Project Title (Project 81927): **A New Method for In-situ Characterization of Important Actinides and Technetium Compounds via Fiberoptic Surface Enhanced Raman Spectroscopy** (SERS)

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Progress Report:

RESEARCH OBJECTIVE

This project serves to fill information gap through the development of a novel surface-enhanced Raman scattering (SERS) spectroscopy to selectively and sensitively monitor and characterize the chemical speciation of radionuclides at trace levels. The SERS technique permits both of these measurements to be made simultaneously, and results in significant improvement over current methods in reducing time of analysis, cost, and sample manipulation. Our overall goal is (a) to develop a scientific basis for this new methodology to detect radionuclides via SERS and (b) to rationally synthesize and evaluate novel sol-gel based SERS substrates tailored to sensitively detect and characterize inorganic radionuclides such as TcO_4^-, actinyl ions (e.g. UO_2^{2+}, NpO_2^+, and PuO_2^{2+}) and other chemical compounds of interest.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes the research after the third year of a three-year project. We have developed SERS substrates coated with dielectric layers to improve the stability of SERS substrates. Surface sol-gel (SSG) and atomic layer deposition (ALD) methods were utilized to prepare thin titania layer on Ag substrates, such as Ag island films. These two coating techniques have the advantage for generating very thin films with the film thickness controlled at molecular level. The ultrathin oxide layers provide protection buffer layers to the metallic SERS substrates. The titania-coated Ag substrates were demonstrated to be SERS active. The current research areas are:

(1)**Improvement of the stability of SERS substrates via surface sol-gel process**: Three SERS active substrates were prepared. Ag island films and Ag-coated silica beads were prepared by depositing Ag particles to glass slides and silica beads with thermal vapor deposition method. Au colloid substrate was prepared by assembling Au colloid to 3-aminopropyltrimethoxysilane (APS) modified glass slides. Surface sol-gel process was then applied to pepare thin titania layer on these SERS active substrates. These titania-coated silver substrates were found to be SERS active when using Rhodamine 6G as a probe molecule. These three substrates were compared and Ag island film is the most sensitive one (Fig.1). The enhancement of Raman scattering is inversely proportional to

the thickness of the titania film, which is consistent with the decay of electromagnetic enhancement. A substantial improvement in the film was achieved as a result of the enhanced stability of this substrate.

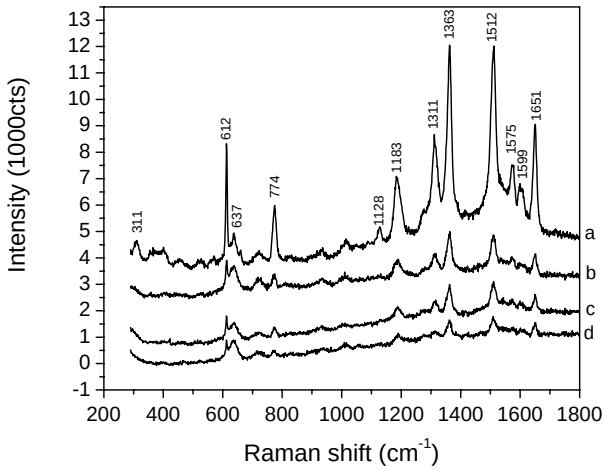

Figure 1. SERS spectra of R6G adsorbed onto silver-island films coated with titania using the SSG process: a) bare silver, b) with one layer of TiO_2, c) with two layers of TiO_2, d) with three layers of TiO_2. The concentration of R6G was 1×10^{-4} M.

(2)**Titania coated Ag island film prepared by atomic layer deposition method**:
The atomic layer deposition (ALD) method is similar to surface sol-gel method but performed in gas phase. In this year, ALD was used for the first time to coat thin titania layers on Ag island films. The substrates characterized using rhodamine 6G as a molecular probe were SERS active (Fig.2). The stability of the substrates was greatly improved. A paper describing these results was submitted to *Israel Journal of Chemistry.*

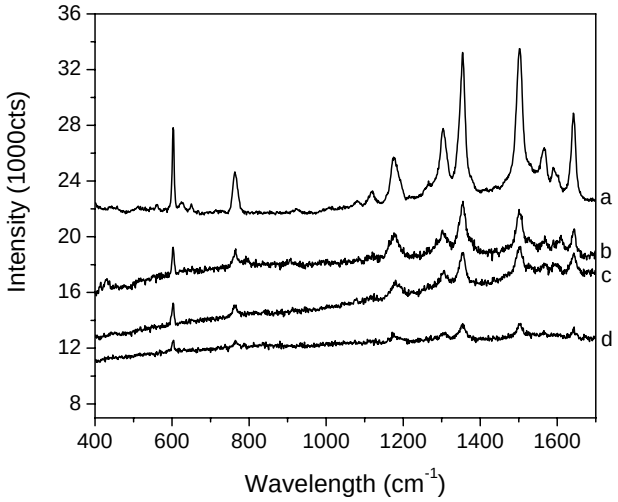

Figure 2. Raman spectra for R6G on titania-coated silver island films using the ALD process: a) MET modified silver, b) 12 cycles, c) 24 cycles, and d) 36 cycles.

PLANNED ACTIVITIES

Efforts will be made to improve the uniformity of Ag-doped sol-gel substrates. Spin coating will be used to cast sol-gel SERS films and various reduction methods such as gas-phase reduction will be used to reduce Ag ions.