

PLASMA-ASSISTED SYNTHESIS OF VANADIUM OXIDE/METAL NANOSTRUCTURES FOR SURFACE-ENHANCED RAMAN SCATTERING (SERS) SPECTROSCOPY

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Abstract

Recently, vanadium oxides and other semiconductor substrates have been intensively studied for surface-enhanced Raman scattering (SERS) spectroscopy due to their advantages such as greater uniformity, stability, and measurement reproducibility compared to plasmonic substrates. Combining vanadium oxide substrates with nanostructures of various noble metals has shown promise for enhancing the signal while retaining the previously mentioned advantages. We prepared the substrates for SERS measurements using a novel plasma-based gas aggregation technique, where a silicon wafer was coated with a vanadium pentoxide/metal (Au) composite. In SERS spectroscopy using methylene blue as a testing analyte, we observed a significant enhancement from vanadium pentoxide/Au composite compared to vanadium oxide substrates without noble metals while maintaining spectral stability. These measurements demonstrate the promising potential of vanadium oxide substrates in combination with metal nanostructures for achieving higher signal enhancements and suggest that further research and exploration of alternative material combinations and shapes of nanostructures are promising for advancements in this field.

Keywords: SERS, heterogeneous nanostructures, plasma-based deposition, vanadium oxide

1. INTRODUCTION

Surface-enhanced Raman scattering (SERS) spectroscopy is a significant analytical method for the detection and identification of chemical substances and biomolecules, first discovered in 70' of the last century [1,2]. This method has found applications across various fields, spanning from biochemistry and medicine to materials research.

SERS signal enhancement primarily occurs through two main mechanisms. The most significant contribution comes from the electromagnetic mechanism (EM), which amplifies the signal by interacting with electromagnetic radiation with localized surface plasmons on nanostructures of plasmonic materials, most commonly rare metals such as Ag, Au, and Cu. This allows for an incredibly strong enhancement of up to 10^{10} in regions known as "hot spots." However, plasmonic materials often suffer from poor signal stability and reproducibility [3].

The second contribution to signal enhancement is the chemical mechanism (CM), which typically involves charge transfer (CT) due to the resonance between incident radiation and the surface-molecular complex, but it is considerably weaker than EM (with enhancements typically around 10^3). Nevertheless, because it does not require the presence of "hot spots", it offers better signal stability. Due to the different mechanisms of SERS enhancement, different materials than noble metals must be used. As shown in recent studies, oxides of transition metals represent a highly promising class of SERS-active materials based on CM (e.g., Ta₂O₅ [4], Nb₂O₅ [5] or V₂O₅ [6,7]).

An intriguing approach, therefore, could be the combination of plasmonic and non-plasmonic materials. This study explores the potential of plasma-assisted synthesis of vanadium oxide/metal nanostructures as a method to enhance SERS using rare metals while concurrently preserving the signal stability typical of non-plasmonic materials.

2. EXPERIMENTAL

2.1 Samples preparation

The procedure employed for the preparation of samples is schematically depicted in **Figure 1**. Vanadium nanoparticles (NPs) were produced using an original custom-built gas aggregation source (GAS) of NPs identical to the one described in detail in our previous work [8]. The nanoparticle source was based on a 3-inch, water-cooled planar magnetron equipped with a 0.125-inch-thick vanadium target (declared purity of 99.9% purity, Kurt J. Lesker Ltd) and powered by a DC power source (MDX 500, Advanced energy). The magnetron was mounted into a water-cooled, stainless steel aggregation chamber 100 mm in diameter and ended with a focussing orifice (20 mm long and 3.5 mm in diameter). The whole GAS was mounted onto a main deposition chamber, which was pumped by turbomolecular (TMH 261 P, Pfeiffer) and scroll (XDS 10, Edwards) pumps to a base pressure of 10^{-3} Pa. Vanadium NPs were deposited onto one-side polished Si substrates (thickness 525 ± 25 μm , MicroChemicals GmbH). The substrates to be coated were introduced into the main deposition chamber by a differentially pumped load-lock system and positioned at a distance of 150 mm beneath the exit orifice of the GAS. V NPs were produced using Ar as a carrier gas (gas flow 4 sccm, pressure in the aggregation chamber 40 Pa) and at magnetron current of 300 mA, i.e., under the conditions previously reported to ensure stable and efficient synthesis of V NPs [8]. The deposition time of V NPs was 120 seconds in this study.

