Contract No:

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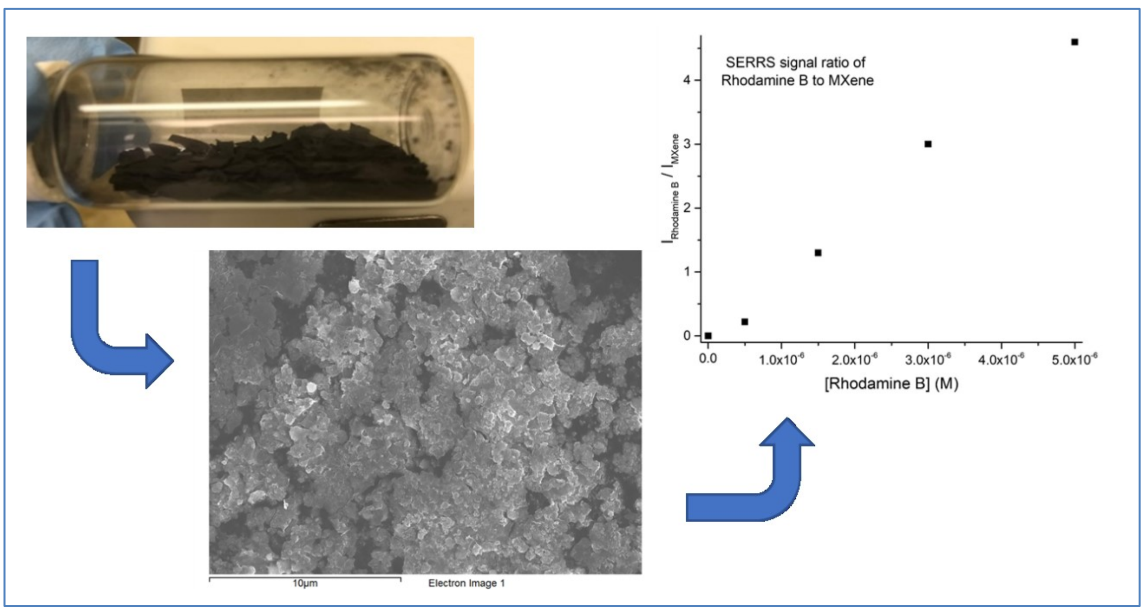
Exploring the suitability of MXenes for sensing applications

The development of sensitive, yet easy-to-use methods for the detection of actinides (uranium, plutonium, etc.) is of continual interest for ensuring nuclear safety, enhancing nuclear nonproliferation efforts, and tracking nuclear species in the environment. In this project, researchers from SRNL and Fayetteville State University explored using films based on titanium carbide nanoparticles ("MXenes") as sensing materials to support trace-level measurements. We showed that MXenes could be used to measure low levels of a test molecule (Rhodamine B). The signal was linearly dependent on concentration, indicating that the method could be used for quantitative measurements and not just detection. We identified several ways to make the films better able to support routine measurements. Once these improvements are implemented, we will demonstrate their use for measuring uranium under conditions typical for environmental samples and waste streams in nuclear materials processing facilities.



Awards and Recognition

None (to date).

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

Signature **Date**

LDRD-2019-00253
LDRD Report

Exploring the suitability of MXenes for sensing applications

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Subcontractor:

Thrust Area: NMM

Project Start Date: July 1, 2019
Project End Date: September 30, 2019

Two-dimensional titanium carbide nanoflakes (MXenes) were synthesized by several methods and tested for use as sensing platforms via surface-enhanced Raman spectroscopy (SERS). Films made from MXenes formed by etching with LiF/HCl were successful in generating SERS signal for the test molecule Rhodamine B, with a linear relationship to concentration to at least as low as 5×10^{-7} M. Several ways to improve the reliability of the measurement were identified. MXene films hold promise for eventual development as an alternative to existing optical spectroscopy methods for trace detection of uranium species.

