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

Sheng Dai, Baohua Gu, and LiLi Bao

Chemical Sciences Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831

dais@ornl.gov, 865-576-7307
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Background

In-situ characterization of actinides and technetium compounds in high level wastes is essential to achieve shorter turn-around times for analytical results or to facilitate tank closure after retrieval. Currently, techniques for monitoring and characterizing radionuclides rely primarily on

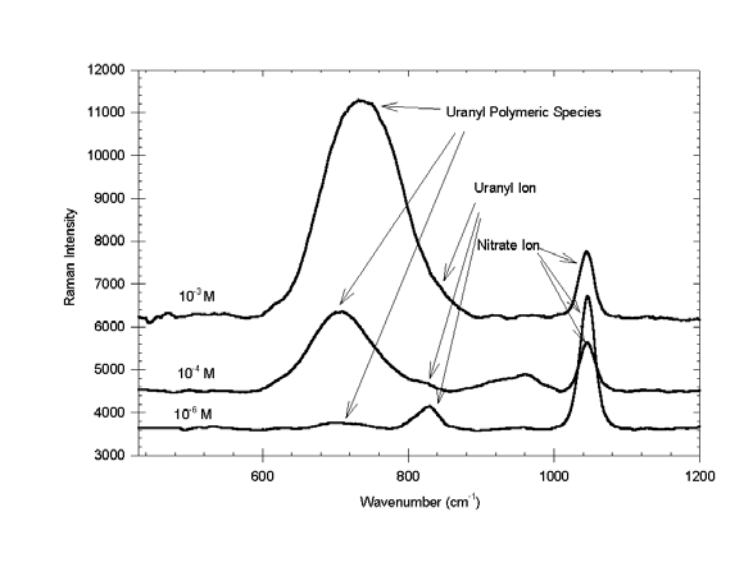
- **liquid scintillation counting,**
- **ICP-MS, and**
- **some limited use of the spectrofluorimetry.**

These techniques require chemical handling, e.g., the use of complexing media, scintillation cocktails, phosphoric acids, in order to enhance signals. Furthermore, only fluorescent radionuclides [UO_2^{2+}, Cm(III), Am(III)] can be detected by the last technique. **Many environmentally-important radionuclides such as plutonium, neptunium, and technetium species have no strong fluorescence signals and therefore can not be characterized via fluorescence spectroscopy.**

Objectives

- To develop a scientific basis for a new methodology to sensitively detect and characterize radionuclides such as actinyl ions (e.g. UO_2^{2+}, NpO_2^{+}, and PuO_2^{2+}) and TcO_4^{-} via SERS
- To incorporate molecular recognition into sol-gel SERS substrates to further improve selectivity and sensitivity

SERS Spectra of UO_2^{2+}
Dai, S, et. al *Appl. Spectrosc.*, **1996**, 50 (4), 536



This proposed research serves to fill this 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**.

Four principal sets of results are expected from this research:

- A new and highly-sensitive methodology for radionuclide monitoring and characterization at the molecular level will be developed via SERS. No inherent chemical handling, such as the addition of chelating agents, is required in this method.
- Structural information concerning speciation and chemical states of important radionuclides (e.g., TcO_4^-, UO_2^{2+}, NpO_2^+, and PuO_2^{2+}) obtained via SERS will provide essential information to cost-effectively remediate and separate the radionuclides from contaminated media.
- This research will lead to a new generation of SERS substrates and a combinatorial chemical methodology for developing and evaluating chemical sensors.
- The interface of our SERS substrates with fiberoptic instrumentation for remote *in-situ* sensing will be conducted to gain understanding of speciation of radionuclides under real environmental conditions.

Why SERS?

- **The majority of the radionuclide species relevant to the DOE environmental problems exist in forms of <u>distinct covalent molecular groups</u> under most environmental conditions.**

  Uranium, neptunium, and plutonium are present under most environmental conditions as monomeric or polymeric actinyl (MO_2^{2+} or MO_2^{+}) species. The oxygen-actinide bond in this group is known to be strongly covalent in nature. For instance, the bonding energy of U=O in uranyl ion is very close to that of the carbon-oxygen bond in CO_2.

  - **Denning, R.G., "Electronic Structure and Bonding in Actinyl Ions," in Structure and Bonding, Springer-Verlag:Berlin, Vol 79, 1992, p216.**
- **Large Raman cross sections**
- **Extremely Sensitive Molecular spectroscopy**
  - **Single molecule detection**

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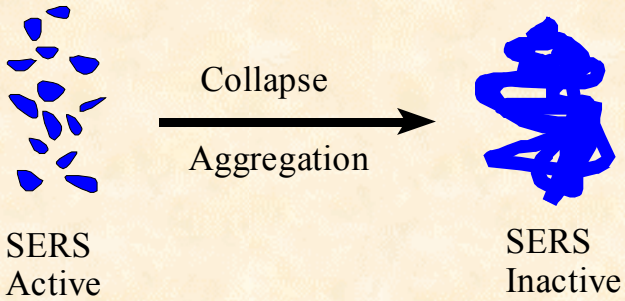
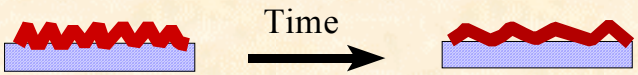
Problems With Conventional SERS Substrates

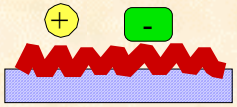
- Colloidal Solution



- Silver SERS Films



- No Molecular Recognition

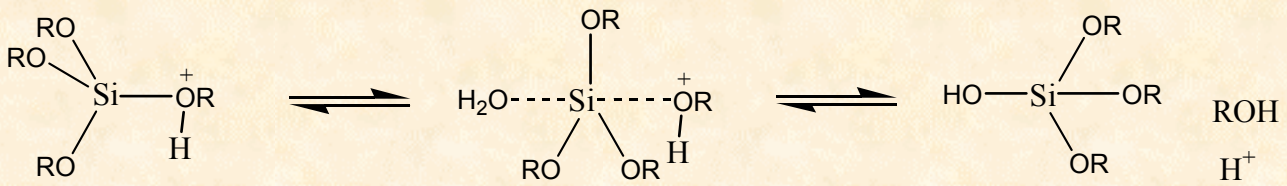


Two Strategies

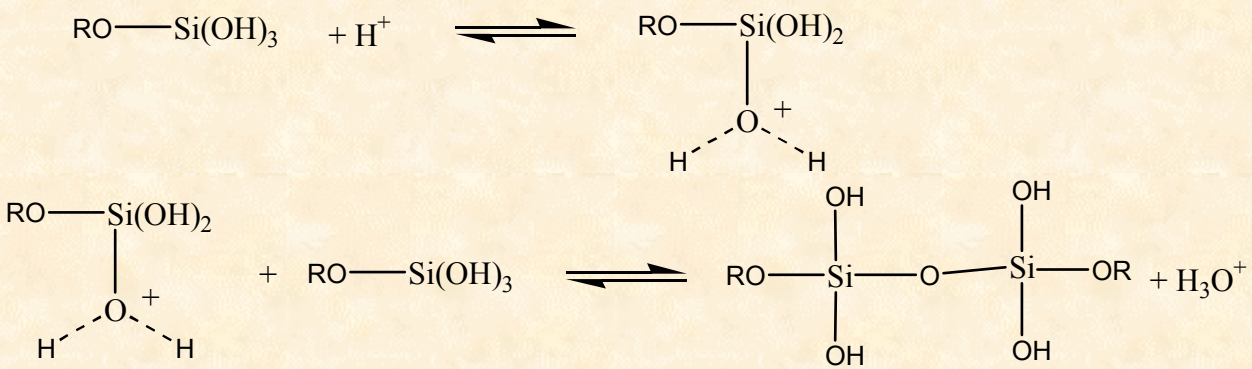
- SERS films prepared by Sol-gel methodologies
  - Isolated Ag particles
  - Functionalities
  - Potential combinatorial search
- SERS films prepared by coating Ag on nanostructured materials
  - Stabilities
  - Functionalities

