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14. ABSTRACT Currently, there exists an urgent need for efficient, rapid detection of chemical nerve agents (CNA) and organophosphorus (OP) compounds and at part per trillion (PPT) level. OP compounds are prominently used by the agricultural industry in the United States and worldwide in the form of pesticides and insecticides. OP compounds also occur in the form of chemical warfare nerve agents such as sarin, cyclosarin, VX, and tabun. We propose to develop a new method for detection of OP compounds by using simple detection methodologies without using the enzyme. We will fabricate polystyrene core with ZnO shell nanoparticles to detect OP compounds such as					
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Report Title

Final Report: Portable Sensor for Chemical Nerve Agents and Organophosphorus compounds

ABSTRACT

Currently, there exists an urgent need for efficient, rapid detection of chemical nerve agents (CNA) and organophosphorus (OP) compounds and at part per trillion (PPT) level. OP compounds are prominently used by the agricultural industry in the United States and worldwide in the form of pesticides and insecticides. OP compounds also occur in the form of chemical warfare nerve agents such as sarin, cyclosarin, VX, and tabun. We propose to develop a new method for detection of OP compounds by using simple detection methodologies without using the enzyme. We will fabricate polystyrene core with ZrO₂ shell nanoparticles to detect OP compounds such as demeton and malathion and CNA compounds such as paraoxon and parathion by using simple and portable reflectance method. Also, the porous thin film of Zirconium Oxide film and Zirconium Oxide sol-gel film will be developed as OP and CNA compound sensors by using simple and portable Fourier Transform Infrared Spectroscopy-Attenuated Total Reflectance (FTIR-ATR). Zirconia (ZrO₂) is an inorganic oxide with thermal stability, chemical inertness, and a lack of toxicity. It has been reported that ZrO₂ has a strong affinity for the phosphoric group in OP and CNA compounds by forming Zirconium- Phosphate bonding. These sensors could be used for visually monitoring OP compound levels in groundwater and air in a PPT level. We will explore the best inexpensive, simple, portable and easy method as a sensitive and reliable sensor of OP and CNA compounds.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received

Paper

- 08/04/2015 12.00 Minh-Phuong Ngoc Bui, Seong S. Seo. Electrochemical Analysis of Parathion-ethyl using Zirconium Oxide-Laponite Nanocomposites Modified Glassy Carbon Electrode, Journal of Applied Electrochemistry, (04 2015): 365. doi:
- 08/04/2015 14.00 Seong S. SEO, Minh-Phuong N. BUI. Fabrication of Polymerized Crystalline Colloidal Array Thin Film Modified γ -Cyclodextrin Polymer for Paraoxon-ethyl and Parathion-ethyl Detection, Analytical sciences, (05 2014): 1. doi:
- 08/04/2015 13.00 Kristopher Brown, Hyungie Doo, Honest Makamba, Seong S. Seo. Spectroscopic Studies on Iron and 2,4-DinitrotolueneComplex and Electrochemical Analysis of 2,4-Dinitrotoluene, Analytical Letters, (07 2015): 2482. doi:
- 08/26/2013 5.00 Brittany Souder, Pandya Prashant, Seong S. Seo. Hafnium Polystyrene Composite Particles for the Detection of Organophosphate Compound, Soft Materials, (01 2013): 0. doi: 10.1080/1539445X.2011.570633
- 08/28/2014 6.00 Phuong Bui, Seong Seo, Juan Otano. Determination of DNA Hybridization on Gold Nanoparticle Conjugated Polystyrene Particle Thin Film Using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy, Analytical Letters, (01 2014): 167. doi: 10.1080/00032719.2013.831429

TOTAL:

5

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
08/04/2015 11.00	Kristopher Brown, Hyungie Doo, Honest Makamba , Seong S. Seo. Spectroscopic and Electrochemical Characterization of Iron (II) and 2,4-Dinitrotoluene , Analytical Letters, (07 2015): 2482. doi:
08/28/2014 7.00	Phuong BUI , Seong SEO. Fabrication of Polymerized Crystalline Colloidal Array Thin FilmModified γ -Cyclodextrin Polymer for Paraoxon-ethyl andParathion-ethyl Detection, Analytical sciences, (05 2014): 581. doi:
TOTAL:	2

Number of Papers published in non peer-reviewed journals:

