Armenta, S. Garrigues, and M. de la Guardia, "FTIR determination of aspartame and acesulfame-K in tabletop sweeteners," *Journal of Agricultural and Food Chemistry*, vol. 52, no. 26, pp. 7798–7803, 2004.

[15] J. D. A. Nóbrega, O. Fatibello-Filho, and I. D. C. Vieira, "Flow injection spectrophotometric determination of aspartame in dietary products," *The Analyst*, vol. 119, no. 9, pp. 2101–2104, 1994.

[16] W. Yang, Z. Li, and Z. Y. Lu, "Graphene-Ag nanoparticles-cicada wings hybrid system for obvious SERS performance and DNA molecular detection," *Optics Express*, vol. 27, no. 3, pp. 3000–3013, 2019.

[17] Z. Y. Lu, H. P. Si, and Z. Li, "Sensitive, reproducible, and stable 3D plasmonic hybrids with bilayer WS2 as nanospacer for SERS analysis," *Optics Express*, vol. 26, no. 17, pp. 21626–21641, 2018.

[18] P. Kumar, R. Khosla, M. Soni, D. Deva, and S. K. Sharma, "A highly sensitive, flexible SERS sensor for malachite green detection based on Ag decorated microstructured PDMS substrate fabricated from Taro leaf as template," *Sensors and Actuators B: Chemical*, vol. 246, pp. 477–486, 2017.

[19] M. Soni, T. Arora, R. Khosla, P. Kumar, A. Soni, and S. K. Sharma, "Integration of highly sensitive oxygenated

graphene with aluminum micro-interdigitated electrode array based molecular sensor for detection of aqueous fluoride anions," *IEEE Sensors Journal*, vol. 16, no. 6, pp. 1524–1531, 2016.

[20] S. Kumar, D. K. Lodhi, P. Goel, N. Neeti, P. Mishra, and J. P. Singh, "A facile method for fabrication of buckled PDMS silver nanorod arrays as active 3D SERS cages for bacterial sensing," *Chemical Communications*, vol. 51, no. 62, pp. 12411–12414, 2015.

[21] J. P. Singh, H. Chu, J. Abell, R. A. Tripp, and Y. Zhao, "Flexible and mechanical strain resistant large area SERS active substrates," *Nanoscale*, vol. 4, no. 11, p. 3410, 2012.

[22] C. H. Lee, M. E. Hankus, L. Tian, P. M. Pellegrino, and S. Singamaneni, "Highly sensitive surface enhanced Raman scattering substrates based on filter paper loaded with plasmonic nanostructures," *Analytical Chemistry*, vol. 83, no. 23, pp. 8953–8958, 2011.

[23] I. Choi, Y. Shin, J. Song et al., "Effective delivery of antigen–encapsulin nanoparticle fusions to dendritic cells leads to antigen-specific cytotoxic T cell activation and tumor rejection," *ACS Nano*, vol. 10, no. 8, pp. 7339–7350, 2016.

[24] J.-X. Dong, C. Xu, H. Wang et al., "Enhanced sensitive immunoassay: noncompetitive phage anti-immune complex assay for the determination of malachite green and leucomalachite green," *Journal of Agricultural and Food Chemistry*, vol. 62, no. 34, pp. 8752–8758, 2014.

[25] A. S. Urban, X. Shen, Y. Wang et al., "Three-dimensional plasmonic nanoclusters," *Nano Letters*, vol. 13, no. 9, pp. 4399–4403, 2013.