Sol-Gel Preparation of Materials

Acid-Catalyzed Hydrolysis

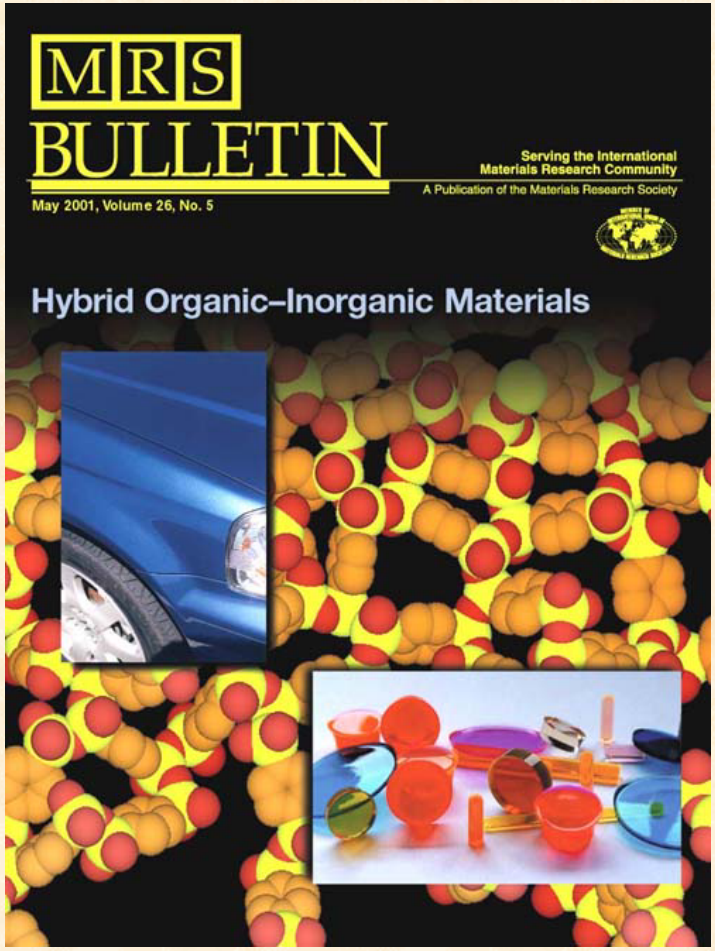


Acid-Catalyzed Condensation

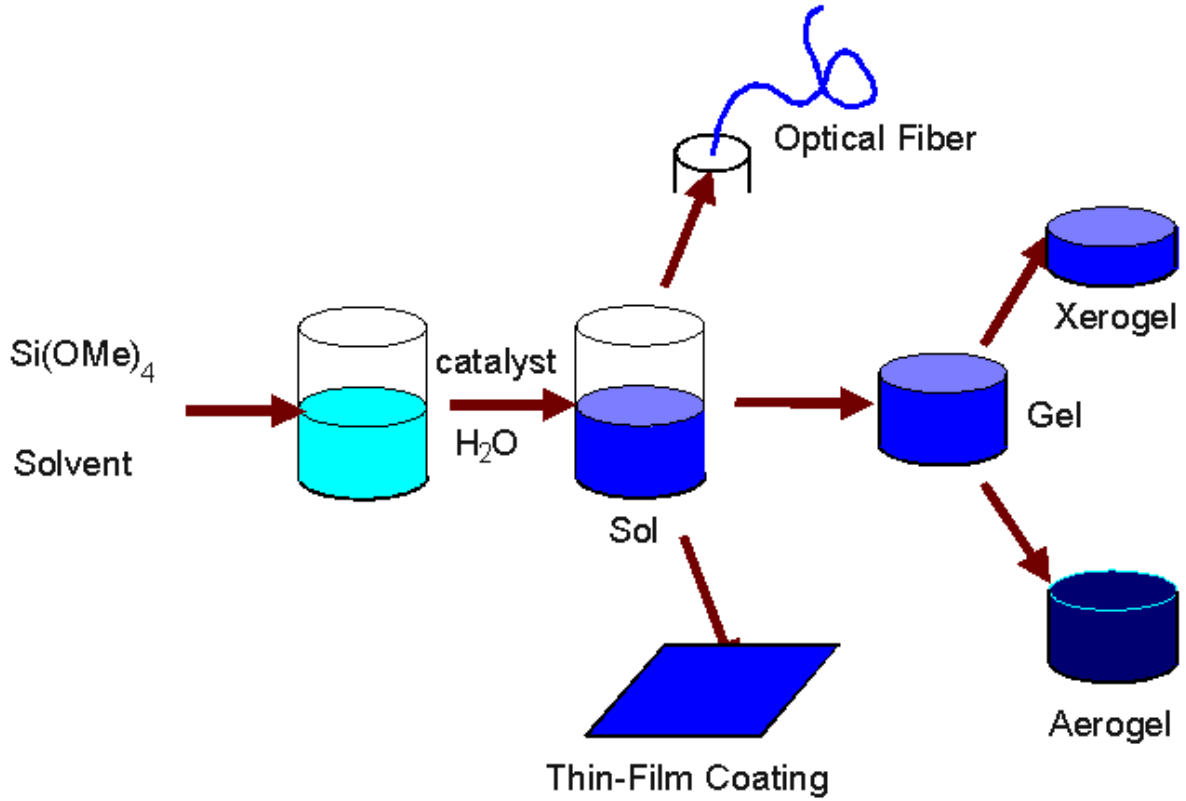


Why Sol-Gel Materials?

- Room-Temperature Processing
- Inexpensive
- Transparent
- Compatible with Inorganic and Organic Dopants

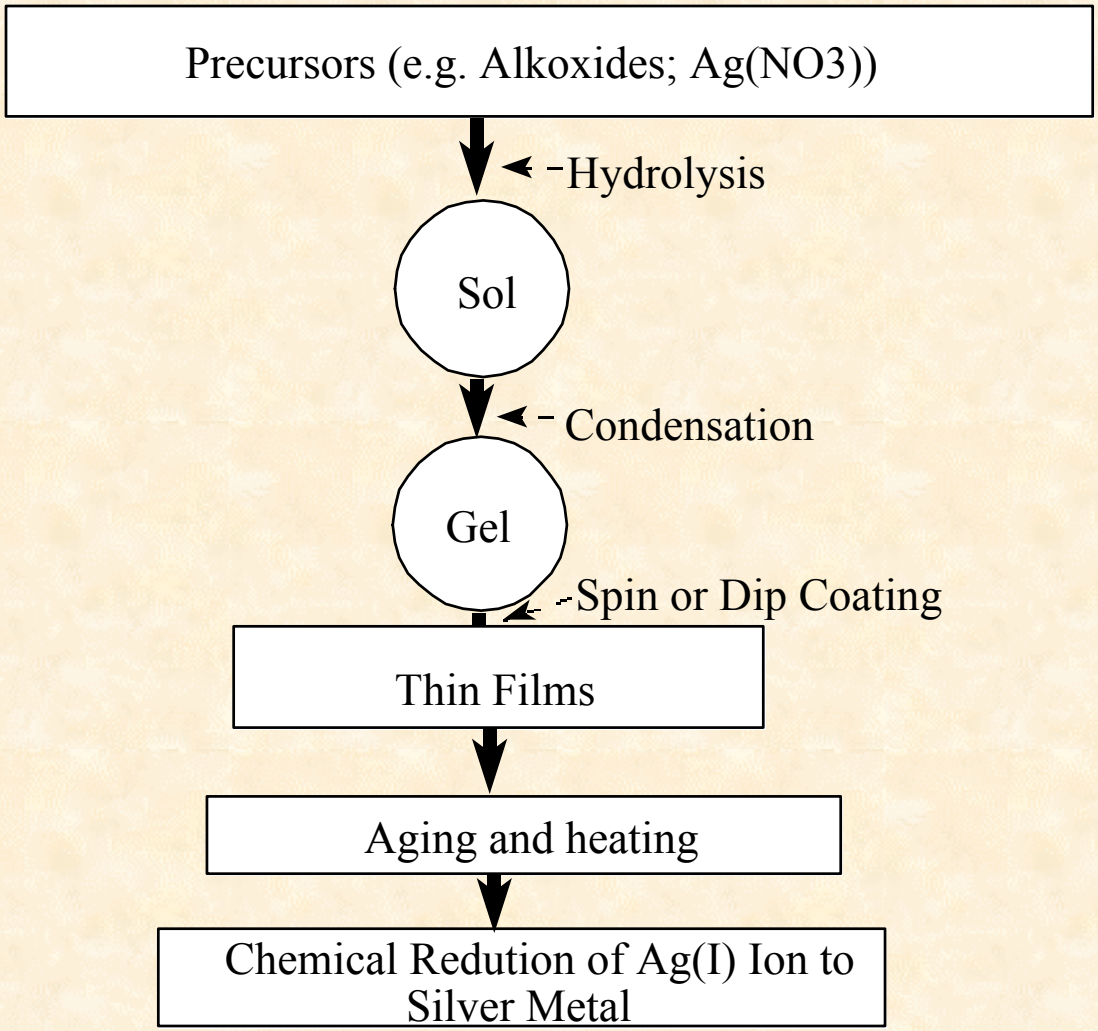


Materials Derived From Sol-Gel Processing



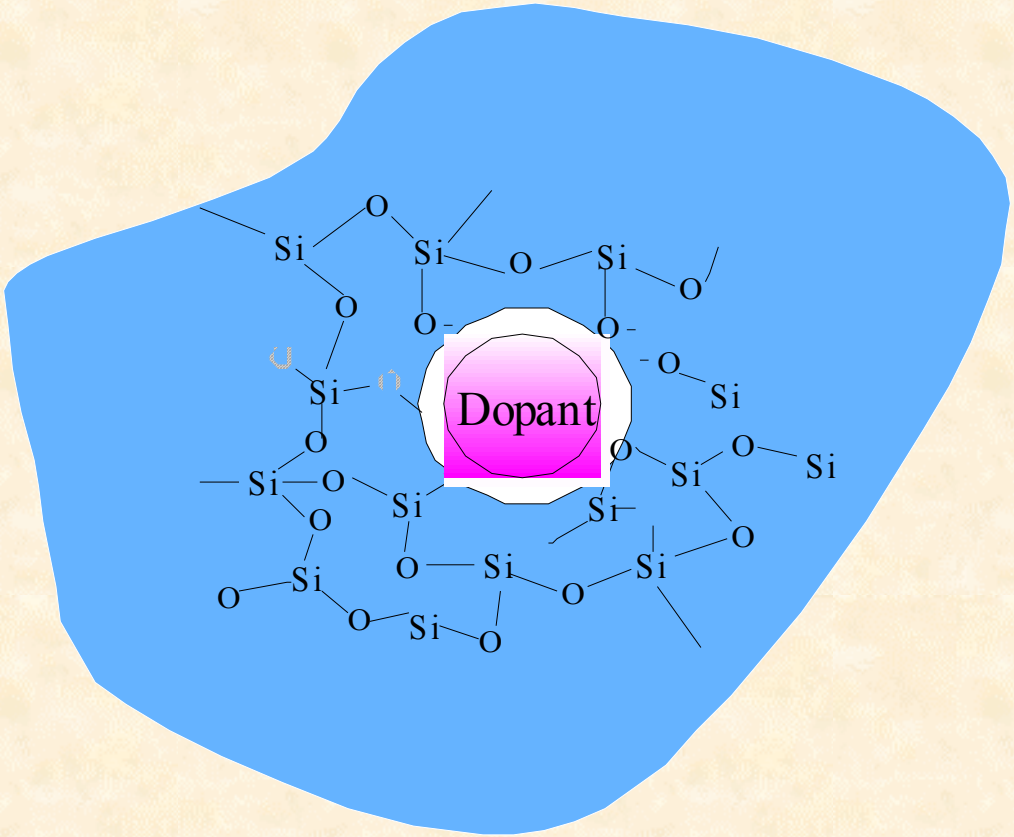
Brinker, C. J and Scherer, G. W., "Sol-gel Science: the Physics and Chemistry of Sol-Gel Processing", Academic Press: Boston, 1990.

