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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Principal Investigator: Sheng Dai
Chemical Sciences Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831
Tel: (423) 576-7307
E-mail: i9d@ornl.gov

Co-Principal Investigator: B. Gu

Postdocs: Lili Bao.

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 year after the first 9 months of a three-year project. We have successfully prepared silver-doped sol-gel SERS substrates with acid-catalyzed procedure. This type of substrates is very sensitive to uranyl and neptunyl ions. The current focus areas are:

(1) **Preparation of silver-doped sol-gel film as a SERS substrate for sensitive detection of uranyl and neptunyl ions**: Silver-doped sol-gel substrates were prepared with an acid-catalyzed sol-gel procedure. Sols containing silver ions were prepared by mixing tetramethyl orthosilicate (TMOS), water, nitric acid, silver nitrate, and Tween 80. The sols were cast on glass slides to form xerogel films. Subsequently, the silver ions in the films were reduced by sodium borohydride to produce silver particles. These substrates were very sensitive for the enhancement of Raman signals from uranyl. (see the SERS spectrum shown in Fig.1, uranyl Raman peak around 710 cm^{-1}). A detection limit of 8.5×10^{-8} M was achieved. There is a great improvement in the sensitivity compared to previous silver-coated silica bead substrates whose detection limit is 10^4 times lower. The new substrates were further applied to study the Raman spectrum of another actinyl ion (Neptunyl). A strong SERS signal for neptunyl ions was observed (see Figure 2, neptunyl peak around 680 cm^{-1}). This is the first observation of SERS for neptunyl ions. Accordingly, the SERS technique provides a new sensitive method for characterization and detection of

neptunyl ions. Being different from uranyl ions, neptunyl ions don't fluoresce under normal conditions so that neptunyl ions cannot be characterized by the fluorometric method. In this case, the applications of the SERS detections offer significant advantages.

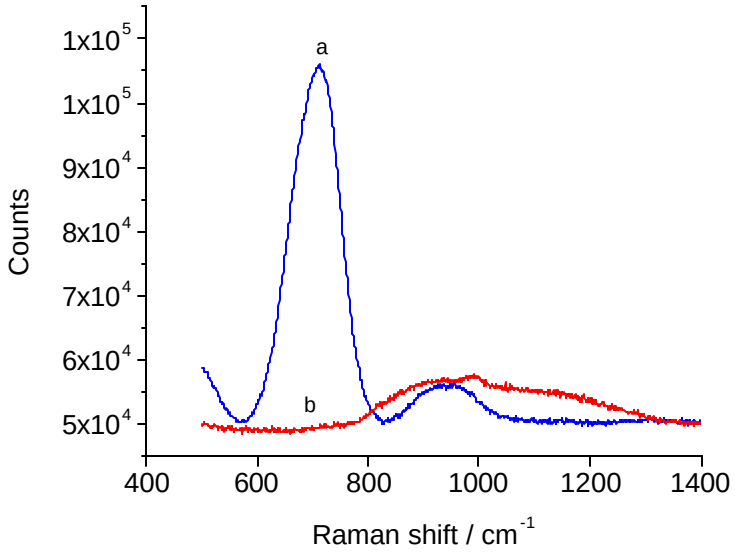

Fig.1 SERS spectrum of (a) uranyl (8.5×10^{-6} M) adsorbed onto the silver-doped sol-gel substrate (b) substrate in the absence of uranyl

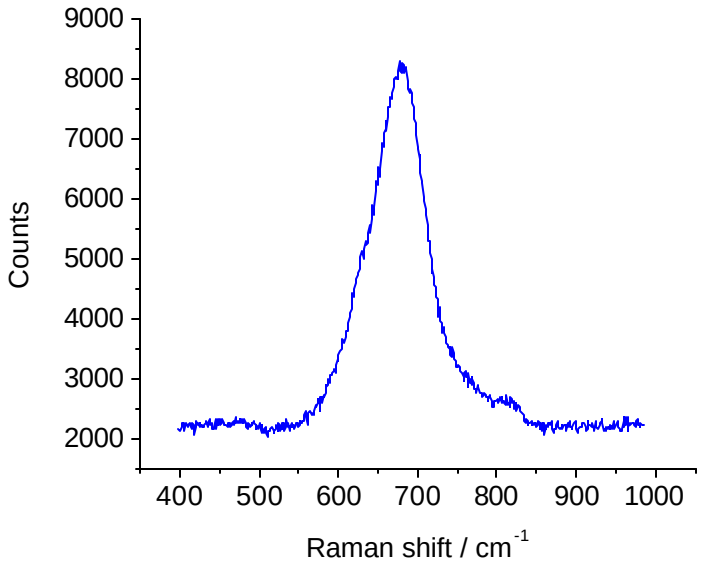

Fig.2 SERS spectrum of Neptunyl, contains 0.08 μCi Neptunium 237 in 0.1 M HCl

(2) **Characterization of uranyl ion complexation with humic acid by SERS**: The complexation of natural humic substances with uranyl ions is very important for understanding the migration of uranium species in the geosphere. The new silver-doped sol-gel substrates were applied to characterize such complexes. A very strong SERS signal from uranyl ions and a complex feature from humic acid were

observed (seeeFigure 3, uranyl Raman peak around 708 cm^{-1}; humic acid peaks at 1370 and 1580 cm^{-1}). Compared with the currently used technique of fluorimetry and UV-Vis absorption spectrometry, SERS is advantageous that it can provide not only the structural changes of the uranyl species, but also those of humate ligands in the complexes.

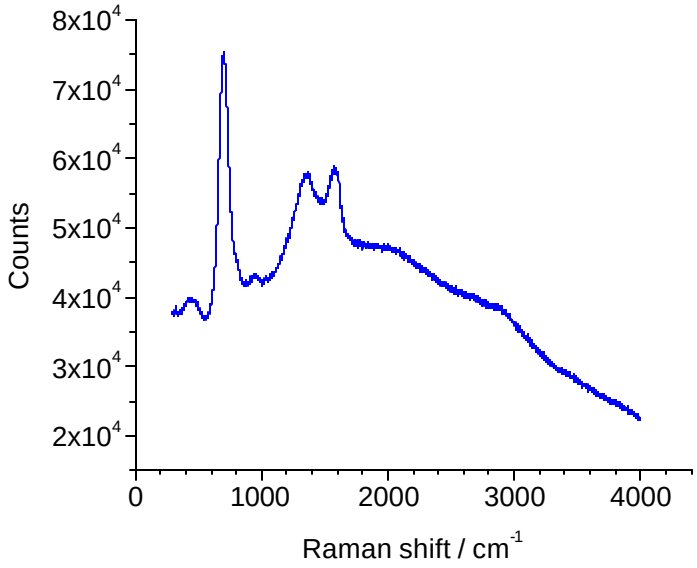

Fig.3 SERS spectrum of complex of uranyl (10 ppm) with humic acid (10 ppm)

PUBLICATION

Li-Li Bao, Shannon M. Mahurin, Cheng-Du Liang, Sheng Dai, "Study of silver films over silica beads as a surface-enhanced Raman scattering (SERS) substrate for detection of benzoic acid," *J. Raman Spectr.* 2003, *34*, 394-398

PLANNED ACTIVITIES

In the next year, several other types of SERS substrate will be explored such as gold-doped sol-gel films, silver and gold nano-rod and nano-wire arrays in sol-gel matrix.