FY2019 Objectives

- Determine that MXene synthesis methods likely to yield good sensing materials
- Demonstrate the viability of MXenes as sensing platforms for trace-level detection by optical methods (Raman spectroscopy, fluorescence)
- Demonstrate the use of MXenes to sense trace concentrations of uranium

Introduction

MXenes are two-dimensional materials composed of layered transition metal carbides, nitrides, or carbonitrides. They have the general formula $M_{n+1}X_nT_x$, where M is an early transition metal, X is C and/or N, and T are surface termination groups such as -F, -OH, and -O. The most common form of these materials is $Ti_3C_2T_x$. MXenes have been used as a surface-enhanced Raman spectroscopy (SERS) substrate [1], with the SERS effect arising from both surface plasmon properties and chemisorption and charge transfer effects. MXenes have also been experimentally observed [2] and theoretically predicted [3] to strongly and selectively adsorb uranyl ion from neutral to slightly acidic (pH = 2.5-7) solutions.

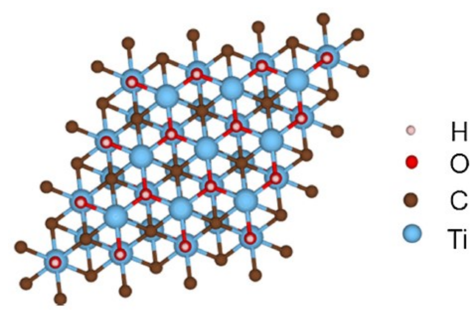

Figure 1. Hydroxylated Ti_3C_2 structure (from Ref. 3).

The combined facts of SERS activity and selectivity for uranyl suggest that optical interrogation of uranyl ions attached to MXenes could be the basis of a sensitive detection method. There have not been any studies reported in the literature which examine this question. The long-term goal of the project was to study both the Raman spectroscopy and the fluorescence of adsorbed uranyl. If successful, MXene based sensing could be developed into a process/field portable alternative to kinetic phosphorescence assay (KPA) as an optical low assay U measurement.

Approach

FSU supplied MXenes that had been synthesized from titanium aluminum carbide precursors by two different etching processes (LiF/HCl and HF). The materials were sonicated, suspended, and centrifuged to prepare solutions that were deposited drop-wise onto a substrate. The drops were characterized for elemental composition, particle size and distribution, and for use as a SERS sensor with a test analyte (Rhodamine B). If time permitted, the materials would have been exposed to uranyl and tested for detection of the latter by SERS and/or fluorescence spectroscopy.

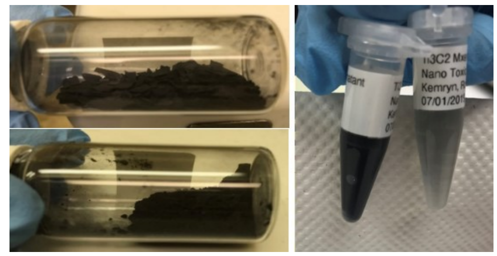

Figure 2. LiF/HCl- (top left) and HF- (bottom left) etched MXenes and prepared aqueous solutions (LiF/HCl, left; HF, right).