(c) Presentations

- 1) Hyungie Doo, Alycia Lewis, Lilya Heggs, and Seong Seo, Novel Hydrophobic Hydrogel to deliver Anti-cancer Drugs into targeted Cancer, UKC 2015 Conference, July 29-August 1, 2015, Hyatt Regency Atlanta, Atlanta, GA
- 2) Kristopher Brown, Minh-Phuong Ngoc Bui, Honest Makamba and Seong S. Seo, "Spectral Properties and Determination of 2, 4-Dinitrotuene by Using Modified Glassy Carbon Electrode", 2014 CBD S&T Conference 17-21 November, 2014, St. Louis, MO
- 3) Charlene N. Middlebrooks, Minh-Phuong Ngoc Bui, Honest Makamba and Seong S. Seo "Determination of Dinitrotuene isomers by Using Silver Modified Glassy Carbon Electrode", 2014 CBD S&T Conference 17-21 November, 2014, St. Louis, MO
- 4) Hyungie Doo, Anil Khanal and Seong Seo, "Investigation of microgel mediated taxel based drugs for the treatment of breast cancer", The 66th Southeastern Regional Meeting of the American Chemical Society 2014, Nashville TN, Oct. 18th, 2014.
- 5) Minh-Phuong Ngoc Bui, and Seong Seo, "Electrochemical Analysis of Parathion-ethyl Pesticide by Zirconium Oxide-Laponite Composite Modified Glassy Carbon Electrode" (Oral) SERMACS 2013, Atlanta, GA, USA.
- 6) Minh-Phuong Ngoc Bui, and Seong Seo, "Sol-gel Thin Film of Zirconium Oxide for Detection of Organophosphate Compounds and Pesticides" (Poster) SERMACS 2013, Atlanta, GA, USA.
- 7) Minh-Phuong Ngoc Bui, and Seong Seo, "Gold Nanoparticle Conjugated Polystyrene Particles Thin Film For DNA Hybridization Detection Using ATR-FTIR Spectroscopy", (Poster) SERMACS 2013, Atlanta, GA, USA.
- 8) Minh-Phuong Ngoc Bui, and Seong Seo, "Fabrication of polymer colloidal crystal array thin film for chemical nerve agent detection", (Poster) 90th Georgia Academy of Science Conference, Valdosta, GA, USA. 2013
- 9) Minh-Phuong Ngoc Bui, and Seong Seo, "Polymer colloidal crystal array thin film for detection chemical nerve agent using optical reflectance measurement", (Oral) 2013 Korean-American Scientists and Engineers Association Southeastern Regional Conference, Atlanta, GA, USA. Feb 23, 2013
- 10) Kristopher M. Brown, Minh-Phuong Ngoc Bui, and Seong Seo "Spectral Analysis of Iron Complex Formation to Different Derivatives of Dinitrotulene isomer compounds" (Oral) 2013 Korean-American Scientists and Engineers Association Southeastern Regional Conference, Atlanta, GA, USA. Feb 23, 2013

Number of Presentations: 10.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) ManuscriptsReceivedPaper

- 08/26/2013 3.00 Minh-Phuong Ngoc Bui and Seong S. Seo*. Fabrication of Polymerized Crystalline Colloidal Array Thin Film Modified β -Cyclodextrin for the Detection of Organophosphate Compounds, Analytical and Bioanalytical Chemistry (07 2003)
- 08/26/2013 4.00 Juan Otano, Minh-Phuong N. Bui, and Seong S. Seo*. Determination of DNA Hybridization on Gold Nanoparticle Conjugated Polystyrene Particles Thin Film using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy, Analytical Letters (03 2013)
- 08/27/2012 1.00 Bruttany Souder, Prashant pandya and Seong S. Seo. Hafnium Polystyrene Composite Particles for the Detection of Organophosphate Compound, Soft Materials (06 2011)
- 08/28/2014 9.00 Phuong Bui , Seong Seo. Inclusion Complexes of Paraoxon-ethyl and Parathion-ethyl with β -Cyclodextrin modified Zirconium Oxide Thin Film Using ATR-FTIR Spectroscopy, Analytical sciences (08 2014)
- 08/28/2014 10.00 Phuong Bui and Seong Seo. Electrochemical Analysis of Parathion-ethyl using Zirconium Oxide-Laponite Nanocomposites Modified Glassy Carbon Electrode, Analytical sciences (08 2014)

