Contract No:

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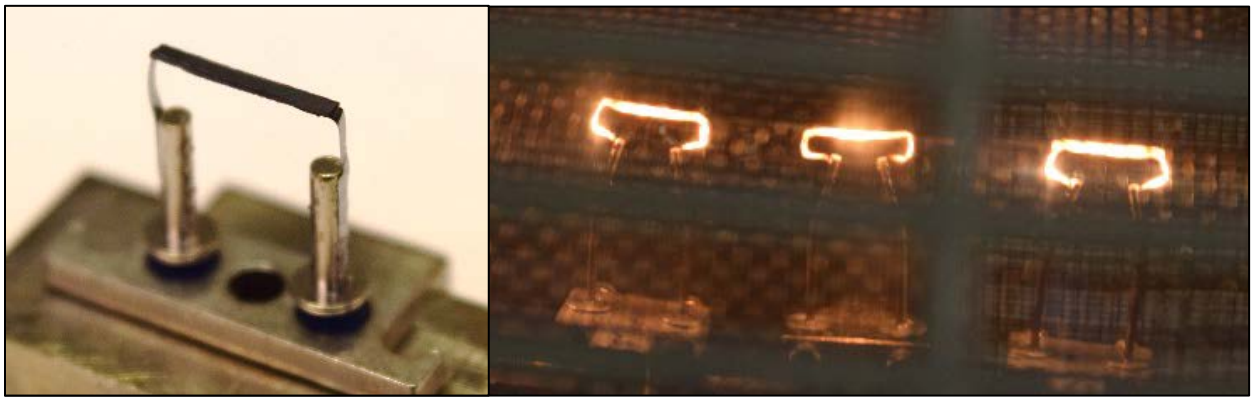
Disclaimer:

Reduced Graphene Oxide as a Filament Material for Thermal Ionization Mass Spectrometry

Isotopic information can be informative as to the intended use and/or production history of special nuclear material. For uranium and plutonium samples, thermal ionization mass spectrometry (TIMS) is the benchmark technique for determining isotope ratio data. Sample utilization in thermal ionization, however, is low with typical ionization efficiencies between 0.1% and 0.5% - i.e., only 0.1% to 0.5% of the sample contributes to the detected signal. One barrier to improving the ionization efficiency is thermodynamic limits related to the work function of the ionization filament. Graphene oxide, having a tunable work function, has the potential to greatly improve ionization efficiencies over Re or W-based filaments. The bulk work function of graphene can be tuned through doping or incorporating metal particulates in the graphene oxide matrix. In the first year of this LDRD project reduced graphene oxide (RGO) filaments were constructed using 3D printing techniques and mated to commercial filament posts. The second year of this LDRD produced ultra-low U background RGO filaments and RGO-composite filaments that are more robust than Re filaments at high temperatures and high vacuum conditions. Preliminary results using a commercial TIMS instrument demonstrate a 500 % ionization enhancement for Uranium when using Re-RGO composite-based filaments over traditional Re filaments when direct loading sample solutions onto filaments.



Reduced graphene oxide filament as-prepared (left) and heated to 1400 ^{o}C (right)

Awards and Recognition

None.

Intellectual Property Review

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

SRNL Legal Signature

Signature	**Date**

LDRD-2017-00025
LDRD Report

Reduced Graphene Oxide as a Filament Material for Thermal Ionization Mass Spectrometry

Project Team: J. M. Mannion, R. M. Achey, J. H. Hewitt, C. R. Shick Jr., M. J. Siegfried

Thrust Area: National Security

Project Start Date: October 1, 2017
Project End Date: September 30, 2018

Isotopic information can be informative as to the intended use and/or production history of special nuclear material. For uranium and plutonium samples, thermal ionization mass spectrometry is the benchmark technique for determining isotope ratio data. Sample utilization in thermal ionization is, however, quite low with ionization efficiencies typically between 0.1% and 0.5%. One barrier to improving the ionization efficiency is thermodynamic limits related to the work function of the ionizing filament. Graphene oxide, having a tunable work function, has the potential to greatly improve ionization efficiencies over Re- or W-based filaments. The work function of RGO can be tuned through doping or incorporation of metal particulates. Work this year produced ultra-low background RGO and RGO-composite filaments that remained stable at high temperature under high vacuum conditions. Preliminary results using a commercial instrument demonstrate a 500 % ionization enhancement for Uranium using Re-RGO composite-based filaments over traditional Re filaments when direct loading sample solutions onto filaments.

