

SERS OF ORGANIC ANALYTE ON THE FILTER PAPER WITH TiO₂ ALD COATING AND Ag NANOPARTICLES

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<https://doi.org/10.37904/nanocon.2022.4618>

Abstract

Surface Enhanced Raman Spectroscopy (SERS) is an important method for characterizing different materials and chemical analytes at low concentrations. The Raman signal plasmonic amplification is strongly dependent on the surface nanostructure. The filter paper could be used as the substrate for the chemical analysis of organic materials. We investigated the influence of different TiO₂ thicknesses deposited on the ashless filter paper surface on the signal efficiency. TiO₂ is hydrophilic and biocompatible. High-surface area TiO₂ on the filter paper will help create 3D heterostructure to collect more analyte molecules. We used Sentech SI 500 thermal Atomic Layer Deposition (ALD) System with 10, 20, and 50 growth cycles and the TTIP precursor. Surface structure was investigated by Atomic Force Microscopy (AFM). The silver (Ag) colloid solution was dropped on the filter paper before standard R6G biomarker solutions were deposited. The Raman signal measured by In Via Renishaw spectrometer was compared for the different samples. TiO₂ ALD-20 cycle gave the highest enhancement factor (~2.3 X 10⁵) compared to other ALD-coated samples. Interestingly, the TiO₂ ALD coating generally results in an enhancement factor more than 20 times higher than the reference sample (namely filter paper without the ALD coating). SERS mapping results suggest the uniformity and reliability of SERS measurements across a large area (40 x 40 μm²). The finding paves a new direction for preparing simple, flexible, and biocompatible SERS substrates, which could be readily applied in detecting various biomolecular or organic analytes in our coming works.

Keywords: Surface enhanced Raman spectroscopy, filter paper, titanium oxide, atomic layer deposition

1. INTRODUCTION

Surface-enhanced Raman scattering (SERS) is a non-destructive sensing technique in which inelastic light scattering by molecules is enhanced in comparison with classical Raman scattering by the orders of magnitude when the molecules are adsorbed onto corrugated metal surfaces such as silver or gold nanoparticles (NPs). The enhancement is produced by localized field of the plasmonic oscillations between the nanoparticles. SERS enables the examination of small numbers of molecules. SERS has increasing number of applications in several different directions, including electrochemistry, catalysis, biology, medicine, art conservation, materials science, and others [1-3]. SERS substrates are produced mainly by metallic nanostructures on glass substrates or silicon wafers. However, three-dimensional (3D) structures are more suitable because they enlarge both the interaction volumes and total interaction surface areas between the localized field and the molecules to be detected. But the complexity of the fabrication and low-flexibility of the substrates, limit the practical application of these SERS devices. The new methods of the preparation of 3D SERS substrates use

polymer nano-fibers or paper fiber networks as the frame for the plasmonic nanostructures [4]. Particular advantages attributed to filter paper-based SERS are the ability to create greater hotspot sites and to concentrate analyte. Filter paper based SERS substrates have recently shown strong capability in detecting trace amount of small molecules [5]. The crystalline TiO₂ with Ag NP or silica-titania fibers obtained by sol-gel and electrospinning processes were also successfully used for SERS substrate preparation [6,7]. Rhodamine 6G (R6G) is often used as a model molecule in the SERS spectroscopy with resulting EF up to 10⁸ on roughened nano-Au films or detection limit of 10⁻¹³ M R6G on urea and formaldehyde (UF) microsphere with Ag NP [8 - 11]. Here we report a study of the properties of the Ag NP covered ashless filter paper with different TiO₂ coverage and the resultant surface enhanced Raman scattering (SERS) activity using R6G as a analyte.