Synthesis Protocol

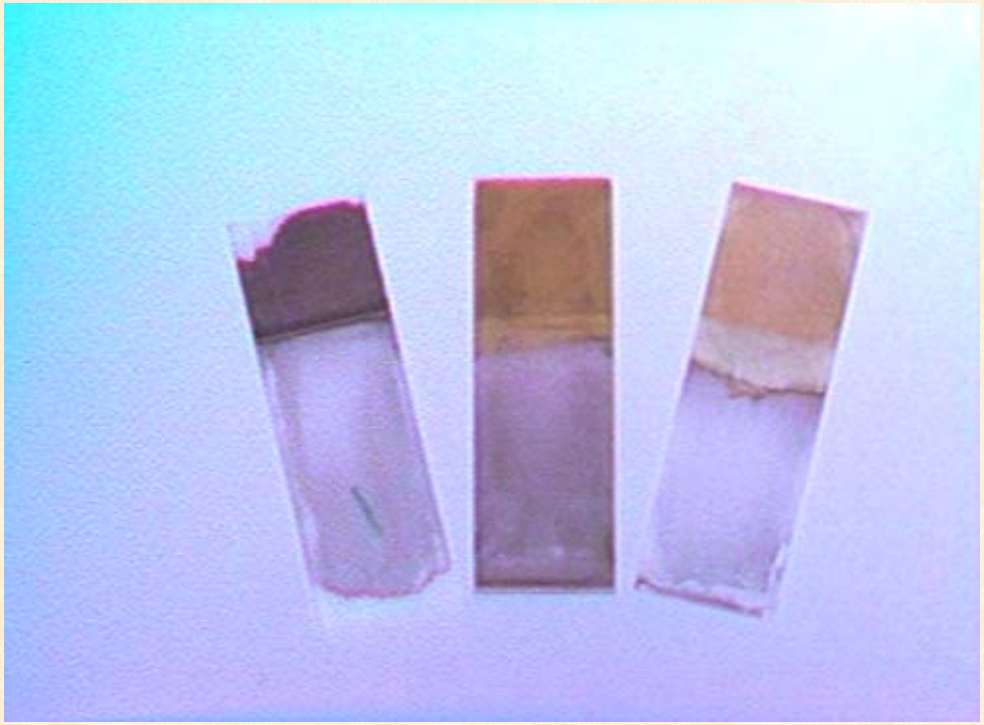


A Dopant Molecule or Particle Entrapped in Sol-Gel Glasses

- *Stabilities*
- *Porosities*

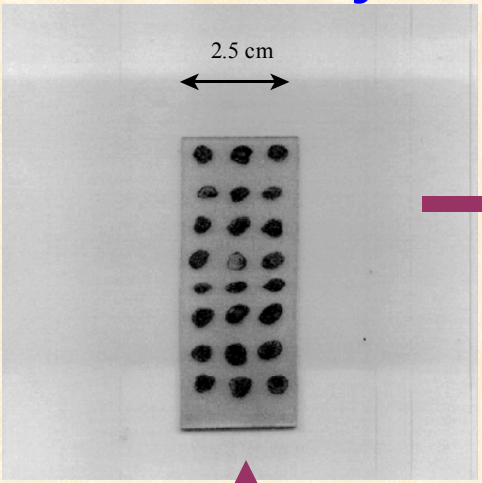


SERS Sol-Gel Films

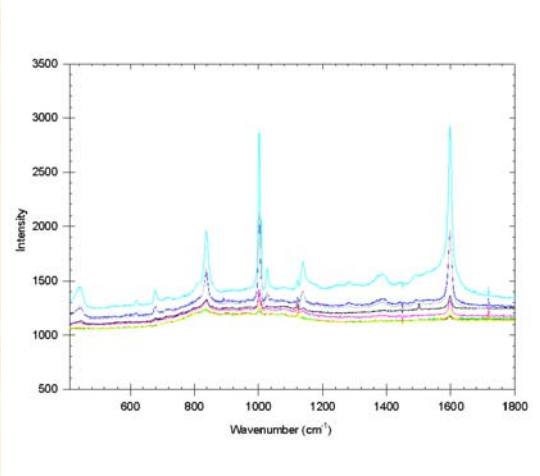


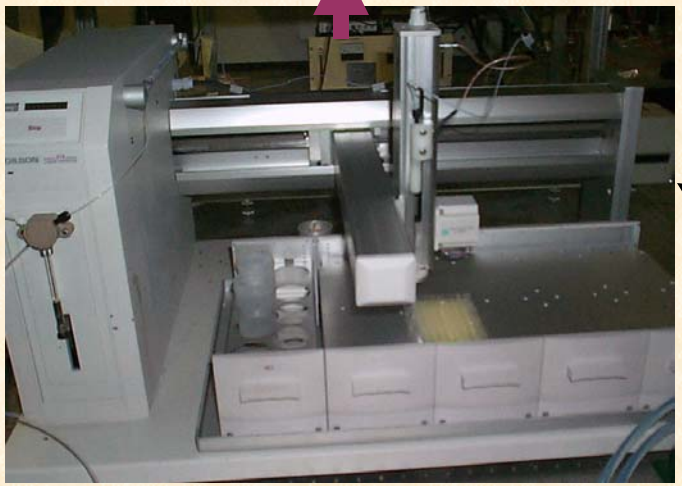
Generation of SERS Film Library

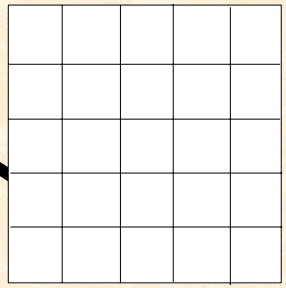
SERS Library



Screening of SERS Films







Microtiter Plate

High-Throughput Synthesis

	A’	B’	C’	D’	E’
A	AA’	AB’	AC’	AD’	AE’
B	BA’	BB’	BC’	BD’	BE’
C	CA’	CB’	CC’	CD’	CE’
D	DA’	DB’	DC’	DD’	DE’
E	EA’	EB’	EC’	ED’	EE’

Combinatorial Libraries

Generation of Library

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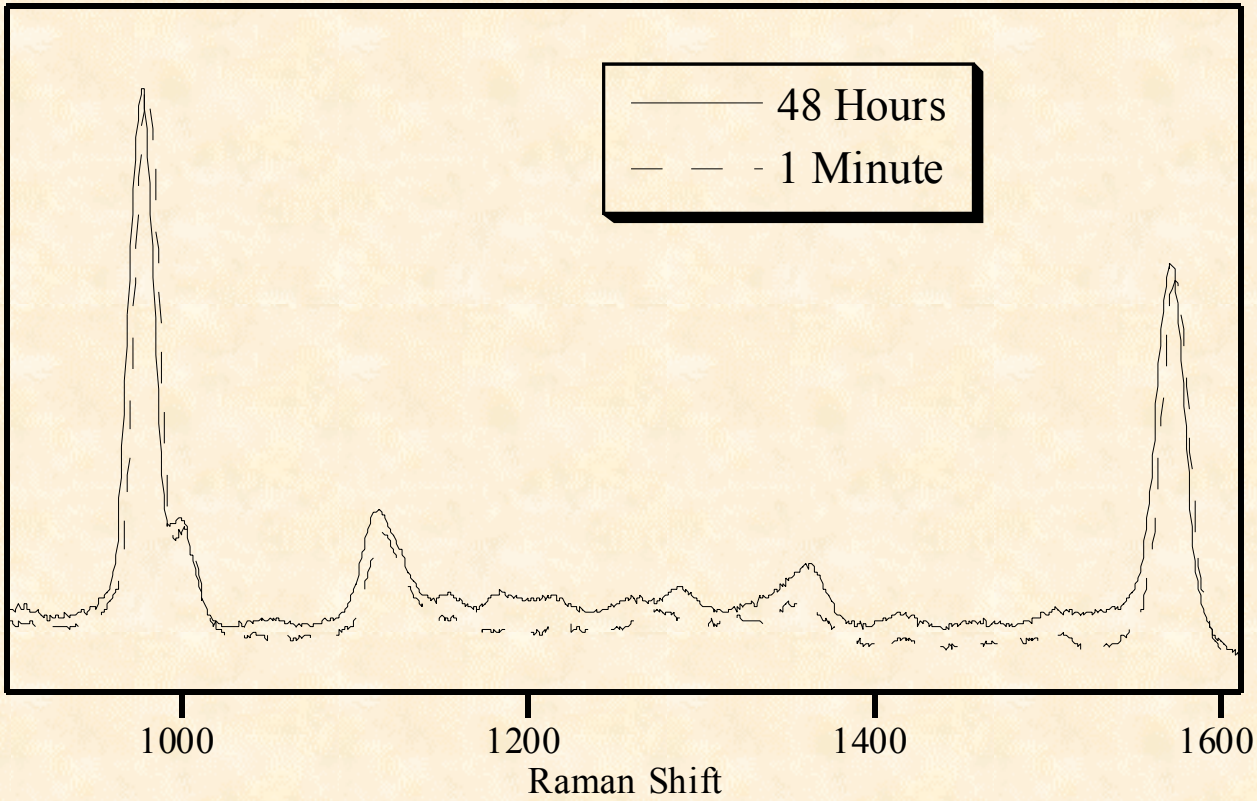
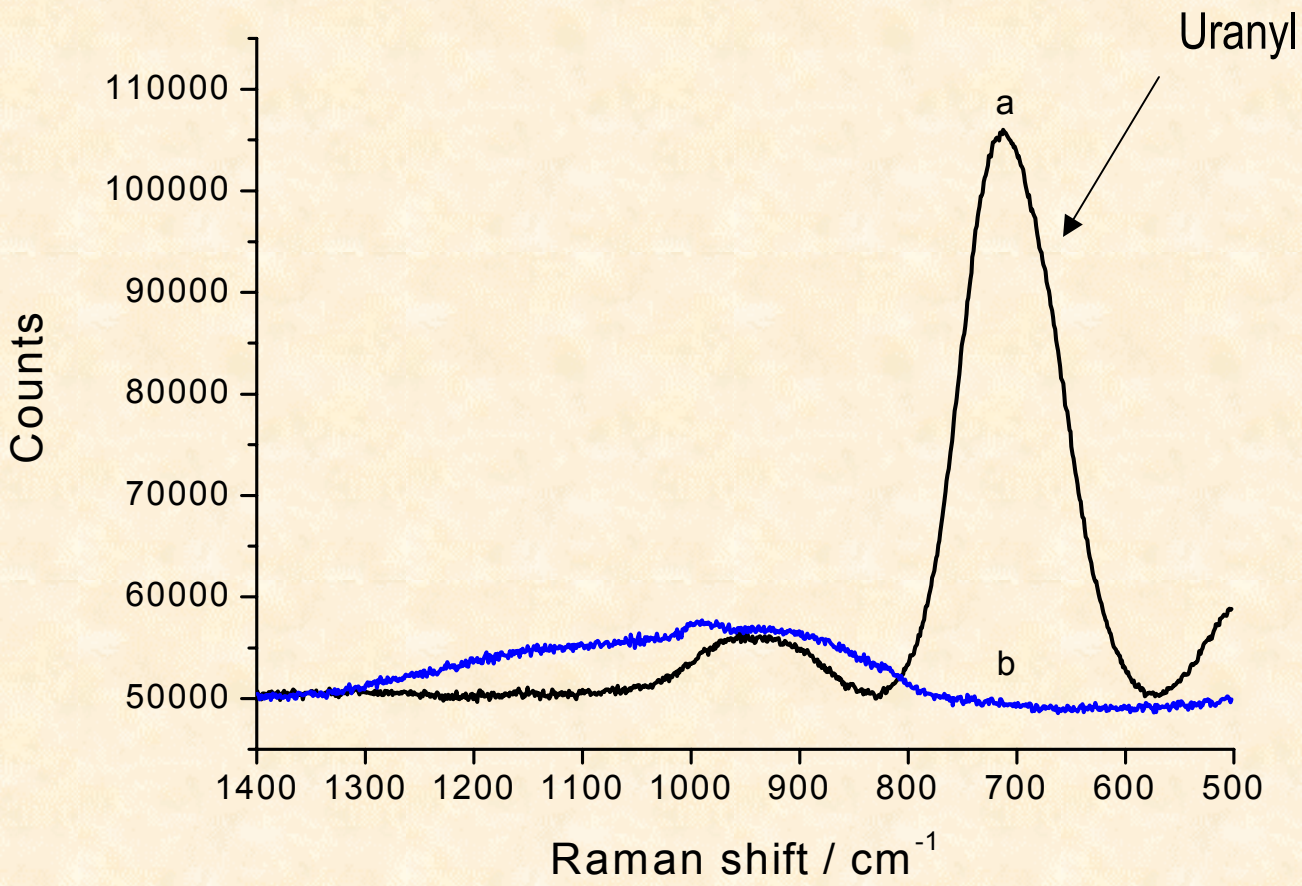
Stability of SERS Sol-Gel Film

