



# Ultrasensitive and quantitative detection of paraquat on fruits skins via surface-enhanced Raman spectroscopy



Hui Fang<sup>a,b</sup>, Xin Zhang<sup>a,b,\*</sup>, Shang Jie Zhang<sup>a,b</sup>, Luo Liu<sup>a</sup>, Yong Mei Zhao<sup>c</sup>, Hai Jun Xu<sup>a,b,\*</sup>

<sup>a</sup> Beijing Key Laboratory of Bioprocess, Beijing University of Chemical Technology, Beijing 100029, China

<sup>b</sup> College of Science, Beijing University of Chemical Technology, Beijing 100029, China

<sup>c</sup> Engineering Research Center for Semiconductor Integrated Technology, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

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## ABSTRACT

In our study, we introduced a rapid, low-cost and nondestructive ‘surface spray’ method to achieve the quantitative detection of the pesticide residues on fruits skins. Taking advantage of the high enhancement ability of the surface-enhanced Raman spectroscopy (SERS) of the optimized Ag nanoparticles colloid, the limit of detection (LOD) of paraquat (PQ) on the peels of pears and apples could reach the order of magnitude of  $10^{-9}$  M, much lower than the maximum residue limit of 0.05 mg/kg ( $\sim 10^{-4}$  M) in a large number of countries including the USA and China. The quantitative detection of PQ was achieved as well. This opens a new avenue for advancing the applications of SERS technique in the fields of food safety, drug security, and environment monitoring.

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## 1. Introduction

As the majority of pesticides are poisonous, the distribution and use of them were strictly controlled by food safety related departments in the world, and the maximum residue limits for pesticides on raw agricultural products were established based on the evaluation of human health. Among the pesticides, paraquat (PQ) with moderate toxicity is widely used in the agricultural practices, and its allowable residue limit for fruits, such as apples and pears, is regulated to be as low as 0.05 mg/kg ( $\sim 1.0 \times 10^{-4}$  M, see the supplementary material) in a large number of countries including the USA and China [1]. Excessive intake of PQ can cause renal tubular necrosis, the central lobular liver cell damage, necrosis, and pulmonary artery thickening middle, and there is no specific drug for it till now [2]. Up to date, the main methods to detect PQ residue on fruits include chromatographic methods, UV, mass spectroscopy, etc. [3–5]. For example, the liquid chromatography method permits a limit of detection (LOD) of PQ as low as 50 ng/ml ( $\sim 0.19$  nM) in human serum [3], and the LOD even reaches 0.5 ng/ml in blood using the liquid chromatography-electrospray ionization-mass spectroscopy [4].

Although outstanding capacities for trace detection are demonstrated by these methods all of them have the limitations of complex sample preparation process, high cost of the instruments, and requirement of well-trained operators and a laboratory. Therefore, it is still necessary to develop a much simpler and faster low-cost analytical method that can be used in open environment [6].

Over the past several decades, surface-enhanced Raman spectroscopy (SERS) as a powerful analytical tool has gained more and more attention and played an important role in the detection of biomolecules and the interactions between substances, because of its perfect properties to provide unique vibrational signatures of analytes associated with chemical and structural information [7–11]. The pesticide detection using SERS has been reported in several articles, and those studies provide good references for the peak assignments of common pesticide molecules [12–17]. Nevertheless, the studies before did not solve the problem of ultrasensitive and quantitative detection of pesticide residues on raw agricultural products such as fruits at low cost. Therefore, developing new methods based on SERS principle to solve the above problem is of great sense. Several kinds of metal nanoparticles (NPs), especially Au and Ag, have been used to make SERS-active substrates [18–25], and Ag NPs have attracted much more attention than Au NPs because of its simpler preparation process and stronger surface plasmon resonance (SPR) which could create more ‘hot spots’ to give a higher enhancement factor (EF) [26]. However, Ag NPs also have some limitations in application, mostly

\* Corresponding authors at: Beijing Key Laboratory of Bioprocess, Beijing University of Chemical Technology, Beijing 100029, China. Tel.: +86 10 64442357.