2. EXPERIMENTAL

Several samples were prepared for the Raman and SERS measurement. The reference samples were placed on the silicon substrates. SERS samples were prepared on the ashless filter paper by two methods: The first with the synthesized rutile TiO₂ and Ag NP, the second with the thin TiO₂ layers prepared by 10, 20 and 50 cycles of the thermal Atomic Layer Deposition (ALD) SI 500 Sentech covered again by the Ag NP. The rutile TiO₂ was synthesized by mixing of 0.75 M of urea (99.5 %) and 1 M of TiCl₄ (99.9 %) in an autoclave by 200 °C for 2 hours. TiO₂ nanoparticles were obtained by centrifugation, washing, and drying in the vacuum oven at 80 °C overnight. The filter paper surface has been characterized by the optical and Atomic Force Microscopy (AFM) as shown in **Figure 1**. The paper fiber diameter is approximately 10 μm and the filter paper structure creates gaps with dimensions of several tens of μm where the analyte could be accumulated. Resulting samples were inspected by the Scanning Electron Microscopy (SEM). In the **Figure 2** the R6G molecule and the surface of the sample with synthesized rutile TiO₂ and Ag NP are shown. The ALD covered sample is shown in the **Figure 3** with different scales. The diameters of the Ag NP are in the range 40 – 120 nm.

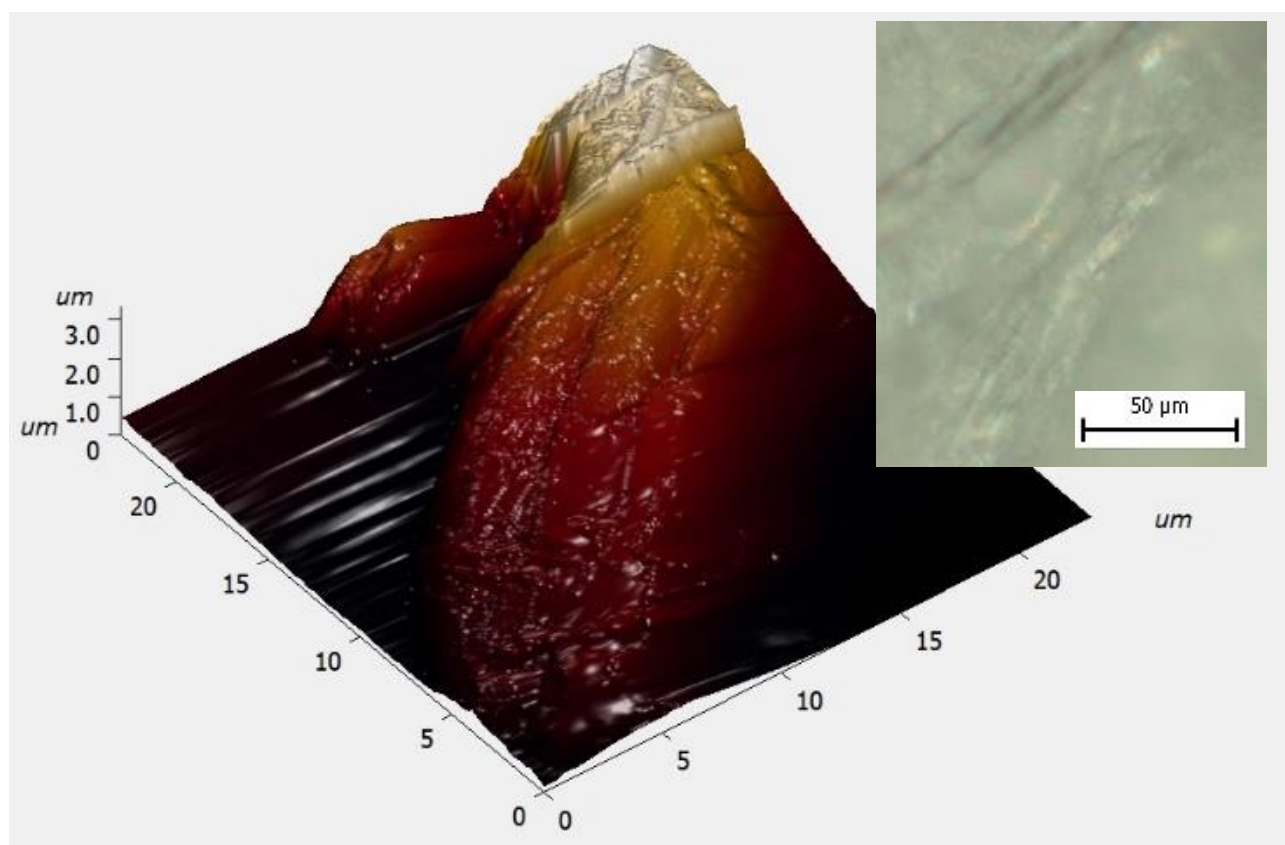


Figure 1 The AFM and optical microscope (insert) picture of the filter paper surface