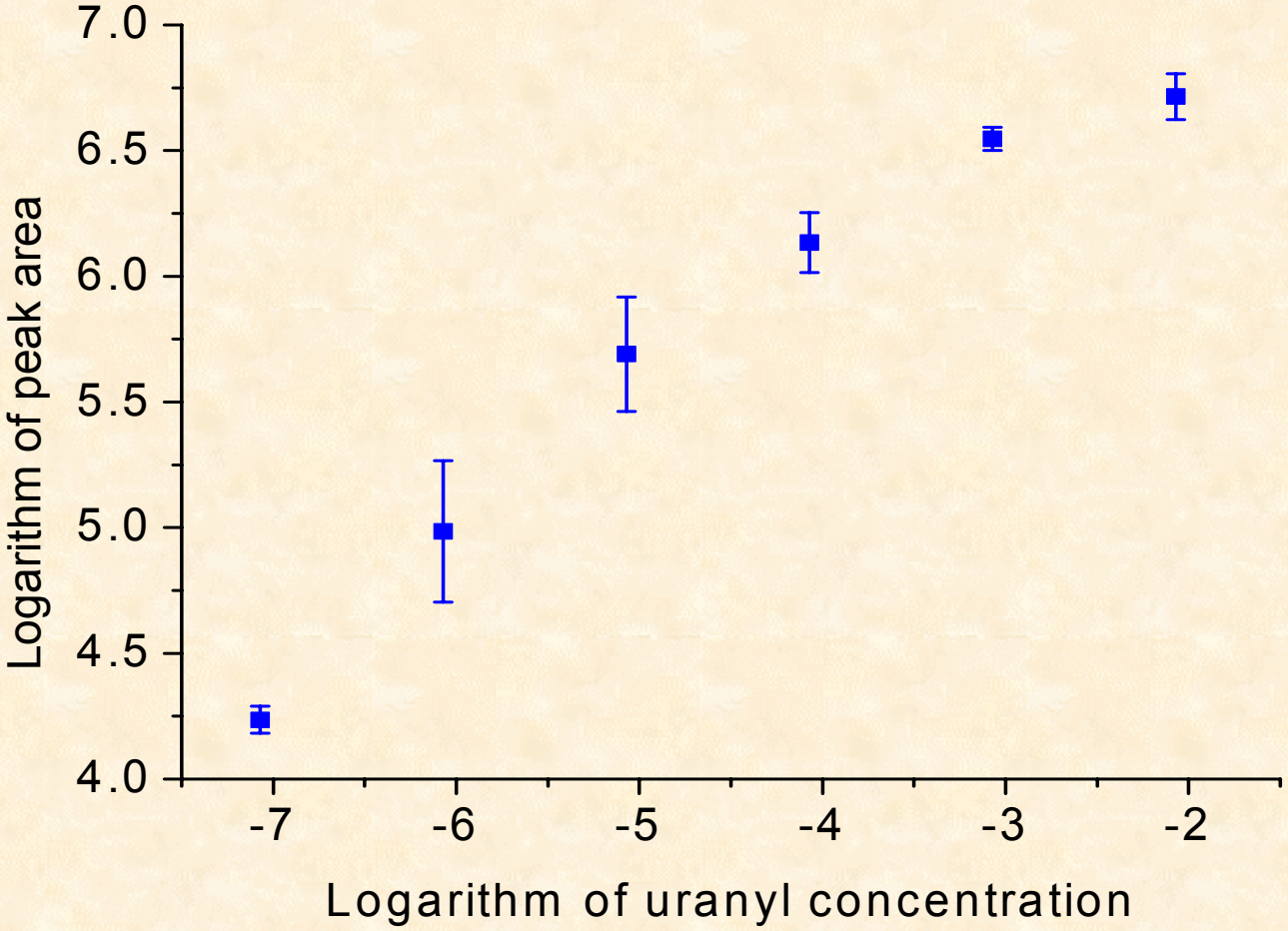


Time Dependence of Raman SERS Spectrum for Benzoic Acid

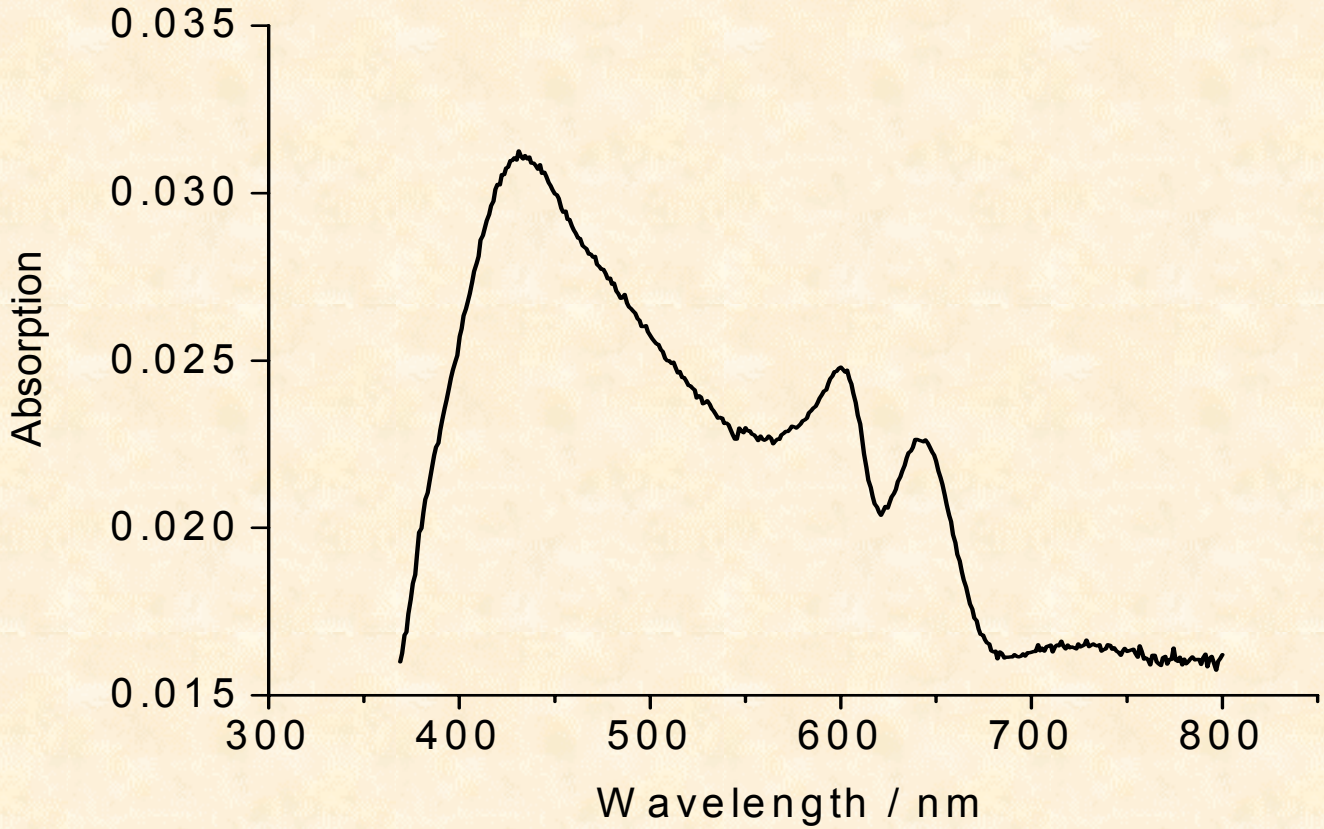
SERS spectrum of (a) uranyl (8.5×10^{-6} M) adsorbed onto a silver-doped sol-gel substrate (b) substrate in the absence of uranyl.