FY2018 Objectives

- Improve RGO filament stability
- Reduce RGO off-gassing
- Operate RGO-based filaments in source chamber of commercial TIMS instrument
- TIMS analysis of U/Pu on RGO filaments
- Investigate RGO filament doping strategies

Introduction

Thermal Ionization Mass Spectrometry (TIMS) is an analytical technique that still sees widespread use in the fields of nuclear safeguards,[1,2] nuclear forensics,[3,4] and environmental monitoring[5,6] for the measurement and characterization of actinide species. TIMS is currently considered the benchmark technique for determining uranium and plutonium isotopic information.[2] Sample utilization in TIMS is, however, typically quite low due to poor ionization efficiencies – normally in the range of 0.1% - 0.5% for Pu and U.

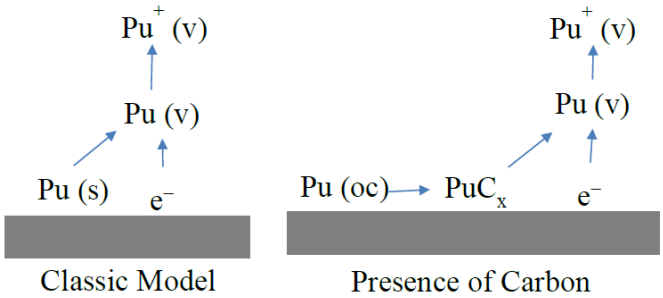


Figure 1: The presence of carbon is believed to benefit thermal ionization through the creation of actinide carbides which stabilize the sample on the ionization surface to higher temperatures, resulting in greater ionization efficiencies due to decomposition of the carbide.[15]

Research to try and increase ionization efficiencies has focused on geometry modifications of the typical rhenium filament material.[7-9] Because of thermodynamic limits related to work function of the analyte and the ionizing filament, entirely new materials (i.e., not Re or W) are needed in order to greatly improve ionization efficiency. Additionally, it has been theorized that carbonaceous filament additives may improve ionization efficiencies by promoting the creation of actinide carbides which stabilize the sample on the filament surface (Figure 1).[15] Thermal decomposition of actinide carbides at elevated temperatures (compared to in the absence of carbon) results in greater thermal ionization efficiency, as described by the Saha-Langmuir equation. Creating a carbon-based filament may further promote the creation of actinide-carbides by providing an abundant excess of carbon.

Developing new materials to be used as TIMS filaments is non-trivial. In a typical Pu or U analysis, filaments can reach temperatures greater than 1500 ^{o}C , requiring high-temperature stable materials. Recent work has shown that graphene-based materials can be 3D printed into small form factors that can be resistively heated to more than 2000 K (1727 ^{o}C).[10] This suggests a graphene-based TIMS filament is possible and could represent an entirely new substrate material for TIMS analyses. Moreover, because the work function of graphene is tunable,[11,12] the thermodynamic constraints that lead to poor ionization efficiency in Re- and W-based filaments could be overcome (orders of magnitude increases in ionization efficiency could be realized). Such improvements would be directly translated into reduced sample size requirements and/or enhanced analytical capabilities which would support the nonproliferation, safeguards, and forensics communities.

The first year of this LDRD project focused on developing the technical knowhow to reproducibly manufacture graphene-based filaments, testing different methods to mate RGO filaments to commercial TIMS filament assemblies, and initial durability studies of heated filaments under high vacuum conditions. Efforts this year focused on producing ultra-low background RGO and RGO-composite filaments that remained stable at high temperature under high vacuum conditions and characterizing Pu and U ionization. RGO and RGO-composite filaments were heated in the source chamber of a commercial TIMS instrument to temperatures greater than 1500 ^{o}C. Preliminary results demonstrate a 500% ionization enhancement for direct-loaded Uranium when using Re-RGO composite-based filaments over standard Re filaments and provide evidence for actinide-carbide intermediates in thermal ionization.

