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.

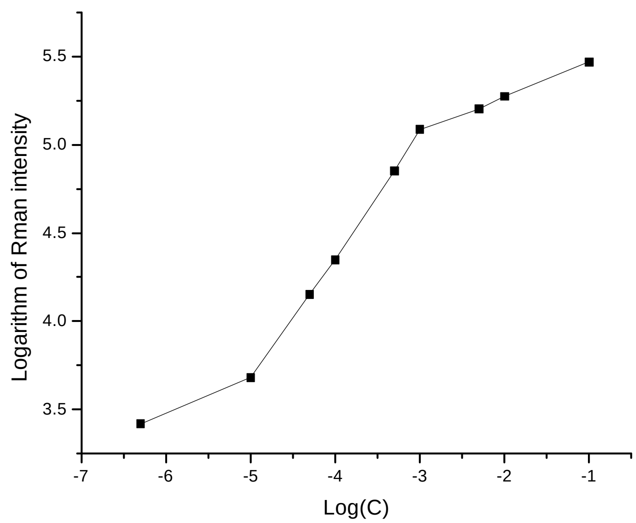
RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes research of the first 9 months of a three-year project. We have successfully prepared a variety of sol-gel SERS substrates for sensitive detection of our target radionuclides. The current focus areas are :

(1) **Synthesis of amine-functionalized sol-gel substrates**: Amine-functionalized sol-gel substrate was prepared by using silver nitrate, 3-aminopropyltriethoxysilane (APTS), ethanol, tetraethyl orthosilicate (TEOS). The silver ion was then reduced by sodium borohydrate. In the sol-gel process, the amine group was covalently linked to the backbone of the sol-gel and can be permanently fixed in the sol-gel matrix. The doped amine group interacts strongly with some species of radionuclides, thereby enhancing their adsorption affinity on the SERS substrate. Accordingly, the selectivity and sensitivity of the SERS substrate can be increased. The substrate was utilized to detect uranyl ions and a detection limit of 10^{-5} M was obtained. Heating of the film at 300° C was found to be helpful to increase the sensitivity because of the remove of some interference organics.

(2) **Development of sol-gel nanoparticles coated with silver for SERS application**: Monodisperse silica nanoparticles were prepared by the hydrolysis of tetraethyl orthosilicate (TEOS) in aqueous ethanol solutions containing ammonia (Stober synthesis). The silica beads were then coated with

silver by vacuum deposition method. The silver film on the silica beads was found to be a good SERS substrate. This substrate was first applied to detect benzoic acid and a detection limit of 5×10^{-7} M was obtained. The sensitivity is better than that of our sol-gel substrate (detection limit of 10^{-6}M by silver- doped sol-gel film). The experimental parameters including Ag film thickness and the size of silica bead were optimized. The SERS response reached a maximum value with the increase of thickness of Ag. Excessive coating of Ag resulted in a decrease of the response, which may be due to the decrease of the surface roughness. The sizes of the silica beads were varied from 200 nm to 800 nm. The maximum response was obtained with the silica beads of 800 nm.



Calibration curve of Raman detection of benzoic acid.
Silica bead is 700nm and Ag film with deposition time of 40min.

PLANNED ACTIVITIES

In the next few months, we will apply the substrate of sol-gel nanoparticles coated with Ag for the uranyl detection. The method of sonochemical deposition of silver nanoparticles on silica beads will be explored to prepare the SERS substrate.