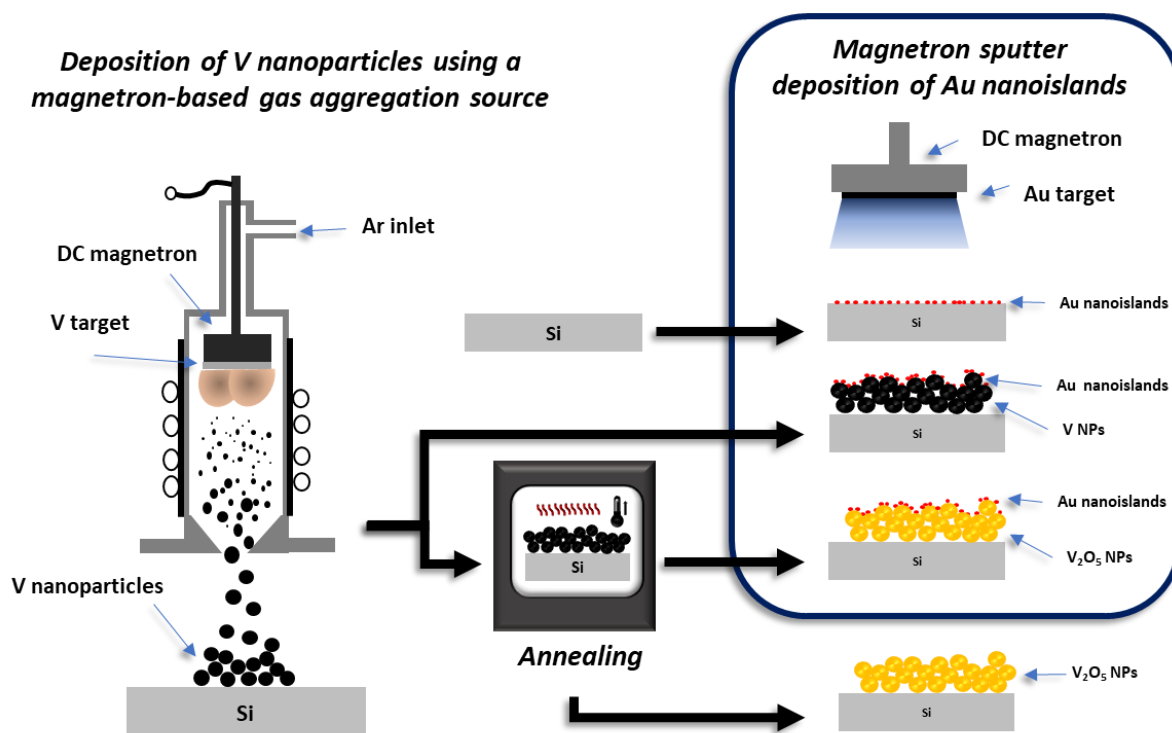


Figure 1 Schematic representation of the procedure used for the preparation of samples.

In order to transform vanadium NPs into vanadium pentoxide ones, the as-deposited nanoparticle films were annealed in an industrial furnace (MP05-0.1, Alexandr Martínek Laboratorní pece) on air. Based on the

previous investigations, the annealing temperature was 450 °C and the annealing time was 60 minutes, which led to the complete structural transformation of predominately metallic V NPs to purely crystalline V₂O₅ NPs [9].

The gold nanoislands, selected as a model plasmonic material that exhibits SERS activity due to the EM mechanism, were deposited either on Si substrates or Si substrates precoated with vanadium or vanadium pentoxide nanoparticle films. The Au deposition was performed in a separate high-vacuum deposition chamber. This chamber, which was pumped by turbomolecular (TMH 261 P, Pfeiffer) and scroll (XDS 10, Edwards) pumps to a base pressure of 10⁻³ Pa, was equipped with a 2-inch planar magnetron with Au target (thickness of 0.125 inches, declared purity 99.99%, Safina a.s.). The deposition was performed in Ar, at a pressure of 3.5 Pa, gas flow rate of 5 sccm, and magnetron current of 100 mA. The deposition time was 90 seconds.

The morphology of Au, vanadium, V₂O₅, Au/V and Au/V₂O₅ samples was evaluated using a field-emission scanning electron microscope (SEM, JSM-7200F JEOL) operated in secondary electron mode. The SEM imaging was performed at an accelerating voltage of 20 kV and a working distance of approximately 10 mm.