Approach

Efforts in FY18 focused on iteratively improving RGO-based filament design, developing reduction strategies to reduce/eliminate organic background and off-gassing, demonstrating viability for U and Pu ionization in a commercial TIMS instrument, and preliminary investigation into RGO doping strategies. Initial filament testing was performed in a custom-built “mock-TIMS” system with a vacuum chamber, a thermal ionization source, and a residual gas analyzer. Experiments with refined RGO-based filaments progressed to a commercial TIMS instrument where U and Pu ionization performance was characterized.

Results/Discussion

The RGO filament design was iteratively improved to obtain robust filaments ultimately capable of withstanding greater than 8 A of current (vs. ~5 A for Re) in ultra-high vacuum. Specifically, strips of RGO were cut from thin sheets of graphene oxide fashioned from dried GO paste. GO strips were them mounted on a commercial TIMS post assembly using GO paste and welded Re metal strips. To generate hybrid or doped filaments, a similar procedure was followed with dopant precursors (e.g., Teflon, Re, ReO, Pt) mixed with the initial GO paste. A combination of thermal annealing and joule heating was used to reduce the GO filaments to a robust, usable form. Scanning Electron Microscope (SEM) images shown in Figure 2 reveal the distribution of dopant materials on the surface of RGO filaments.

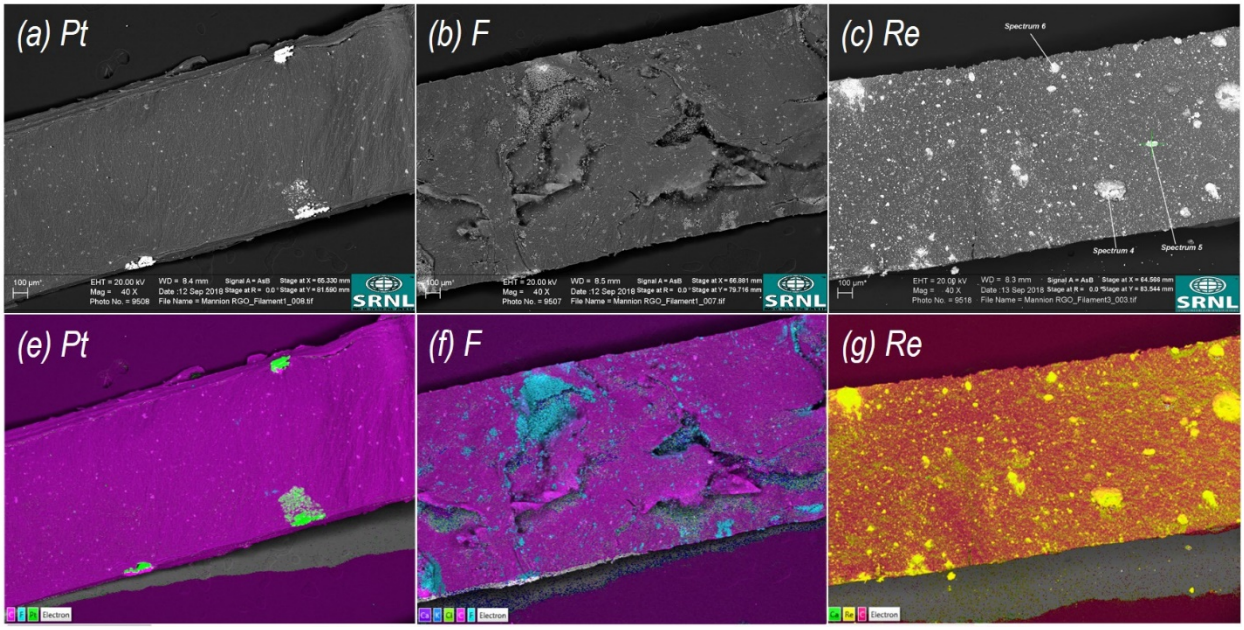


Figure 2: (a-c) Scanning Electron Micrographs and (e-g) Energy dispersive X-ray spectral maps of (a,e) Platinum, (b,f) Fluorine, and (c,g) Rhenium hybrid GO filaments showing the distribution of selected elements on the surface.

