

# Surface-enhanced Raman spectroscopy for highly sensitive detection of Methyl Parathion

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**Abstract**—Methyl Parathion (MP) is a common organophosphorus pesticide, which may pollute the environment. A sensitive method was explored for quantification of MP in water samples as surface-enhanced Raman spectroscopy (SERS) substrate by using silver nanorod (AgNR) array substrates. The AgNR array substrates were fabricated by oblique angle deposition technique, which exhibited an excellent SERS activity. A good linear relationship was demonstrated between the intensity of characteristic peak and MP concentration in the range of 3 ~ 50 mg/L, and a limit of detection was determined to be 3 mg/L. This SERS based method enables the rapid and highly sensitive detection of PM without any sample pretreatment, and has the potential in water quality monitoring application.

**Keywords**—AgNR; Methyl Parathion; SERS

## I. INTRODUCTION

Organophosphate (OP) insecticides are widely used in agriculture, vector control and domestic purposes. About 70% of the pesticides in current use are OP compounds, which constitute a total consumption of around 90 million pounds per year [1]. In the world, it is unavoidable to use the pesticides on agricultural and urban areas, but the usage of pesticide was indiscriminate and injudicious, which has resulted in widespread contamination in lakes, rivers, and streams and through subsurface transport to aquifers. Therefore, it demands to establish the methods for sensitive and accurate analysis of OPs. Traditional analytical protocols used to determine OPs are gas chromatography, high performance liquid chromatography or coupled to mass spectrometry. Over the past few years, enzyme-based inhibition electrochemical biosensors have emerged as an alternative to ease detect pesticides [2]. Nevertheless, the operational conditions are mostly limited by the denaturation of enzymes. Gong *et al.* designed a sensitive electrochemical stripping voltammetric sensor for pesticides based on solid-phase extraction [3]. These methods are highly efficient, but very expensive, time consumed, and not suitable for real-time analysis. A great challenge remains to develop a fast, reliable and real-time monitoring system. Raman spectroscopy, a molecular vibration spectroscopy technique, resulting from an inelastic scattering process, can provide information about the structural characteristics of a molecule. Surface-enhanced Raman spectroscopy (SERS), as a means of chemical identification and analysis, is characterized by high sensitivity, high selectivity, non-destructive, and high repeatability [4]. Samir Kumar *et al.* demonstrated a simple “paste and peel off” method for directly extracting trace amount ( $10^{-9}$  g/cm<sup>2</sup>) of thiram pesticide from fruit peels [5]. In this paper, we used the highly sensitive silver nanorod (AgNR)

substrates to detect Methyl Parathion (MP) in water samples. The detection ability of AgNRs for MP in ultrapure water and in pool water was investigated systematically.

## II. MATERIALS AND METHODS

### A. Sample collection

Materials Silver (99.999%) and titanium (99.995%) pellets were attained from Kurt J. Lesker Co., Ltd. MP (99.9%) and ethanol were acquired from J&K China Chemical Ltd. Briefly, the pool water sample was collected from a pool in Xuzhou, and the pure water sample was collected directly and filtered the ultra-pure water ( $\geq 18.2$  M $\Omega$ ), and the PH of water sample is neutral. MP was spiked into the water samples at concentrations between 0.5 mg/mL and 1 mg/mL, which were then used for SERS analysis.

### B. SERS substrate preparation

SERS-active AgNR array substrates were fabricated in a custom built electron beam evaporation system as described in our previous studies. Briefly, glass slides were cut into pieces of glass with an area of  $1 \times 1$  cm<sup>2</sup> and soaked in an ethanol solution. Then pieces of glass washed with an ultrasonic cleaner for 5 minutes, and repeated three times. Finally, the treated glass pieces were loaded into the deposition chamber. Evaporation process is mainly the following sections. Firstly, the glass substrates were deposited a 20 nm film of titanium and 100 nm of silver film at rates of 0.2 nm/s and 0.3 nm/s, respectively. These films were deposited at an incident angle =  $0^\circ$  relative to the normal of the substrate. Next, the substrates were rotated to an oblique angle of =  $86^\circ$  with respect to the vapor incident direction, and 2000 nm of silver was deposited at a rate of 0.3 nm/s [6].

### C. SERS measurements

All SERS measurements were performed using a Raman analyzer (ProRaman-L-785A2, Enwave, Optronics, Irvine, CA) equipped with a 785 nm diode laser. The substrate used to obtain SERS with a laser power of 100 mW and an integration time of 10 s. 2  $\mu$ L drop of MP solution with different concentrations was placed on the surface of the AgNR substrate. Then SERS spectra were taken from the substrate. Each drop were measured at least nine random sampling locations. Origin 8.5 software (Origin Lab, Northampton, MA) was applied to plot all of the SERS spectra. The raw spectra without further processing obtained from the Raman analyzer were used unless otherwise specified.