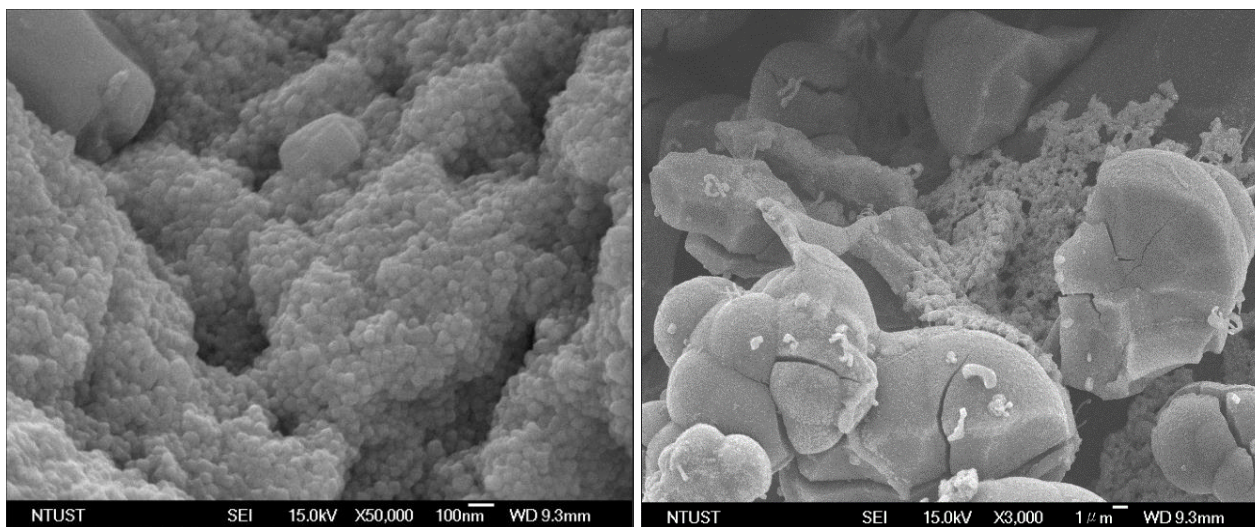


Figure 2 SEM picture of R6G molecule (left) and rutile/Ag NC surface (right)

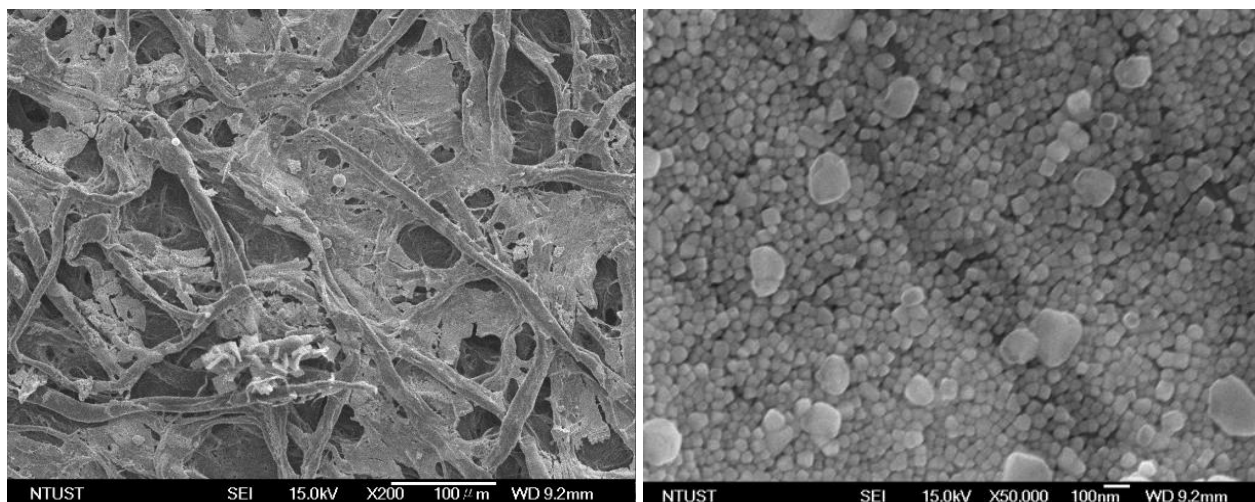


Figure 3 SEM picture of ALD TiO₂/Ag NC surface in microscale (left) and in nanoscale (right)