2.2 SERS measurements

As a test molecule for measuring SERS spectra, we selected methylene blue (MB) purchased from Sigma-Aldrich. To record the spectra, we used an integrated Raman system LabRAM HR800 (Horiba Jobin-Yvon) equipped with a confocal microscope connected to a spectrograph with an 800 mm focal length. We employed an integrated He-Ne laser with a wavelength of 632.8 nm as the excitation source, which was directed through a confocal slit with a width of 400 μm and focused by a 100x objective onto the prepared sample. The laser power at the sample was ~2 mW. The scattered light was further directed to a Czerny-Turner spectrograph with a grating of 300 grooves/mm and recorded by a CCD detector cooled with liquid nitrogen. For SERS measurements, MB was pipetted in a volume of 5 μl of an aqueous solution with a concentration of 10⁻⁶ M and left to dry at room temperature.

3. RESULTS AND DISCUSSION

As can be seen in **Figure 2**, where are presented examples of SEM images of V NPs acquired immediately after their deposition and after their annealing in the air at the temperature of 450 °C for 30 minutes, the originally close-to-spherical V NPs (mean diameter of 40 nm) undergo upon heating significant morphological changes; the NPs grow into much bigger rod-like structures with lengths exceeding 100 nm. As demonstrated in our previous study [9], such changes in the morphology of the samples are accompanied by the structural transformation of initially metallic NPs into fully crystalline vanadium pentoxide NPs. Despite these changes, the NPs films retain their high porosity characterized by a high surface-to-volume ratio, i.e., a property that assures a large amount of analyte-surface interaction sites needed for an effective photoinduced CT required for CM SERS enhancement.

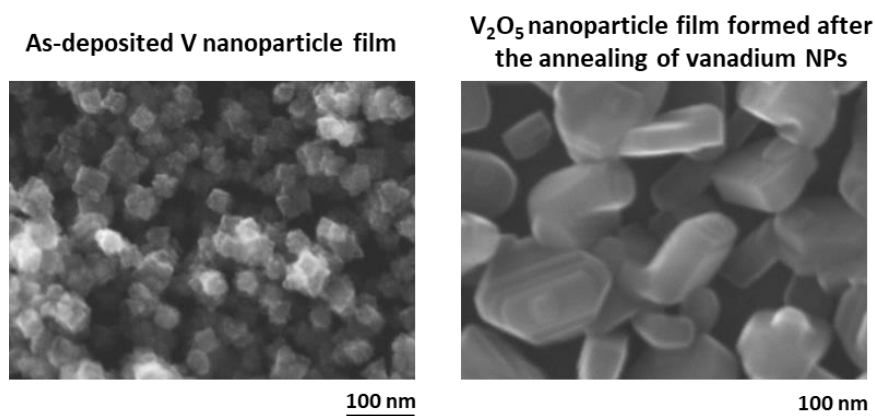


Figure 2 SEM images of as-deposited (left) and annealed (right) vanadium NP films.

In order to demonstrate the possibility of enhancing the SERS performance by combining the V_2O_5 NPs with noble metal nanostructures, pristine Si wafers and Si wafers coated either with V or V_2O_5 NPs were sputter coated with Au. Under the deposition conditions employed in this study, the sputtered Au formed on all three types of substrates inhomogeneous film of Au nanoislands. This is well-visible in **Figure 3**, where corresponding SEM images are presented. However, the morphology of Au nanoisland films differs for pristine Si used as a substrate and on V and V_2O_5 NPs, whereas on Si substrate Au forms relatively large, interconnected grains, considerably smaller Au nanostructures were observed on both types of NPs films. This difference is due to the larger surface area of NPs films as compared to the smooth substrate. Because of this, the larger surface area implies under the same fluence of Au atoms a lower number of incoming Au atoms per unit area that does not allow in our case formation of larger Au grains at the nanostructured surface of NPs films.

