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 research of the third year of a three-year project. We have developed a new class of SERS substrates based on silver-coated zeolite films and a cation selectivity in SERS detection has been demonstrated. The combinatorial method of high-throughput synthesis and screening of sol-gel films was initialized and tested for viability, and the methodology was developed and instituted as a foundation for generating sol-gel libraries of SERS substrate responses to actinides. Preliminary experiments have been conducted to further improve the stability of SERS substrates via the surface sol-gel process. The current focus areas are:

(1) **Development of silver-coated zeolite crystal film as a SERS substrate for selectively detection of uranyl:** A novel silver-coated zeolite substrate, which is a crystalline aluminosilicate with unique pore structures, was prepared by a physical vapor deposition procedure. The large surface area and cation-exchangeability of zeolite materials enhance the adsorption of small cationic molecular species such as uranyl ions (UO_2^{2+}), leading to an increased SERS sensitivity. Zeolite A nanocrystals were first synthesized hydrothermally followed by dispersion in ethanol and deposition onto a glass slide to form a film. Silver was deposited onto the zeolite film by using a vacuum evaporator. This substrate was active for the enhancement of Raman scattering of uranyl ions and a band at approximately 720 cm^{-1} assigned to the symmetric stretch of O=U=O was observed (Figure

1). The detection limit obtained was ~10^{-5} M. An important advantage of the zeolite-based substrate is that the negatively charged framework of the zeolite provides selectivity to adsorption based on static electric forces. The SERS effect for positively charged uranyl ions was approximately 100 times greater than the corresponding effect for neutrally charged benzoic acid. A paper describing these results was published. (*Appl. Spectrosc.* **2004**, *58*, 18-25.)

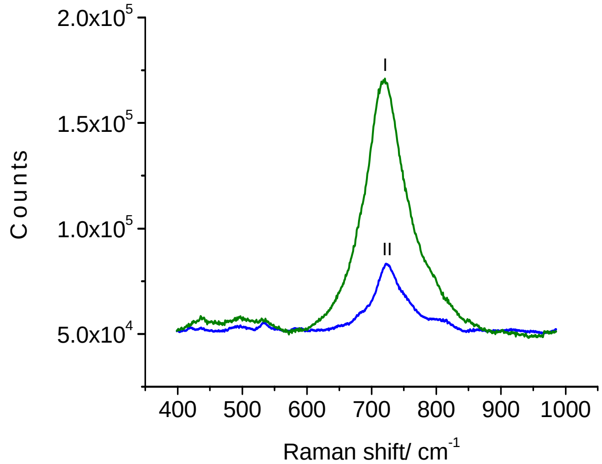

Figure 1. SERS spectra of uranyl adsorbed on Ag-coated zeolite A film, uranyl is 10^{-4}(I) and 10^{-5} M

(2)**Establishment of the combinatorial methodology for synthesizing sol-gel silver films**: The physical properties of sol-gel films and the embedded silver particles, such as silver particle size and morphology, and film stability, are primarily determined by the composition of the silver-doped sol-gel. In order to fully investigate the effect of these compositional variations on the SERS response and to optimize the substrate for maximum sensitivity, it is necessary to measure the SERS signal of a test molecule as the concentrations of every components are varied. This is an extremely difficult and time-consuming task. Our approach to this problem is the development of a combinatorial methodology that utilizes an automated liquid handling instrument to dispense a predetermined amount of each component into a standard 96-well microtiter plate where each well contained some compositional variations. A small quantity of each combination was dispensed onto a microscope slide using a second automated instrument. Figure 2 shows a picture of two slides that were synthesized according to this procedure where each spot represents a distinct compositional variation. These films exhibited a response to both benzoic acid and uranyl that was comparable to the larger films synthesized in the traditional manner. Thus, we have successfully reduced the size of each film to a 500µm spot and demonstrated the use of the combinatorial methodology for preparing SERS-active substrates. There are a number of clear advantages associated with the combinatorial methodology including (1) a large number of films can be quickly and easily synthesized and deposited onto a single slide and (2) the effect of compositional variations on the SERS response can be readily investigated. Finally, this methodology can be viewed as a precursor to a large scale production of SERS-active films.

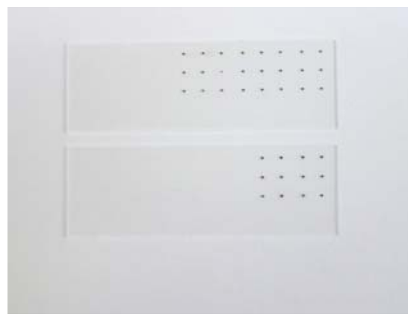

Figure 2. Picture of two slides of SERS active substrates where each spot represents a compositional variation.

(2)**Further improvement of the stability of SERS substrates via the surface sol-gel process**: Preliminary experiments have been conducted to further improve the stability of SERS substrates via the surface sol-gel process. Silver island films prepared by the physical vapor deposition method were coated with a controlled titania layer by the surface sol-gel method. The titania-coated silver island films were found to be SERS active when using Rhodamine 6G as a probe molecule. 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 compared to the silver island films without a titania coating (Figure 3). A paper describing these results will be publised. (*Anal. Chem.* **2004**, ASAP.)

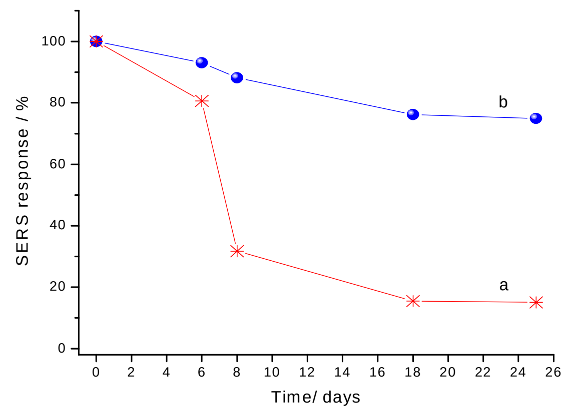

Figure 3. Stability of silver island film. (a) bare Ag film, (b) coated with 1 layer of TiO_2. The concentration of R6G is 1×10^{-4} M.

PLANNED ACTIVITIES

In the next year, molecular recognition will be introduced into SERS substrates to further develop and optimize SERS substrates tailored for detection and characterization of radionuclides relevant to DOE high-level wastes.