Initial studies to produce RGO filaments led to significant off-gassing and organic background signals during filament heating. Published graphene oxide reduction strategies were not adequate to eliminate organic backgrounds below the detection limits of high sensitivity TIMS. A reduction strategy was developed to analyze RGO reduction products *in situ* utilizing a custom-built mock thermal ionization source with a residual gas analyzer. This equipment enabled analysis of off-gassed species as a function of filament current and time (Figure 3). Optimal reducing conditions were found to be heating in air at 115 ^{o}C for 48 hours (higher temperatures resulted in exfoliation from entrapped water), followed by heating in a tube furnace with an inert atmosphere at 700 ^{o}C for 30 minutes and joule heating to greater than 5 A of filament current for at least 2 h.

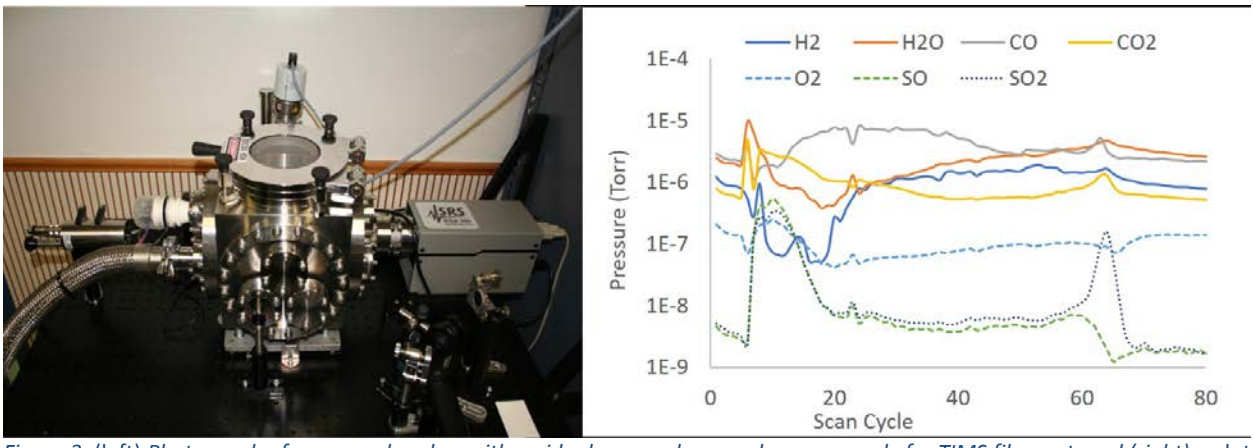


Figure 3: (left) *Photograph of vacuum chamber with residual gas analyzer and power supply for TIMS filament, and (right)* a plot of intensity of select off-gas species as a function of time and filament heating.

U and Pu samples deposited on RGO filaments were analyzed utilizing an IsotopX commercial single stage magnetic sector TIMS. Bead loading was initially investigated; however, beads were found to not adhere to the hot RGO surface. Direct loading was used for all subsequent sample analyses, involving

simply drop-drying a sample on the RGO filament surface. After adequate reduction, non-doped RGO was found to perform well in terms of ion beam stability and low background, however, the lower work function of non-doped RGO resulted in poor ionization efficiencies compared to Re direct loading and Re bead loading. Surface fluorination was investigated as a means of improving ionization efficiency and was found to produce a two-fold improvement, however, ionization efficiencies were still lower than that of Re, suggesting low fluorine conversion utilizing this method. Achieving higher levels of doping was then attempted by mixing relatively large quantities of dopants into RGO paste prior to filament construction. Teflon and platinum were difficult to disperse in aqueous RGO paste and led to filament failure as these large deposits melted/sublimed at high temperature. In contrast, RGO/Re hybrid filaments were found to perform comparably to the bead loading method and surpassed Re direct loading by ~500% in terms of ionization efficiency (Figure 4). The improvement (with RGO/Re hybrid filaments) over Re direct loading, and similar performance to Re bead loading, supports the theory that actinide carbides are beneficial intermediates in the thermal ionization of actinides, as the work function of RGO/Re filaments is not expected to exceed that of metallic rhenium.