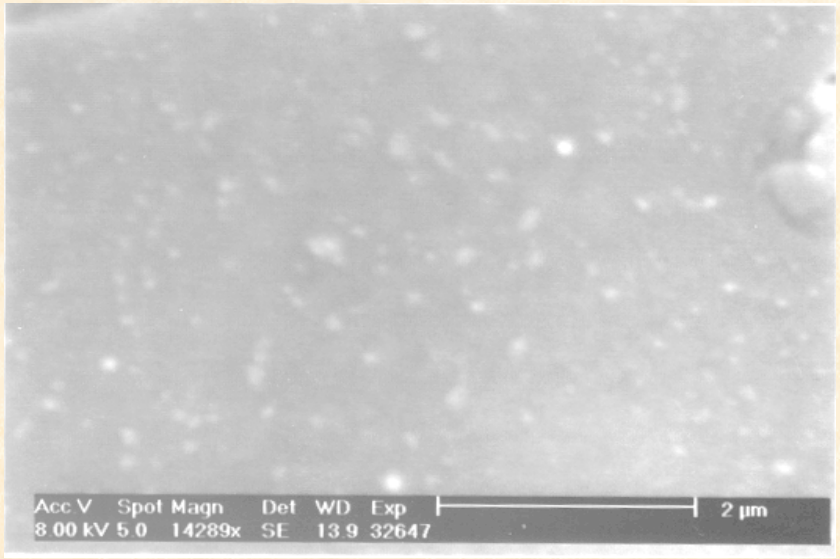
Logarithmic calibration graph of uranyl adsorbed on to silver-doped sol-gel substrate using SERS band of 710 cm^{-1}.



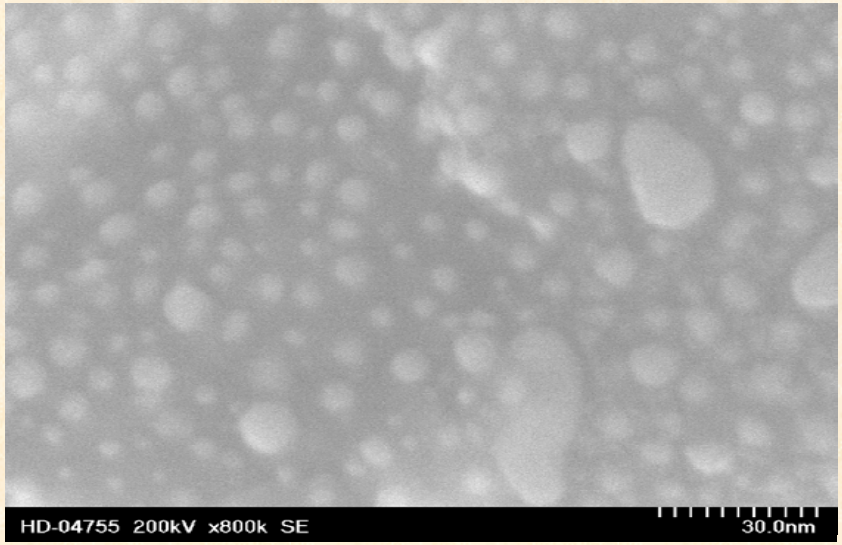
UV- visible absorption spectrum of silver-doped sol-gel substrate



SEM micrographs of silver-doped sol-gel substrates: image (a) obtained by field emission scanning electron microscope and image (b) by scanning transmission electron microscope.

