

SPR-based Surface-enhanced Raman Scattering for the Detection of Organophosphorus Pesticide

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Detection of organophosphorus compounds (OPs) is becoming more and more urgent due to the requirement of food safety and environmental protection. Among various detection techniques currently available (e.g. HPLC (high-performance liquid chromatography), gas chromatography, fluorometry, enzyme linked immunosorbent assay, etc.),¹ surface-enhanced Raman scattering (SERS) has received much attention since it does not require any complicated and cumbersome workload between samples and test analysis.² The SERS technique allows rapid measurements of the order of several minutes without any labeling of the analyte, whereas conventional Ag⁺ or Au⁺ nanoparticles SERS suffers from the challenges to synthesize nanostructures with uniform size, shape and crystallinity.³ In the paper, a novel surface plasmon resonance (SPR)-based SERS is proposed for OPs detection. The gold-plated photonic crystals (PCs) present the appealing characteristics of wide spectrum across visible and IR wave band are highly SERS sensitivity, while it barely requires sample and sample preparation.

Superprism phenomena in PCs has been used for the realization of signal decomposition. The periodic arrays are characterized by a period of 1 μm , diameter of 471.2 nm and depth of 17.6 μm (fig. 1), which are much more difficult to fabricate based on silicon technology. To detect the responsibility of PCs, OPs was used as the SERS probe molecule assembled on the patterns of PCs by electrostatic adsorption. It is obviously that the characteristic peaks (1000.6 cm^{-1} and 620.1 cm^{-1}) of trichlorfon are distinguished out, as shown in fig. 2 and fig. 3. The enormous enhancement of Raman signal is clearly observed on gold patterns comparing with pristine silicon-substrates. Moreover, the SERS intensity of trichlorfon deposited on PC patterns (fig. 2b and fig. 2c) is almost 7 times as strong as that on smooth surface (fig. 2a). The intensity of the Raman peak at 1000.6 cm^{-1} decreases linearly with trichlorfon dilution ranging from 10^{-4} mol/L to 10^{-7} mol/L. Note there is no obvious Raman peak below 10^{-7} mol/L as shown in fig. 4. Consequently, the sensitivity is as high as 10^{-7} mol/L, which is similar to other assays⁴.

¹ Shaveena Thakur, M. Venkateswar Reddy, Dayananda Siddavattam, and A. K Paul, *Sensors and Actuators B: Chemical* **163**, 153 (2012).

² G. Goddard, L. O. Brown, R. Habbersett, C. I. Brady, J. C. Martin, S. W. Graves, J. P. Freyer, and S. K. Doorn, *J. Am. Chem. Soc.* **132**, 9 (2010).

³ Xiao Gong, Ying Bao, Chao Qiu, and Chaoyang Jiang, in *The Royal Society of Chemistry*, 2012, edited by Richard R. Schrock.

⁴ A. N. Ivanov, G. A. Evtugyn, Lilia V. Lukachova, Elena E. Karyakina, H. C. Budnikov, S. G. Kiseleva, A. V. Orlov, G. P. Karpacheva, and Arkady A. Karyakin, *IEEE SENSORS JOURNAL* **3**,7 (2003).

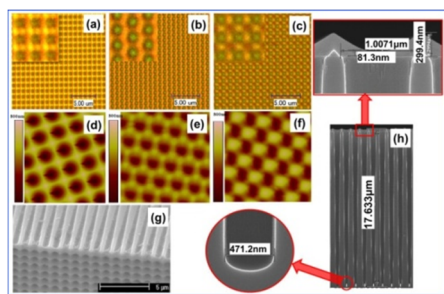


Figure 1: the characteristic images of the patterns: optical images of square pattern (a, c) and hexagonal pattern (b), AFM images of corresponding PC patterns (d)-(f), and SEM images of square PC structure (g, h).

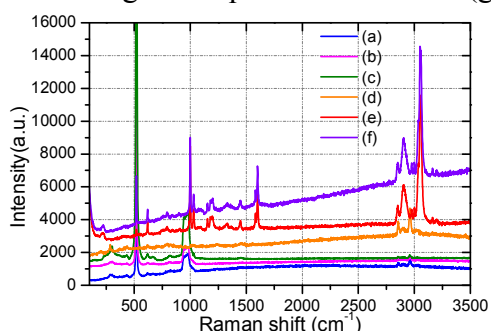


Figure 2: SERS spectra of trichlorfon measured on different substrates: Curves (a)-(c) measured on smooth, square and hexagonal patterns without gold film, respectively. Curves (d)-(f) measured on the patterns corresponding to (a)-(c) with 50nm thick gold film.

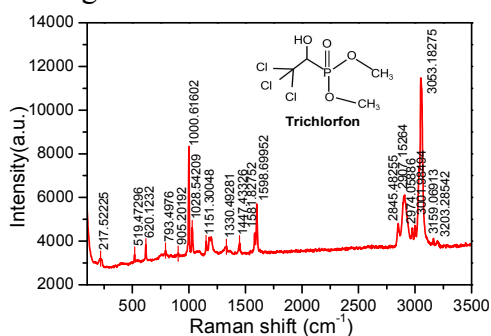


Figure 3: the Raman peaks of trichlorfon deposited on the SERS-active square PC structure: The inset gives the structural formula of trichlorfon.

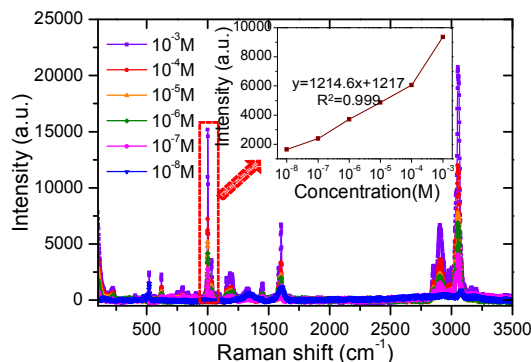


Figure 4: Changes in the trichlorfon SERS spectra via concentrations: The inset shows the relationship of SERS intensity and concentrations of trichlorfon.