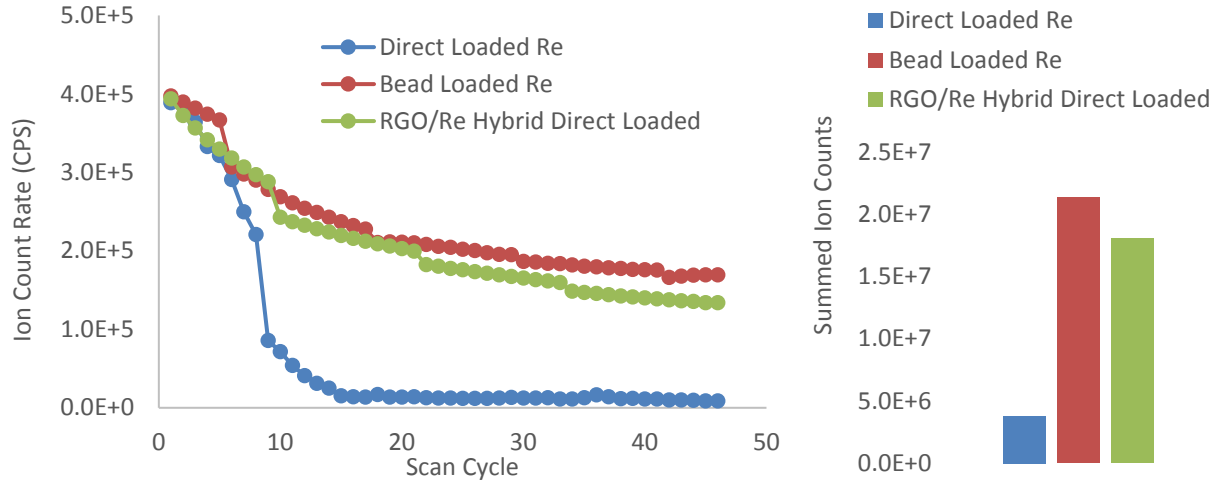


Figure 4: (left) Comparison of *ion count rate decay for 100 ng U sample monitoring the ^{238}U ion signal; filaments with various loading strategies were heated until a count rate of 400 counts per second was achieved and allowed to decay without modification of the filament current to determine sample stability. (right) Comparison of total summed counts detected after sample decay*.

FY2018 Accomplishments

- Furthered the development of RGO and hybrid RGO-based filaments
- Doped RGO filaments with Re, Pt, and F
- Demonstrated RGO filaments are stable at high temperature and high-vacuum conditions
- RGO filaments capable of withstanding 8 A of current (vs. ~5 A with Re)
- Utilized RGO-based filaments in a commercial TIMS instrument
- Re-RGO filaments improved ionization efficiency by 500% over Re direct loading
- Provided evidence that actinide-carbides are intermediates in thermal ionization

Future Directions

Results from this study are promising and warrant further investigation into RGO-based TIMS filaments. Potential future experiments include:

- Investigate alternative methods to increase fluorine conversion in RGO filaments. Possible pathways are improved Teflon dispersion, modification with gaseous fluorination reagents, or pre-assembly fluorination of RGO paste.
- Filament geometries, such as cavity sources, have shown improved ionization efficiency. RGO paste and 3D printing facilitate the creation of unique geometries.
- Further characterize Re/RGO hybrid filaments. Investigate the influence of rhenium dispersion, particle size, loading, and presence of other metals such as platinum.

FY 2017 Publications/Presentations

1. J. M. Mannion, R. M. Achey, J. H. Hewitt, C. R. Shick Jr., M. J. Siegfried, "Reduced graphene oxide as a filament material for thermal ionization mass spectrometry". Expected: Communication in Talanta, Fall 2018.

2. J. M. Mannion, R. M. Achey, J. H. Hewitt, C. R. Shick Jr., M. J. Siegfried, "*In Situ* analysis of graphene oxide reduction products by residual gas analysis". Expected: Communication in Talanta, Fall 2018.

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Acronyms

EDX – Energy Dispersive X-Ray Spectroscopy
GO – Graphene Oxide
RGA – Residual Gas Analyzer
RGO – Reduced Graphene Oxide
SEM – Scanning Electron Microscope
TIMS – Thermal Ionization Mass Spectrometry

Intellectual Property

Invention Disclosure - SRS-16-019 – "*Graphene Based Filaments for Thermal Ionization"*

Patent application - 15/435,976 - *"Graphene/Graphite-Based Filament for Thermal Ionization*"

Invention Disclosure – SRS-18-022 – "*Fluorine Doping of Graphene Based Heaters/Thermal Ionization Filaments"*

Patent application - SRS-18-022 – "*Fluorine Doping of Graphene Based Heaters/Thermal Ionization Filaments*"

Total Number of Post-Doctoral Researchers

1