3. RESULTS

First, the Raman spectra of 10 mM and 1 mM R6G on silicon were performed (**Figure 4**). All measurements were done on Renishaw In Via Raman spectrometer. We used the 633 nm laser with 10 % intensity and we compared the signal at Raman shift on the 1364 cm⁻¹ peak. SERS enhancement factor (EF) is defined as the ratio of SERS intensity contributed by each surface molecule to the ordinary Raman intensity contributed by each free molecule:

$$EF = \frac{(I_{SERS} / C_{SERS})}{(I_{Raman} / C_{Raman})}$$

where I_{SERS} and I_{Raman} are the SERS and ordinary Raman intensities, respectively. C_{SERS} and C_{Raman} are the concentrations of molecules probed by SERS and ordinary Raman. For the samples with synthesized rutile TiO₂/Ag NC layer we obtained the height for 1 mM R6G 452286 a.u. as shown in **Figure 5**. In comparison with the height of reference peak for 10 mM R6G on the silicon wafer (451 a.u.) we obtained EF 10⁴. For the 1 μM of R6G on the ALD TiO₂/Ag NC surface we measured the samples with different thicknesses of ALD TiO₂ layer using 10, 20 and 50 growth cycles on Sentech SI 500 thermal ALD with the TTIP precursor. Resulting SERS

spectra are shown in **Figure 6**. The highest peak 10591 a.u. of 1 μ M R6G at 1364 cm^{-1} was observed for the 20 cycles of ALD (TiO_2 layer thickness 0.4 nm). Resulting EF is 2.3×10^5 .

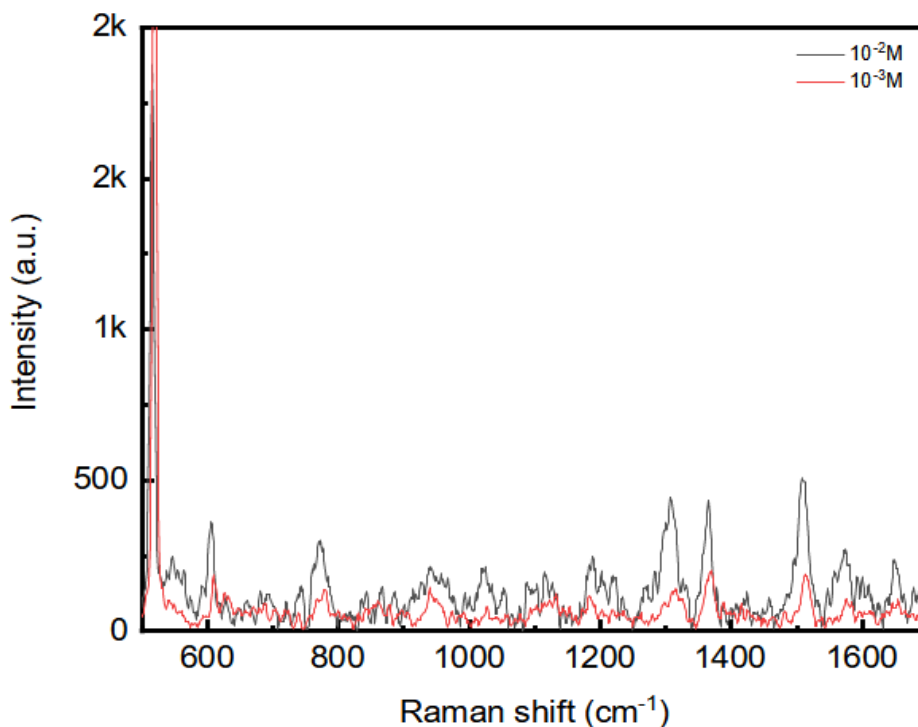


Figure 4 Raman spectra of 10 mM (black) and 1 mM (red) R6G on silicon with 10 % power of 633 nm laser