TOTAL: 5**Number of Manuscripts:**

BooksReceivedBook**TOTAL:**

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Anil Khanal	1.00
Minh-Puong Bui	1.00
Huyngie Doo	1.00
Honest Makamba	1.00
FTE Equivalent:	4.00
Total Number:	4

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Seong Seo	0.30	
FTE Equivalent:	0.30	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Kristopher Brown	0.30	Chemistry
Charlene N. Middlebrooks	0.30	Chemistry
Juan Onto	0.20	Chemistry
KaBreshiya Austin	0.30	Forensic Science
Ana Maldonado	0.00	Chemistry
Kawani L. Brown	0.00	Chemistry
Lilya Heggs	0.00	Chemistry
Alycia Lewis	0.00	Chemistry
Kimberly Gaines	0.20	Chemistry
Trenicia Barner	0.00	Chemistry
FTE Equivalent:	1.30	
Total Number:	10	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 8.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 4.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 3.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 2.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Department of Natural Sciences,
Albany State University
Albany, GA 31705

I. Summary of the most important result

We have developed an alternative approach for GC electrode modification using Laponite clay and ZrO₂ gel nanocomposites. This facile one-step fabrication using drop-and-dry techniques provides affordable, low cost electrode for OP compound detection. The fabrication process was optimized with 1:1 ratio of Laponite 2%:ZrO₂ gel, and the modified electrodes were successfully used for electrochemical detection of parathion-ethyl in acetate buffer, pH 4.0 using DPV technique. The sensors showed good linearity over a wide range of parathion-ethyl from 0 to 58.3 ng.mL⁻¹ (R²= 0.994) with a detection limit of 1.6 ng.mL⁻¹. The electrode exhibited high selectivity of parathion-ethyl detection in the presence of fenitrothion and demeton-S-methyl and showed good repeatability and reasonable stability. Although further investigation is needed for improving the reproducibility and stability, this work has expanded the scope of utilizing low cost Laponite clay-ZrO₂ gel nanocomposite for OP compound detection.

The DoD project has significantly benefited to establish a research laboratory of nanomaterial and microgels to develop sensors for chemical nerve agents and it has benefited the Natural Science department of Albany State University. The research laboratory is equipped with a Scanning Electron Microscopy (SEM). This equipment has enabled us to maintain student presence and interest in our laboratory. There is usually an average three undergraduates working in my laboratory, with 3 students at present for spring 2015. The typical student's experience includes research experience in my lab, conferences travel, numerous presentation opportunities, journal writing and publications. Furthermore, these students have found great success in their continuing education goals.

We published 6 papers in peer reviewed journals and presented 10 papers in regional and national conferences. There is one paper in the press and another one paper is submitted. The research efforts that the DOD project has supported have also incited much recognition from my peers, the community and the press. Our laboratory has been featured in numerous news articles, both internal and external, and upon faculty recommendations. There is excellent result to show that the DoD project has been instrumental in the Natural Science Department and our laboratory's research focus to advance and enhanced scientific knowledge in the areas of nanomaterial science and microgels.

II) Statement of the Problem Studied

Parathion-ethyl is an organophosphorous compound which is widely used as a pesticide in agricultural activities and it presents serious problems in the environment, especially in surface water and in the soil. The pesticides are meant to kill pests, but they are also dangerous to human beings if they are exposed regularly to such chemicals. Organophosphorus compounds act by inhibiting an enzyme called acetylcholinesterase, which regulates nerve function. Because of their poisonous effects, these organophosphorus compounds are also used as nerve agents by rogue governments and terrorist organizations. Therefore it is important to develop analytical methods that can be applied to detect and analyze these dangerous compounds. This report is meant to develop methods that can be used to detect an organophosphorus compound electrochemically but the method can be modified for use in detecting similar organophosphorus compounds. In this report, we have developed a simple electrochemical electrode by surface modification of a glassy carbon electrode (GC) with a mixture of laponite clay and zirconium oxide (ZrO₂) gel nanocomposite, using a natural drop-and-dry technique. The modified Laponite-ZrO₂ nanocomposite electrode was evaluated using cyclic voltammetry (CV) and different pulse voltammetry (DPV) techniques. Also, the effect of interfering pesticides such as demeton-S and fenitrothion was investigated. The stability of the electrode and the reproducibility of the analysis were also evaluated. The results showed that the Laponite-ZrO₂ nanocomposites modified GC electrode improved the sensitivity and selectivity in the detection of parathion-ethyl when compared to bare glassy carbon electrode. The fabricated electrode showed fast response, is cost effective, disposable and easily portable. The fabricated electrode has a potential for use in the detection of dangerous organophosphorus compounds in the environment.