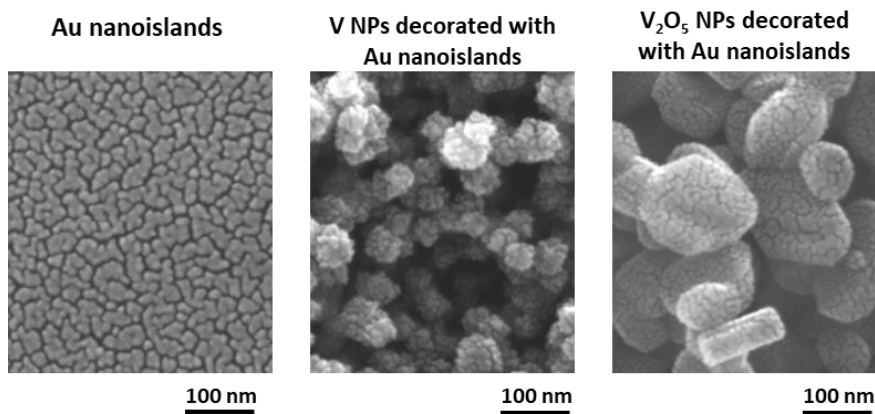


Figure 3 SEM images of Au nanoislands on a flat Si substrate (left), V NPs films decorated with Au nanoislands (middle) and V_2O_5 NPs film decorated with Au nanoislands (right).

The final step was the comparison of SERS activity of Au nanoislands, V_2O_5 NPs without Au, and V and V_2O_5

NPs decorated with gold. The result is depicted in **Figure 4**, where SERS spectra acquired for the same concentration of MB are presented together with a magnified part of the spectra that corresponds to the C-C ring stretching band of MB. As can be seen, neither Au nanoislands alone nor V_2O_5 NPs provide an intense SERS signal corresponding to MB. A slightly higher MB signal was observed when Au was deposited onto metallic V NPs. This enhancement is most likely connected with the highly nanostructured character of this substrate that facilitates the formation of “hot spots” between individual Au nanostructures. However, a dramatic increase in the MB signal is evident when Au nanoislands are deposited onto V_2O_5 NPs; the intensity of the MB band at about 1630 cm^{-1} [10] is an order of magnitude higher as compared to all other samples.

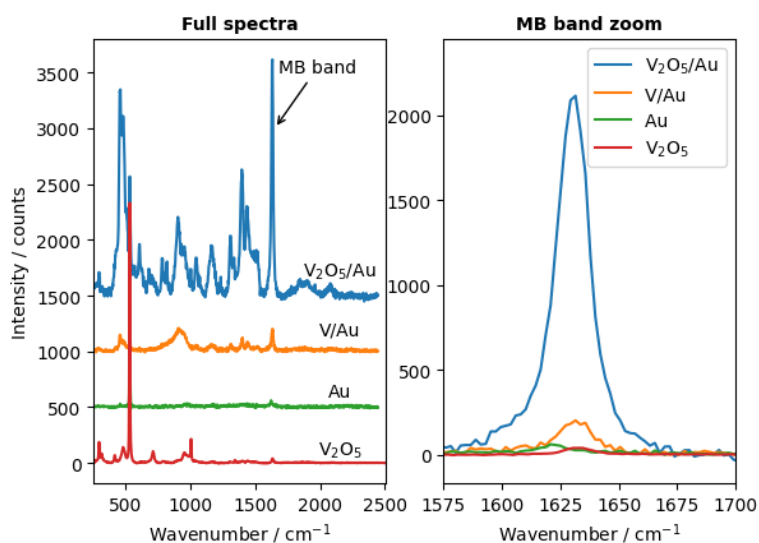


Figure 4 Full SERS spectra of V_2O_5 NP film (V_2O_5), Au nanoislands (Au), V NPs with Au nanoislands and V_2O_5 NPs with Au nanoislands (V_2O_5 /Au) (left). The zoom of the MB band (right).

4. CONCLUSION

To conclude, it was demonstrated that the V₂O₅ NPs decorated with plasmonic Au nanoislands are capable of dramatically enhancing the SERS signal of MB as compared either to Au nanoislands or V₂O₅ NPs alone. Such an enhancement is believed to benefit from the mutual interaction of plasmonic metals with semiconducting metal-oxides and their nanostructured character. Furthermore, due to the relative simplicity of the deposition procedure that does not require any solvents or linkers as well as due to the recent progress in the synthesis of various metal-oxide NPs by gas aggregation sources, the proposed approach is believed to be applicable for a wide range of different combinations of plasmonic metals and metal oxides that can result in the development of novel highly SERS-active platforms urgently needed for ultrasensitive detection.

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