



# Fabrication of flower-like silver nanostructures for rapid detection of caffeine using surface enhanced Raman spectroscopy



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## ABSTRACT

Flower-like silver nanoparticles, with diameters of 450–500 nm and protrusions on the surface up to 10–15 nm, have been successfully synthesized via liquid phase reduction method, by using ascorbic acid as a reductant and polyvinyl pyrrolidone (PVP) as a surfactant. It is found that the proper coating degree of PVP on silver nuclei leads to anisotropic growth of the silver nuclei resulting in the formation of flower-like structure with more protrusions. Furthermore, when the obtained flower-like silver nanostructure is used as Surface Enhanced Raman Scattering (SERS) substrates, SERS signal is still clearly even if the concentration of R6G solution is reduced down to  $10^{-8}$  M. The SERS enhancement mechanism of flower-like silver nanostructures in SERS spectroscopy has been further discussed. SERS technology based on the obtained flower-like silver nanostructure substrates can be also used as an effective way to detect caffeine. In this work, it is found that the average intensity of SERS signals at  $807\text{ cm}^{-1}$  (N—C—H),  $958\text{ cm}^{-1}$  (Pyrimidine ring) and  $1327\text{ cm}^{-1}$  (Imidazole trigonal ring) linear decreased with the  $-\log_{10}C$  ( $C$  is the concentration of caffeine), and the coefficient of determination ( $R^2$ ) is as high as 0.975. This work provides a new way for the quantitative detection of caffeine based on SERS spectroscopy.

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## 1. Introduction

Caffeine is an alkaloid that mainly found in tea, coffee, cocoa, cola nuts and other plants, and is widely used as additive in the field of food, beverage and medicine. The moderate intake of caffeine may improve people's attention and work efficiency, but over intake can cause many unwanted effects [1]. Recent years, many modern techniques have been applied to the analysis of caffeine, such as UV–vis spectrophotometry [2], Ultrasonic Extracting Technique [3], High Performance Liquid Chromatography [4], Near Infrared Spectrum Instrument [5], etc. However, these techniques are generally expensive, complex and time consuming. Herein, a simple, rapid, sensitive, and low cost analytical technique for analysis of caffeine is very essential.

Recently, Surface Enhanced Raman Scattering (SERS) spectroscopy is widely used in materials analysis, environmental monitoring and other fields [6]. Compared with other techniques, SERS has greater potential for caffeine analysis due to its

excellent performance (such as high sensitivity, great flexibility, reproducibility, and reliability) [7]. In addition, by combining well-designed microchannels and SERS substrates, more effective and convenient SERS detecting systems had been realized [8]. Bondesson et al. [9] had simulated the Raman spectra of caffeine in the gas phase and aqueous solution by using hybrid density functional theory, and the calculated spectra are correspond well with experimental results. Baranska and Proniewicz [10] demonstrated that FT-Raman spectroscopy can be used either for the measurement of an isolated molecule as well as for in situ analyses, and they also used FT-Raman mapping technique to investigate the spatial distribution of caffeine in pharmaceuticals.

It has been reported that the cause of SERS enhancement is mainly due to two mechanisms: electromagnetic effect, caused by localized Surface Plasmon Resonance (LSPR) effect [11]; chemical mechanism, caused by charge transfer effect [12]. Electromagnetic enhancement is the main contribution to drastic enhancement of the signal in SERS and indifferently applies to all analytes [13]. Many researches indicated that the LSPR property is very sensitive to particle size, shape, composition, and arrangement [14]. Currently, many methods, including Hydrothermal method, [15] Liquid phase reduction method [16], Template method [17] and Nano lithography [18], have been applied to the fabrication of SERS-

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active substrates with particular size, shape and so on. In all of the SERS substrates, silver nanostructures shows excellent SERS performance, and various silver nanostructures, such as nanowires [19], nanorods [20], nanocubes [21], and dendritic nanostructures [22] have been used as SERS substrates. Many studies have showed that the controllability, stability, repeatability and uniformity of the substrates play a vital role in SERS detection [23]. Therefore, the preparation of SERS-active substrates with great repeatability, sensitivity and uniformity is highly desirable for broadening the application of SERS detection.

In this paper, we propose a simple, convenient, reasonable route for the synthesis of SERS-active silver nanostructures, which is carried out in the aqueous medium, produced no heavy metals or organic matter pollution. Silver nanostructures described in this work exhibit high SERS activity and its detection limit for R6G can reach  $10^{-8}$  M or even lower. In addition, the Raman shift, relative intensity, and assignment of characteristic peaks in SERS spectra of caffeine are summarized in this work, which provides the experimental and theoretical basis for the SERS application in qualitative and quantitative detection of caffeine.

## 2. Experimental

### 2.1. Materials

All the chemicals, like caffeine, silver nitrate ( $\text{AgNO}_3$ ), ascorbic acid, polyvinyl pyrrolidone (PVP), Rhodamine 6 G (R6G), were analytical reagents without further purification. Ultrapure water (18.3 M $\Omega$ ) was also used for all solution preparations.