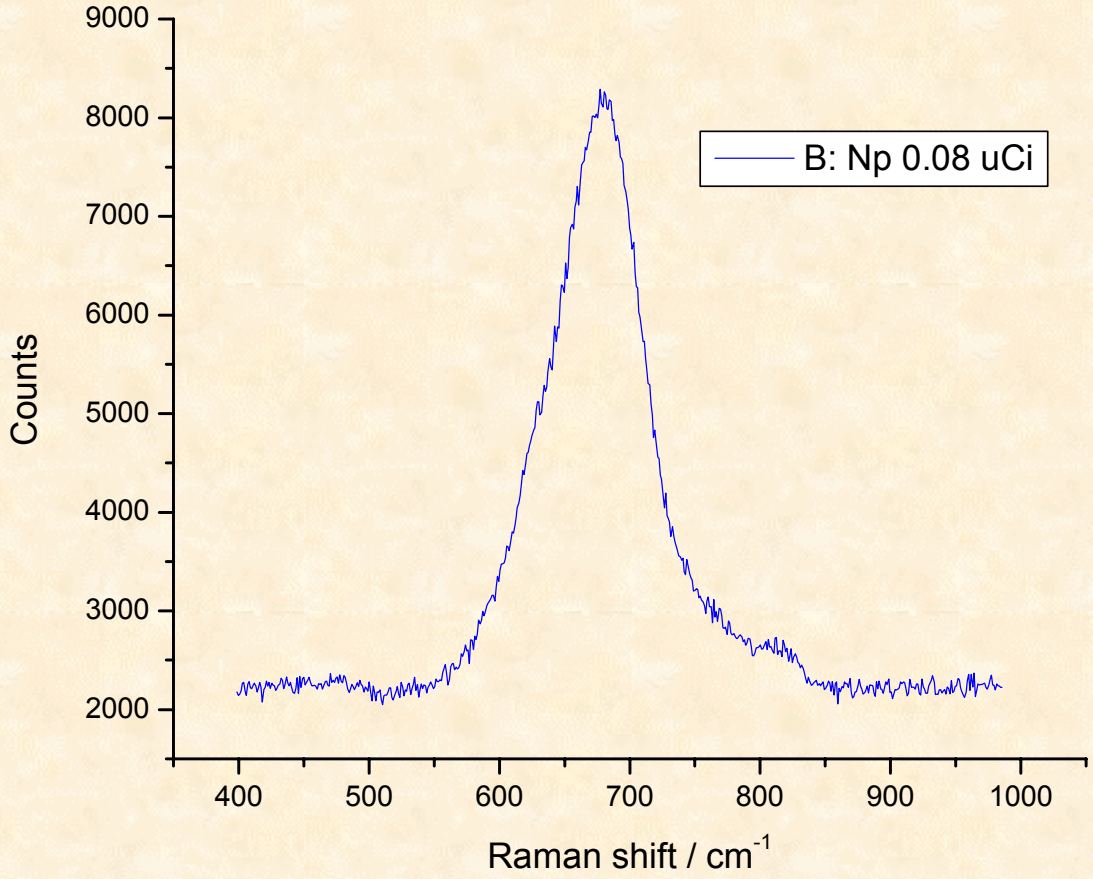


a

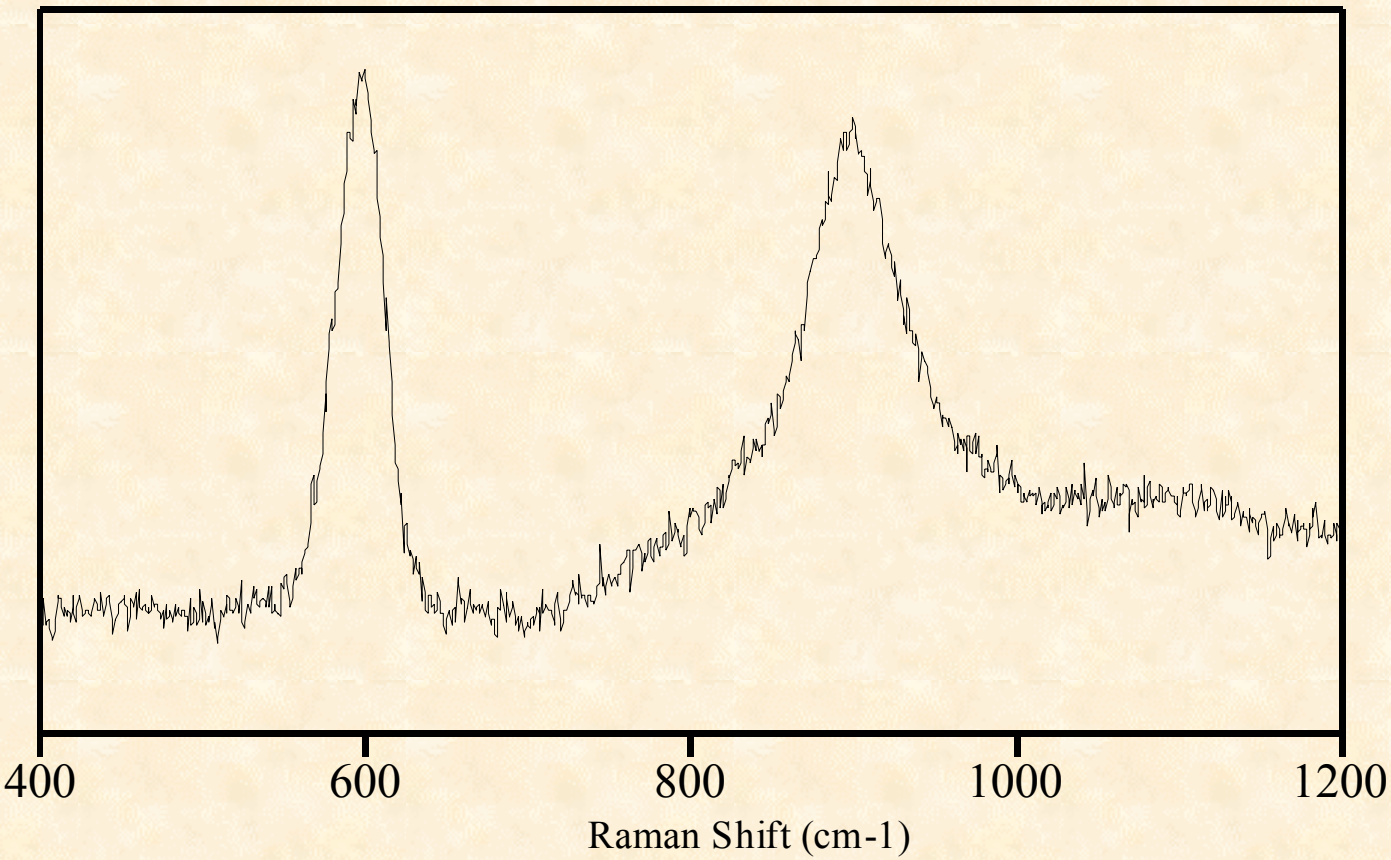


b

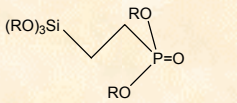
SERS spectrum of NpO_2^+



SERS spectrum of pertechnetate anion

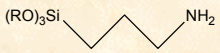


Bifunctional sol-gel precursors for selective and high-affinity SERS films



1

2



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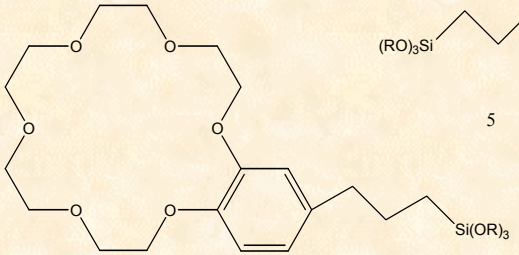
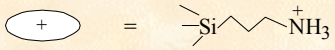
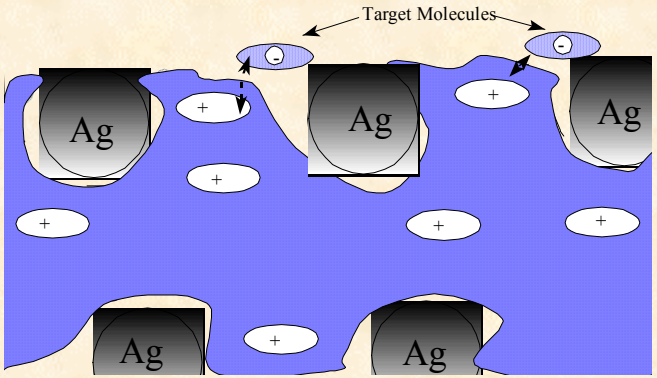


6

(a) S. Dai, *Chem. Euro. J.*, **2001**, *7*, 755. (b) M. C. Burleigh, S. Dai, E. W. Hagaman, and J. S. Lin *Chem. Mater.* **2001**, *13*, 2537. (c) Z. T. Zhang and S. Dai *J. Am. Chem. Soc.* **2001**, *123*, 9204. (d) S. Dai, M. C. Burleigh, Y. H. Ju, H. J. Gao , J. S. Lin , S. J. Pennycook , C. E. Barnes, and Z. L. Xue, *J. Am. Chem. Soc.* **2000,** *122*, 992.