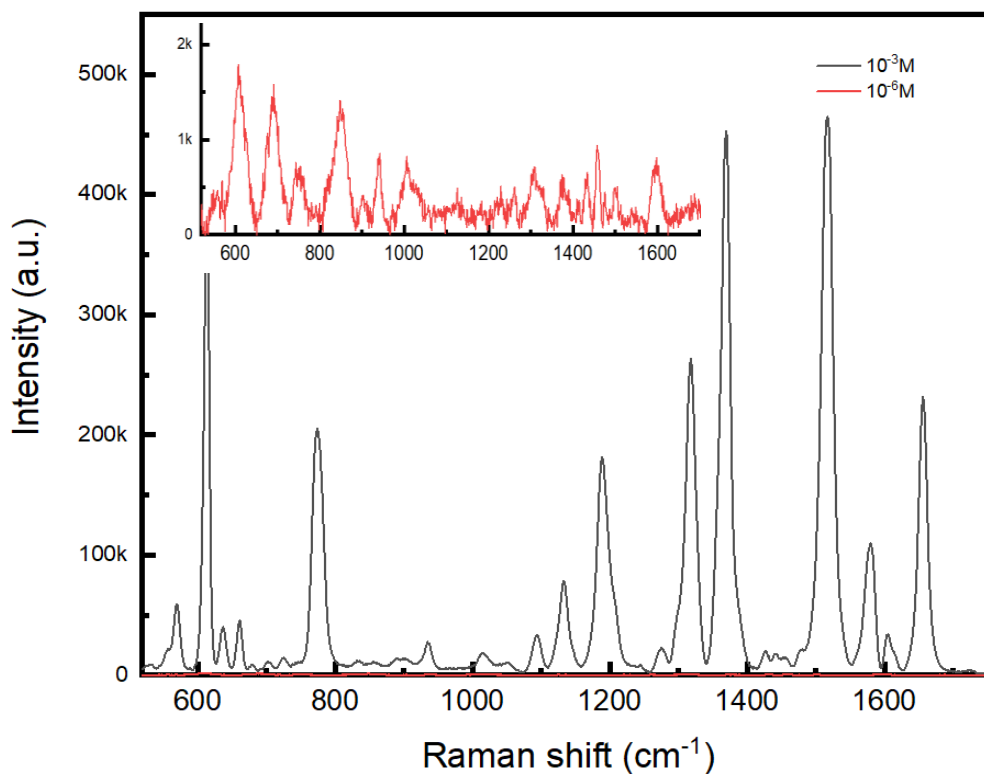


Figure 5 SERS spectra of 1 mM and 1 μ M (insert) R6G (insert) on rutile TiO_2/Ag NP