Results/Discussion

The LiF/HCl etching process resulted in larger flakes than the HF-etched material, which is consistent with the LiF/HCl being a gentler reagent. Elemental analysis revealed that more Al was present in the LiF/HCl material, meaning that the etching process was less complete. The larger LiF/HCl flakes resulted in a more concentrated suspension and thicker drop-cast film (4 μL drops) than the HF-etched material. "Macroscopic" SERS spectra of Rhodamine B were obtained by drying a single 4 μL drop of 0.5 – 5 μM solution onto previously deposited and dried MXene drop-cast films. SERS was measured at 532 nm using a conventional fiber probe with ~100 μm diameter spot size and 50 mW excitation. Spectra were observed with films made from the neat LiF/HCl material, but not from a 1:4-diluted LiF/HCl solution or from the HCl solution. For the neat LiF/HCl films, the SERS response for Rhodamine B was linear with concentration and consistent with prior literature reports [4] obtained with a different substrate. Intrinsic fluorescence of the Rhodamine B was greatly reduced for these samples compared to dried drops of neat Rhodamine B solution. Suppression of fluorescence is a characteristic of plasmonic coupling and supports the conclusion that a surface-enhancement effect is occurring. "Microscopic" SERS spectra of the LiF/HCl samples were also obtained at 532 nm through a microscope with a 20x objective and sub-μW laser powers (~1 μm spot resolution) . Raman spectra were highly spot-dependent. Some spectra roughly resembled the spectra obtained with the macroscopic objectives, while others corresponded to small Rhodamine B particles (with high fluorescence) or to a MXene particle of some kind. Microscopic spectra of the HF material were inconclusive. These results suggest that the SERS spectra observed for LiF/HCl etched MXene with the microscopic Raman probe are probably a spatial average of Raman-active and -inactive regions. Due to time limitations (especially with the limited tenure of the summer intern), we were not able to test the response to uranyl solutions.

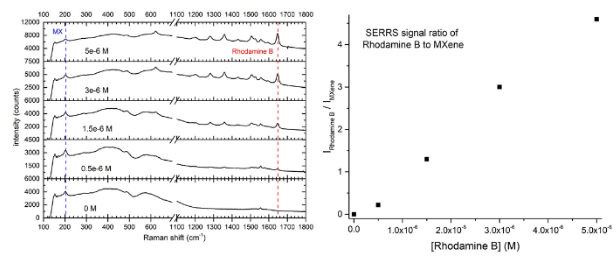

Figure 3. Raman spectra (left) and SERS enhancement signal (right) of Rhodamine B on LiF/HCl-etched MXene.

FY2019 Accomplishments

- We were able to make stable MXene-based sensing films with simple procedures.
- We observed a SERS response for Rhodamine B on LiF/HCl-etched MXenes despite incomplete etching of the original material. Although HF-etched MXene has been reported to have a larger SERS enhancement than LiF/HCl-etched material, the thicker and more uniform surface coverage of the latter makes it a better candidate for subsequent SERS method development.

Future Directions

- Revise etching conditions, especially with the LiF/HCl process, to obtain more complete removal of Al and improve the formation of MXene flakes. (Work to be done at FSU)
- Optimize sensing film formation to obtain more uniform distribution of MXenes within the drops. Develop a reproducible film formation procedure that will allow the films to be a reliable substrate for future method development. Examine utility of mixing MXene and analyte solutions prior to casting films in order to obtain more uniform results.
- Test SERS signal for uranyl solutions, and compare sensitivities to those obtained by other optical techniques (KPA).

FY 2019 Publications/Presentations

A presentation will be made by our undergraduate student (K. Allen-Perry) at the 2020 Emerging Researchers National (ERN) Conference in STEM, Washington, D.C., in February 2020.

References

1. A. Sarycheva *et al.*, *J. Phys. Chem. C* **121** 19983-19988 (2017).
2. L. Wang *et al.*, *Chem. Commun.* **53** 12084-12087 (2017).
3. Y.-J. Zhang *et al.*, *J. Hazard. Mater.* **308** 402-410 (2016).
4. L. Zhang *et al.*, *Applied Spectroscopy* **71** 2395–2403 (2017).

Acronyms

FSU: Fayetteville State University. KPA: Kinetic Phosphorescence Assay. SERS: Surface Enhanced Raman Spectroscopy.

Intellectual Property

None (to date).

Total Number of Post-Doctoral Researchers

None.

Total Number of Student Researchers

1 undergraduate student (MSIPP summer intern). Work performed off-site (materials synthesis) and on-site (sample prep, materials characterization).