E-mail addresses: [zhxin@mail.buct.edu.cn](mailto:zhxin@mail.buct.edu.cn) (X. Zhang), [hjxu@mail.buct.edu.cn](mailto:hjxu@mail.buct.edu.cn) (H.J. Xu).

because the aggregation of NPs will greatly affect the localized SPR and make it very difficult to achieve reliable quantitative detection of target molecules.

In this paper, the dispersity and uniformity of Ag NPs was first well optimized by identifying the dispersity of colloid synthesized upon the addition of different concentrations of AgNO<sub>3</sub> solutions, and then the optimized Ag NPs obtained by using 1.0 × 10<sup>-3</sup> M AgNO<sub>3</sub> solution were successfully applied to detect the PQ molecules on fruits skins via SERS. The LOD reached as low as 3.4 × 10<sup>-9</sup> M and quantitative detection was achieved. The experimental results demonstrated that this SERS detection technology was rapid, ultrasensitive and quantitative, and thus could be applied widely in the fields of food safety and play an important role in daily life.

## 2. Experimental

### 2.1. Materials and instruments

Sodium citrate, PQ and AgNO<sub>3</sub> were of analytical grade and supplied by Aladdin, China. Other reagents used in the experiments were of analytical grade and used as received.

The typical morphologies and microstructures of samples were investigated by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) (Phillips CM200 FEG-TEM), and the UV–vis absorption spectra were monitored by a Shimadzu UV-3600 UV–vis spectrophotometer. The Raman signals of PQ were obtained after the droplet evaporated naturally and all of the signals were obtained at room temperature on the LabRAM ARAMIS Raman system with the 633 nm laser as excitation. The diameter of the light spot area was ~1 μm and the incident power was 0.325 mW. The spectra were recorded with the accumulation time of 15 s and the spectral resolution was 1 cm<sup>-1</sup>. The accumulation time and the laser power were the same for all Raman spectra in the case of no special instructions.

### 2.2. Sample preparation

Ag NPs were synthesized by the reduction of AgNO<sub>3</sub> with sodium citrate [27]. Typically, 300 mL of AgNO<sub>3</sub> solution with a certain concentration was first heated to boil with magnetic stirring during the whole process, then 10 mL of 1% sodium citrate was quickly injected into the boiling solution, and after stirring for 1 h the gray liquid is the expected colloid. Considering that the ratio of AgNO<sub>3</sub> to sodium citrate may affect the sizes of the Ag NPs, which would further affect the Raman signals, AgNO<sub>3</sub> aqueous solutions with five different concentrations of 0.2 × 10<sup>-3</sup>, 0.6 × 10<sup>-3</sup>, 1.0 × 10<sup>-3</sup>, 1.4 × 10<sup>-3</sup> and 1.8 × 10<sup>-3</sup> M were used. PQ solutions with different concentrations from 10<sup>-3</sup> to 10<sup>-11</sup> M were also prepared. For Raman detection, a method named ‘surface spray’ was developed to prepare the samples. A slice of pear or apple skin was first cut and cleaned using ethanol and deionized water successively, and then PQ solution with a certain concentration was sprayed onto the cleaned peels until the liquid got together and ran down. This piece of peel was spread onto a slide glass, followed by spraying the Ag colloid to cover its surface after the PQ solution completely evaporates at room temperature. When the colloid nearly dries, the Ag NPs will be located at the surface and have some interactions with the PQ molecules, thus the SERS signal of the PQ can be detected when the sample was excited by laser. The main procedures for the above ‘surface spray’ method can be illustrated in Fig. 1.