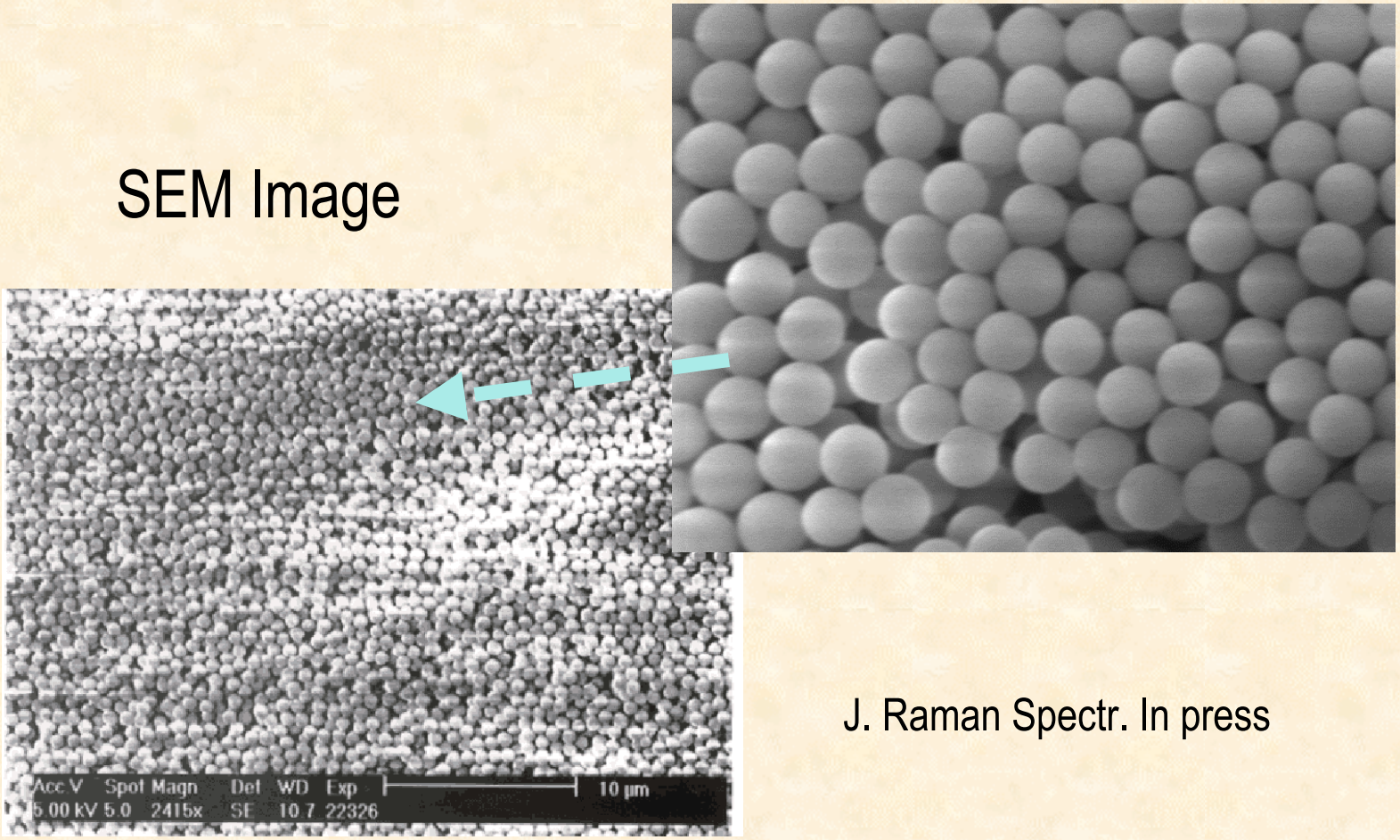
Anion-Selective SERS Film





Silica Nanoparticles by Stöber Synthesis

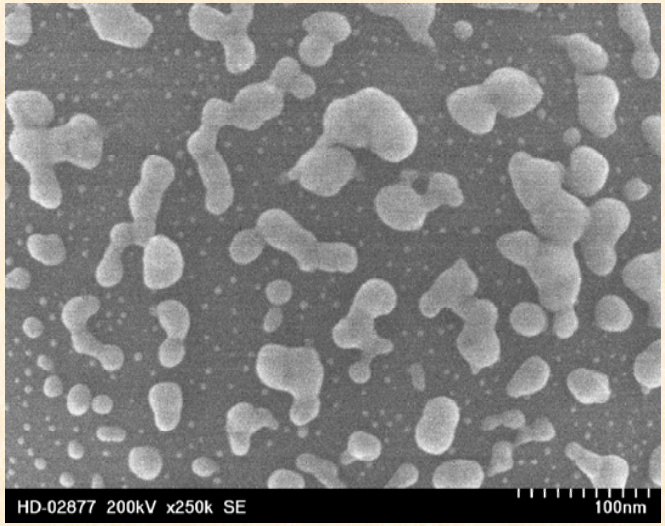
SEM Image



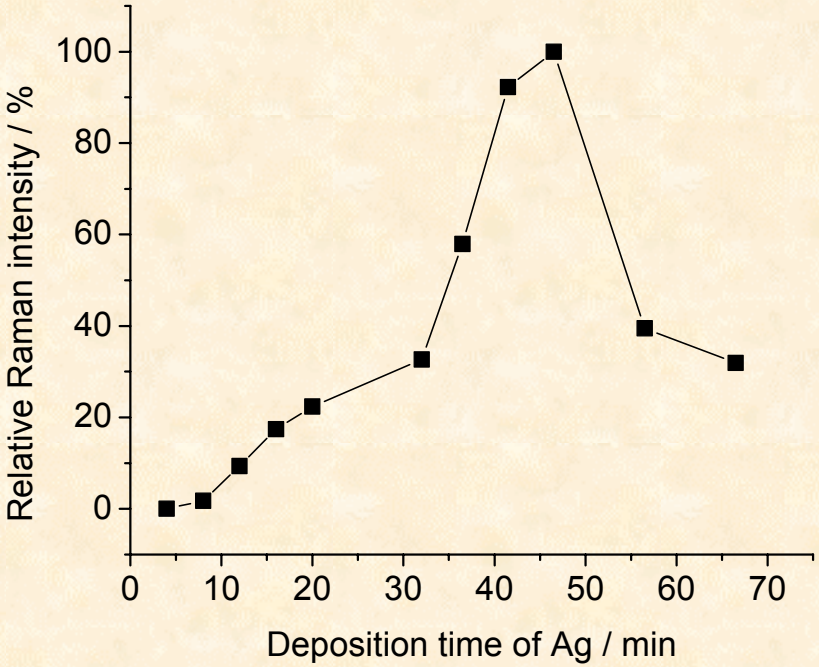
J. Raman Spectr. In press

UT-BATTELLE

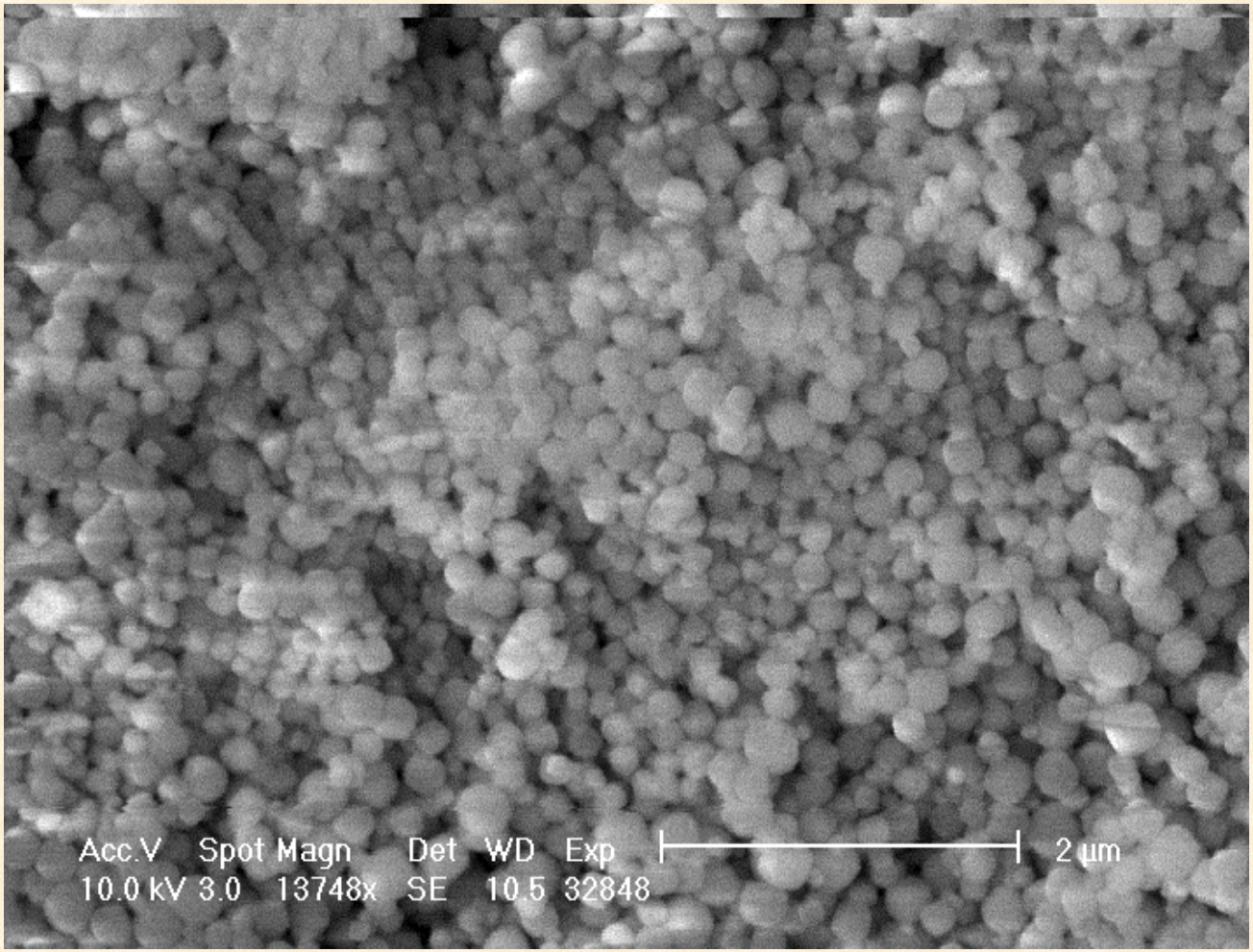
Influence of mass thickness of Ag film on SERS response. The diameter of the silica bead is 650 nm, the benzoic acid tested is 10^{-2} M.