### 2.2. Fabrication of flower-like silver nanostructures

A typical synthesis of flower-like silver nanoparticles proceeds as follows. First, 0.2 ml of  $\text{AgNO}_3$  solution (1 M) and 2 ml of PVP solution (1%) was both added in 10 ml of ultrapure water. After mixing evenly in the thermostat magnetic stirrer at room temperature, 1 ml of ascorbic acid solution (0.1 M) was quickly added into the above mixed solution, and the solution was stirred for next 15 min. Finally, the product of reaction was separated from the solution by centrifugation at 5000 r/min for 10 min, and it was then dispersed again in 10 ml of ultrapure water, plus these two steps were repeated several times in order to remove impurities.

### 2.3. SERS measurement

Preparation of SERS substrates based on flower-like silver nanoparticles: a certain amount of silver colloid was placed on a Si wafer ( $0.5 \times 0.5$  cm) and the Si wafer was transferred to the vacuum oven. Then, the Si wafer was dried at  $40^\circ\text{C}$  in the vacuum oven for 6 h, to deposit silver nanostructure film on the Si wafer. The as-prepared silver nanostructure films were used as SERS substrate for sensing R6G and caffeine.

SERS measurement: 0.5 ml aliquots of R6G solution with different concentrations ranging from  $10^{-8}$  to  $10^{-4}$  M were pipeted onto the SERS substrates, and the solvent evaporated under ambient conditions for SERS measurement. The solutions of caffeine were prepared at different concentrations ranging from  $10^{-9}$  to  $10^{-4}$  M, and the experiments were carried out using the same procedure as described in the above step. In addition, ten different points on each substrate were selected to detect the molecules in this experiment, to calculate the average Raman spectrum.

### 2.4. Characterization

The structure of the silver nanoparticles were characterized by HITACHI SU8010 field-emission scanning microscopy (resolution:

1.0 nm). The EDS spectrum was taken by EDAX TEAM Apollo XL Energy Dispersive Spectrometer (energy resolution: 129 eV). The UV-visible spectra were taken by Purkinje TU-1901 double-beam spectrophotometer. SERS spectra were recorded by the confocal microscope Raman spectrometer system (Horiba, LabRAM HR) using a 785 nm laser excitation source with 25 mW power.

## 3. Results and discussion

### 3.1. Characterization of the flower-like silver nanostructures

The obtained silver samples were first characterized by the field emission scanning electron microscopy (SEM) and the energy dispersive spectrum (EDS). Fig. 1(A) is the SEM image of the obtained silver nanostructures with large scale, and Fig. 1(B) demonstrated the detailed morphology of the silver nanoparticle. As shown in the figures, silver nanoparticles, with diameters of 450 ~ 500 nm and protrusions of surface up to 10 ~ 15 nm, have been successfully synthesized, and these nanoparticles are named as flower-like silver nanoparticles in the following article. In addition, the purity of these nanoparticles was confirmed by the EDS spectrum, as shown in Fig. 1(C).

The formation process of silver nanoparticles can be divided into three stages, that is, the induction stage (pre nucleation stage), the nucleation stage and the growth stage. Firstly, a silver cation was reduced to a silver atom upon to the reducing action of reductant, and the silver glomeration was rapidly formed. As the reaction continuing, the number of silver glomeration increases constantly until the nucleation state is reached. After that, the crystal nucleus rapidly generates, and then begins to grow. At the growth stage, if the growth rate of each crystal surface is equal, the growth rate of crystal nucleus will be isotropic and the final particle morphology will be spherical [24]. However, when the surfactant exists, the growth rate of some crystal surfaces will be influenced [25]. PVP is a kind of non-ionic surfactant with excellent properties. Due to its special structure, PVP has different adhesion coefficients on different crystal surfaces [26]. When the PVP molecules preferentially adsorbed on certain crystal surface, the free energy of these crystal surface changes largely compared to crystal surface with no PVP absorption, and further the growth rate of these crystal surface decreases, which can leads to anisotropic growth of the crystal nucleus resulting to the formation of flower-like structure, as shown in Fig. 2.

Fig. 3 is the SEM image of silver nanoparticles obtained in different ascorbic acid addition. Fig. 3(A) shows that, when the ascorbic acid addition is 0.5 ml, the particle size of the silver nanoparticles is about 550–600 nm, and the protrusions of the surface are blunt. However, when the amount of ascorbic acid increased to 1 ml, as shown in Fig. 1, the particle size of the silver nanoparticles is about 450–500 nm, and more and more sharp protrusions appeared on the surface. These phenomena indicate that the ascorbic acid addition has an important influence on the morphology of silver nanoparticles. As the ascorbic acid addition increased to 1 ml from 0.5 ml, the more relative amount of reducing agent in the system contained, the faster transformation of silver cation to silver atom was, and the more crystal nucleus were produced in the nucleation stage, which led to the decrease of the molar ratio of PVP and crystal nucleus. Furthermore, the decline of molar ratio indicates the descent of coating degree of PVP on silver nuclei. In this case, the number of exposed crystal surfaces (without surfactant adsorption) is relatively high, which leads to more isotropic growth of the crystal nucleus contributing to the more protrusions on the particle surface. Moreover, with the ascorbic acid addition further increase, due to the amount of  $\text{AgNO}_3$  is enough and other conditions are constant, the production of crystal nucleus will be

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