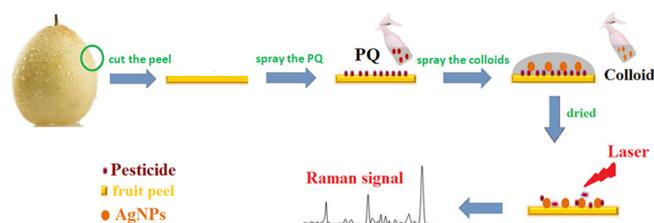


Fig. 1. Schematic illustration of the ‘surface spray’ method to detect the pesticide residues on fruits.

## 3. Results and discussion

### 3.1. Characterization

The transmission electron microscopy (TEM) images of the Ag NPs obtained from different concentrations of AgNO<sub>3</sub> solutions are shown in Fig. S1 in the supplementary material. Clearly, when the concentration of AgNO<sub>3</sub> is low at 0.2 × 10<sup>-3</sup> M, Ag NPs are highly dispersive and have an average particle size of ~50 nm. This kind of colloid will not have significant Raman enhancement because the density of ‘hot spot’ is too low. When the AgNO<sub>3</sub> concentration increases to 0.6 × 10<sup>-3</sup> M, the Ag NPs aggregate obviously and become larger in size. However, the size of Ag NPs decreases sharply when the AgNO<sub>3</sub> concentration increases further to 1.0 × 10<sup>-3</sup> M. The larger size of Ag NPs from the 0.6 × 10<sup>-3</sup> M AgNO<sub>3</sub> than from the 1.0 × 10<sup>-3</sup> M solution may be owing to the effect of relatively excess sodium citrate, which can accelerate the aggregation of NPs [11]. When the AgNO<sub>3</sub> concentration becomes higher than 1.0 × 10<sup>-3</sup> M, the size of Ag NPs shows a positive correlation with it again, and finally Ag NPs aggregated into large networks when the AgNO<sub>3</sub> concentration is too high, up to 1.8 × 10<sup>-3</sup> M. The above characteristic of the dependence of the size of the Ag NPs on the AgNO<sub>3</sub> concentration is different from that reported by Rodríguez-León et al. [28], where Ag NPs were also obtained through the reduction of silver ions in AgNO<sub>3</sub> solutions and a monotonic dependence of the NPs size on the AgNO<sub>3</sub> concentration was shown. The differences in synthesis method and experimental condition in these two studies result in different sizes of Ag NPs (2–40 nm vs 50–100 nm), as well as the different characteristics of the dependence of the NPs size on the AgNO<sub>3</sub> concentration (monotonic vs nonmonotonic).

Larger Ag NPs mean smaller ratio of surface area to volume and less ‘hot spots’, which is disadvantageous to the SERS effect. Therefore, the colloid obtained using the 1.0 × 10<sup>-3</sup> M AgNO<sub>3</sub> was focused on to do further study based on the optimization of experimental parameters. From the TEM image shown in Fig. 2a, it can be seen that Ag NPs have an average size of ~65 nm. Furthermore, as shown in Fig. 2b, high-resolution TEM (HRTEM) image indicates that Ag NPs have well-defined crystalline planes with interplanar spacing of 0.227 nm, corresponding to the (111) planes of face-centered cubic (fcc) Ag according to the fast Fourier transform (FFT). Note that this is different from the result reported in Ref. [28], in which a hexagonal 4H structure of Ag NPs is also displayed besides the crystal symmetry of fcc. The UV–vis absorption spectra of Ag NPs from two distinct syntheses are measured, and the results are shown in Fig. S2. It can be seen that the locations of the absorption peaks in both images of Fig. S2 are identical, indicating the reproducibility of the Ag NPs colloids from the two syntheses is satisfactory. From Fig. S2, it can also be seen that as the concentration of AgNO<sub>3</sub> solution increases the SPR peaks of Ag NPs are broadened obviously with red shift from 430 to 475 nm, and the absorption increase on the whole. Moreover, it can be seen that all the curves in Fig. S2 are not so smooth, implying some non-spherical (such as ellipsoidal, multidimensional) Ag NPs also exist in addition to the spherical particles. The symmetry of plasmon resonance peaks

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