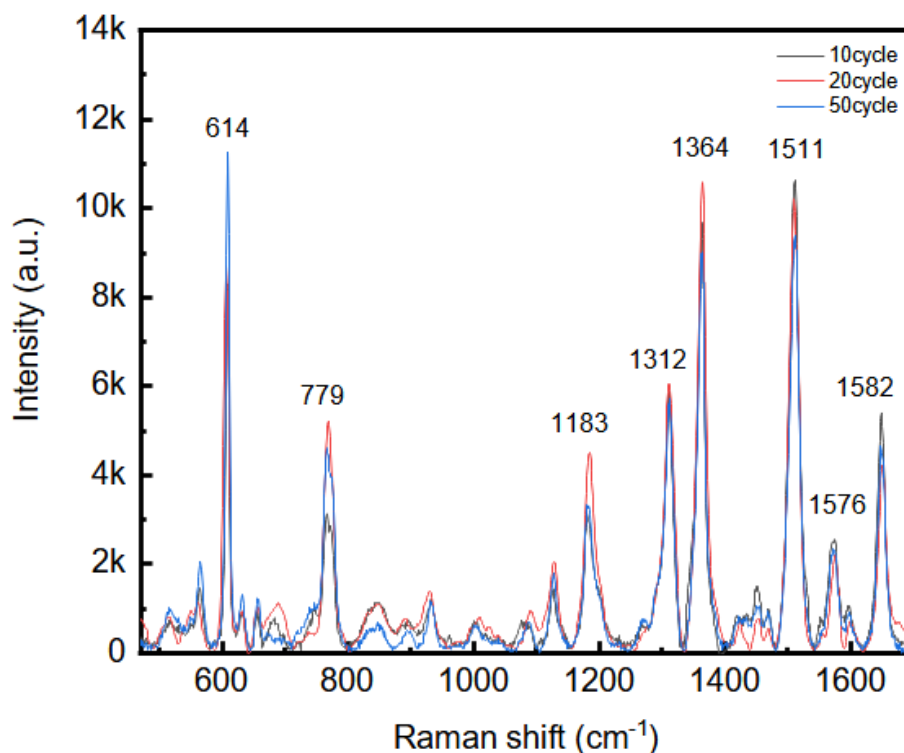


Figure 6 SERS spectra on ALD TiO₂/Ag NP

The SERS signal homogeneity was measured as well by the Raman mapping (**Figure 7**). The 1364 cm⁻¹ peak showed good homogeneity in the area of several tenths of μm.

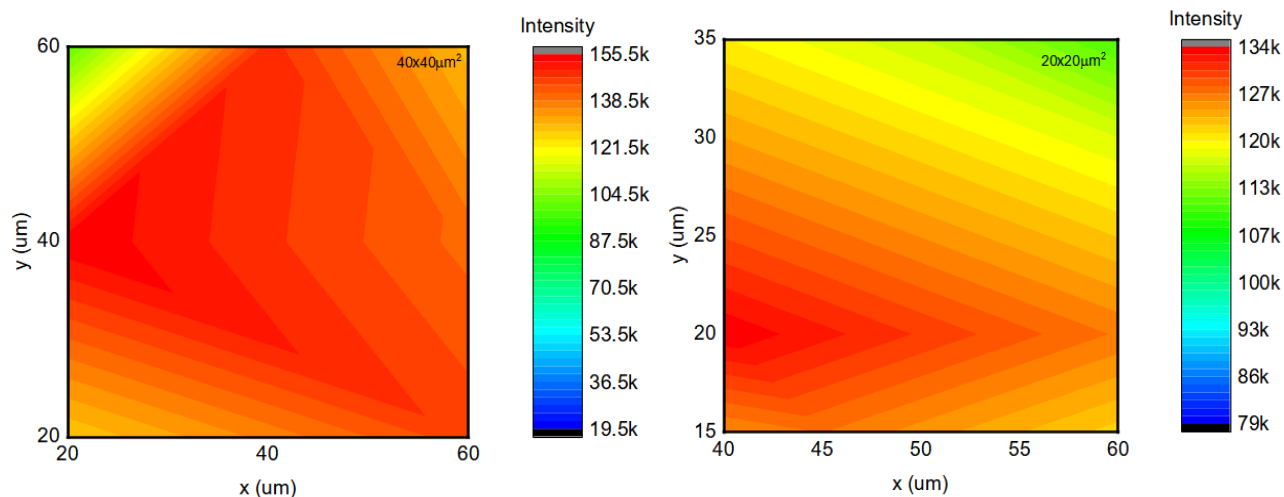


Figure 7 SERS mapping on droplet 50 ALD cycle for 1364 cm⁻¹ (left) and for 1511 cm⁻¹ (right).

4. CONCLUSION

The Raman spectra of the R6G analyte on the pure silicon substrate in comparison with SERS spectra on TiO₂ coated filter paper with Ag NP show the enhancement factor larger than 10⁵. Low costs, thin, and flexible devices are the main advantages of the presented SERS substrate over the conventional 3D designs. The samples with thin ALD TiO₂ coverage have 10 times higher enhancement factor than the samples with

synthesized pristine TiO₂. It probably follows from the retained filter paper 3D structure due to very thin oxide coverage.

ACKNOWLEDGEMENTS

The research has been supported by the grant CTU-NTUST-110-02 of the Joint Research Program between Czech Technical University in Prague and National Taiwan University of Science and Technology, by the student grant of CTU No. SGS20/176/OHK3/3T/13 and by the project Centre of the Advanced Applied Natural Sciences No. CZ.02.1.01/0.0/0.0/16_019/0000778 supported by the Operation Programme Research, Development and Education co-financed by European Community and by Ministry of Education Czech Republic.

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