### III. RESULTS AND DISCUSSION

#### A. The Advantages of Oblique Angle Deposition (OAD)

OAD has been recognized as an effective and stable method applied in the fabrication of nanostructures, which is controllable. Different sizes of AgNR substrates were fabricated for different detection requirements are shown in Fig. 1A. The cross-section SEM of the AgNR surface is shown in Fig. 1B.

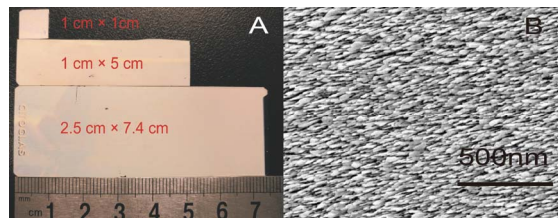


Fig. 1. (A) Three sizes of SERS substrates. (B) SEM of the AgNR surface.

#### B. Detection of MP in ultrapure water

Fig. 2A shows the representative SERS spectra which derived from different concentration MP in ultrapure water. The addition of water led to elevated background and several broad peaks in the spectra even though the AgNR array substrates do not show any significant SERS peaks. But as shown in Fig. 2A, the emergence of MP's characteristic SERS peaks was not affected by the control spectrum of AgNR array substrates. Fig. 2B plots the SERS peak intensities at 1320  $\text{cm}^{-1}$  versus the MP concentration. The current responses were proportional to MP concentrations in the range from 1.0 to 50.0 mg/L. The linear equation of the minimum squares fitting were obtained as  $I_{1320} = 892.29 + 225.17C_{MP}$ . Based on these results, the lowest concentration can be detected as 3 mg/L with the  $3\sigma$  method ( $\sigma$  is the mean square root of the noise signal, which was determined by standard deviation of the spectral intensity at a spectral region at the range of 1700~1800  $\text{cm}^{-1}$ ) [7].

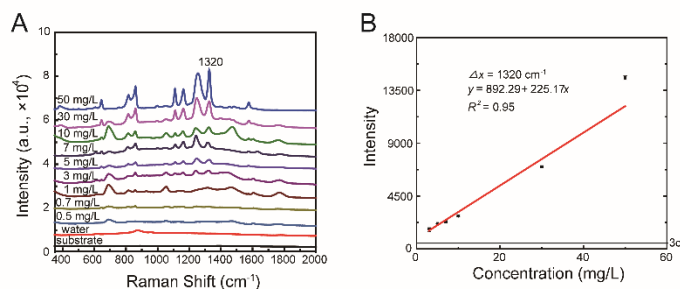


Fig. 2. (A) SERS spectra of MP in ultrapure water at different concentrations. (B) The average intensity were plotted and the error bars represent the standard deviation value).

#### C. Detection of MP in pool water

Fig. 3A shows the SERS spectra of MP in pool water at different concentrations. It can be clearly seen that as the concentration increases, the SERS signal at 1320  $\text{cm}^{-1}$  continues to increase. Spectra showed that MP's concentrations as low as 5mg/L still exhibit an observable SERS signal. Fig. 2B plots the intensities of SERS peak at 1320  $\text{cm}^{-1}$  versus the  $C_{MP}$ :  $I_{1320} = 95.59 + 58.97C_{MP}$ . Based on these results, the

lowest concentration can be detected as 5 mg/L with the  $3\sigma$  method.

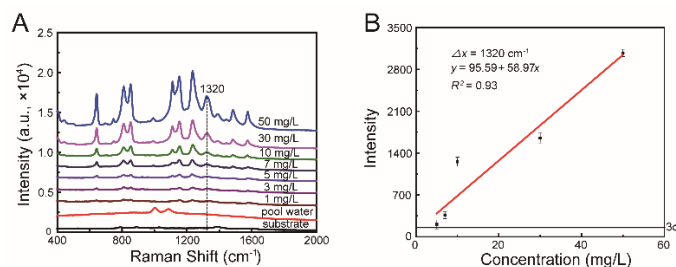


Fig. 3. (A) SERS spectra of MP in pool water at different concentrations. (B) The average intensity were plotted and the error bars represent the standard deviation value).

### IV. CONCLUSION

In this study, the size controllable AgNR array substrates fabricated by oblique angle deposition were applied to the MP detection in water samples, which achieved the limit of detection (LOD) of 3 mg/L. Moreover, the pool water samples, which contain different concentration of MP, were detected by AgNR and reached the LOD of 5 mg/L. The result shows this SERS based method could be an efficient way to control the pesticides in water.

### ACKNOWLEDGMENT

This research was funded by the National Natural Science Foundation of China (Grant No. 61575087), and the National Training Programs of Innovation and Entrepreneurship for Undergraduates (Grant No. 201710320040). We thank for the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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