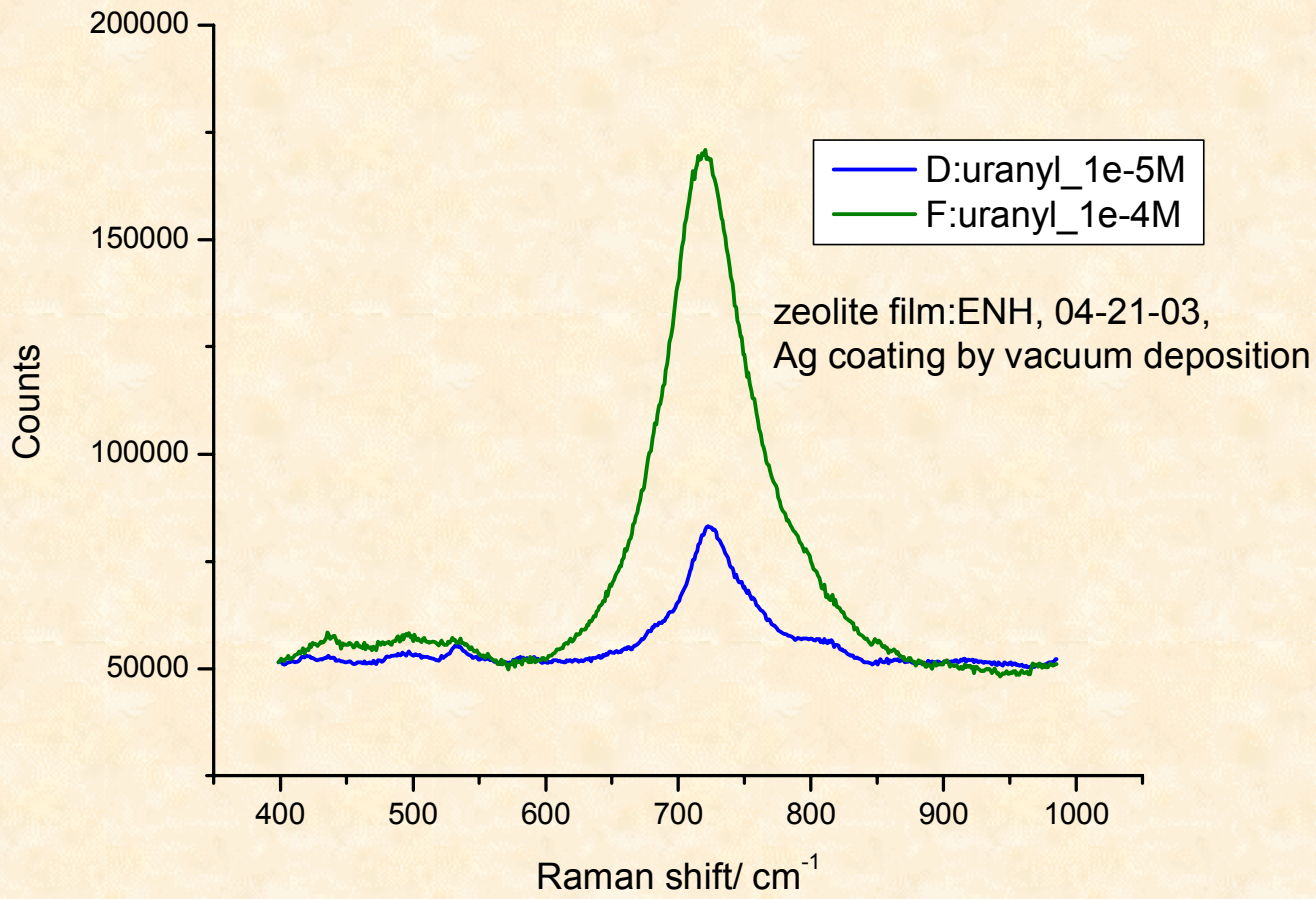
SEM image of single bead surface



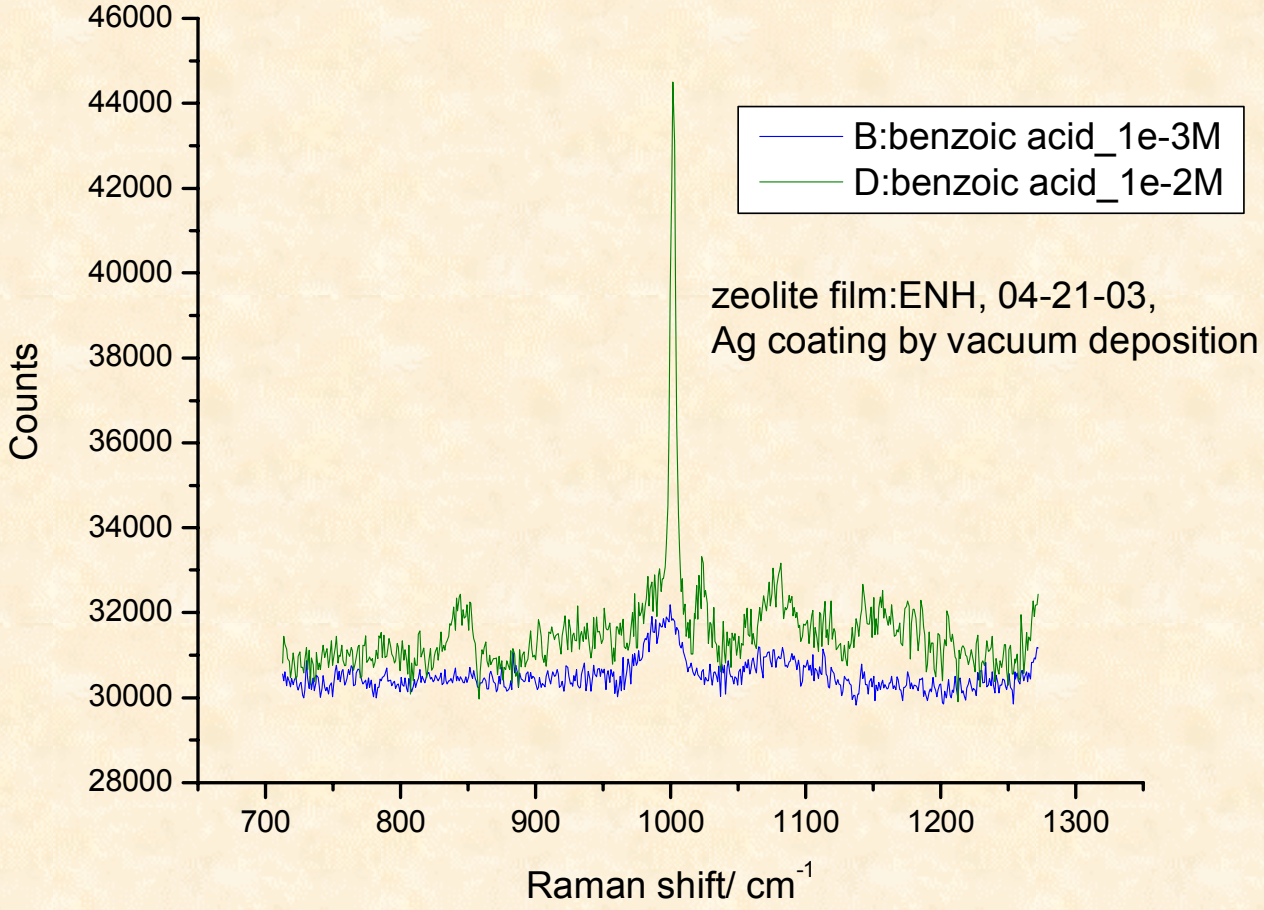
Zeolite SERS Film Prepared by LTA Nanoparticles



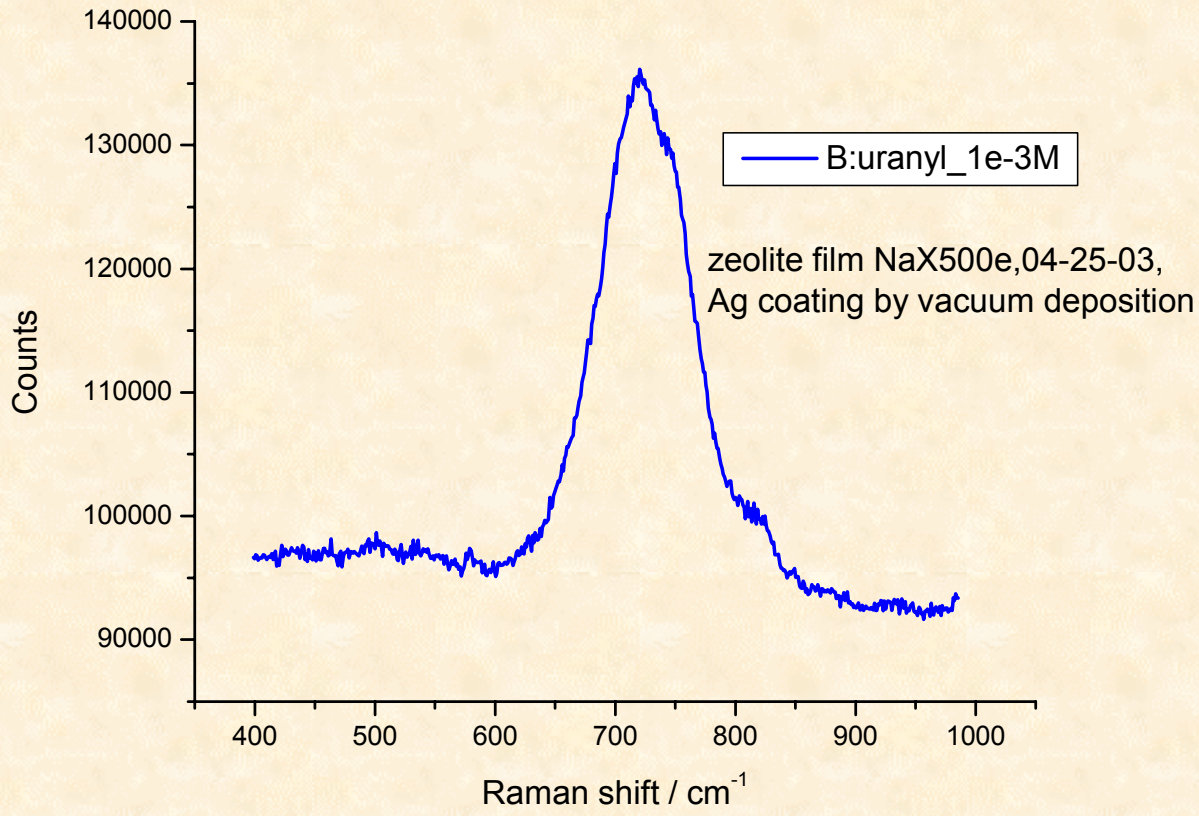
SERS Spectra of Uranyl Ions on Ag-Coated LTA Zeolite Films



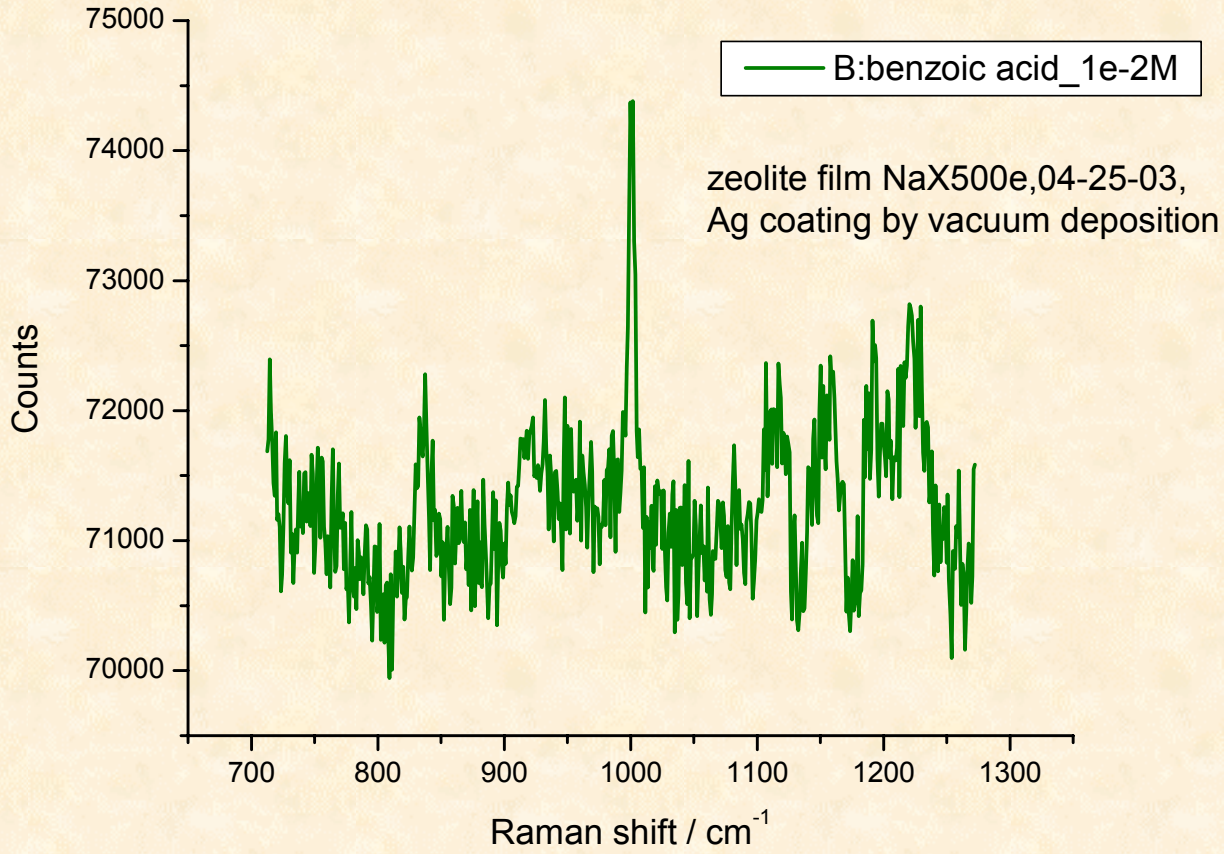
Weak SERS Effect of Benzoic Acid on Ag-Coated LTA Zeolite Film



SERS Spectra of Uranyl Ions on Ag-Coated Zeolite-X Films



Weak SERS Effect of Benzoic Acid on Ag-Coated Zeolite-X Film



Summary

- We have developed Ag-doped sol-gel films tailored for SERS measurement of radionuclides.
- The new sol-gel SERS substrates are very stable.
- We have successfully developed Ag-coated zeolite and silica nanoparticles for SERS applications.
- The measurements of SERS spectra for actinides (detection limit ~ 10^{-8} M and 1μl sample) and potential wastes have been demonstrated.