III. Research Highlights

A) Fabrication of Polymerized Crystalline Colloidal Array Thin Film Modified β -Cyclodextrin Polymer for Paraoxon-ethyl and Parathion-ethyl Detection

Highlights

- 1) The PCCA thin film was modified with β -cyclodextrin (β -CD) polymer as capping cavity for the selectivity detection of paraoxon-ethyl, and parathion-ethyl chemical agents.
- 2) The PCCA thin film was characterized using scanning electron microscopy (SEM).
- 3) The diffraction peak of β -CD modified PCCA thin film showed red shift according to the change of paraoxon-ethyl and

parathion-ethyl concentrations.

B) Inclusion Complexes of Paraoxon-ethyl and Parathion-ethyl with β -Cyclodextrin modified Zirconium Oxide Thin Film Using ATR-FTIR Spectroscopy

Highlights

- 1) The synthesis and modification of zirconium gel with β -cyclodextrin (ZrO_2 - β -CD) via sol-gel process have been established.
 - 2) The surface morphology of ZrO_2 - β -CD gel was characterized by SEM and EDS and ATR-FTIR
 - 3) The inclusion complexes of paraoxon-ethyl, parathion-ethyl on the ZrO_2 - β -CD gel thin film have been studied.
 - 4) The hydrolysis of paraoxon-ethyl by ZrO_2 - β -CD gel thin film give peaks shifted in the ATR-FTIR spectra but that was not observed in case of parathion-ethyl with limit of detection as low as 0.03 μ M.
- C) Electrochemical Analysis of Parathion-ethyl using Zirconium Oxide-Laponite Nanocomposites Modified Glassy Carbon Electrode

Highlights

- 1) The simple electrochemical electrode was developed by surface modification of a glassy carbon electrode (GC) with a mixture of laponite clay and zirconium oxide (ZrO_2) gel nanocomposite, using natural drop-and-dry technique.
- 2) The surface morphology of modified glass carbon electrode was characterized by SEM, EDS and ATR-FTIR.
- 3) The detection limit of parathion-ethyl was calculated at the oxidation potential of 0.07 V with a value as low as 1.6 ng.mL⁻¹ in the linear range from 0 to 58.3 ng.mL⁻¹ ($R^2 = 0.994$).
- 4) The modified Laponite- ZrO_2 nanocomposite electrode was evaluated using cyclic voltammetry (CV) and different pulse voltammetry (DPV) techniques.

IV. Research Focus

- 1) Core/Shell (PS- ZrO_2) Portable Sensor for Chemical Nerve Agents Detection

Abstract

Synthetic chemical nerve agents or organophosphorous compounds such as demeton-S, parathion and paraoxon-ethyl, are widely used in agricultural as pesticides in the US and worldwide. These compounds are neurotoxins which can breakdown neurotransmitter acetylcholine at the neural synapse, resulting in a loss of muscular function, paralysis or death. Because of their high neurotoxicity, chemical nerve agents have been exploited for use as pesticides in crop, livestock, and poultry products and as chemical and biological warfare agents.

As a result of the high toxicity and the important for national security, fast and effective detection of chemical nerve agents in the environment and public place are needed. In recent years, organophosphorous pesticide kits have become commercial that offer advantages, including portability, rapid turnaround time, and cost effectiveness. However, these still involve complicated handling procedures and often lack sensitivity and precision in detecting low concentration at ppm level. Thus, the detection and identification of newly-introduced, OP neurotoxins in air, water and soil remains an extremely difficult challenge. To meet the requirements of rapid warning and field deployment, more-compact low-cost instruments, are highly desirable for facilitating the task of on-site monitoring of organophosphorous compounds. Recent research have become focusing of on the developing of sensor using nanomaterials for fast, high sensitivity and selectivity to detect chemical nerve agent. In this study, we fabricated polystyrene (PS) core with zirconium oxide (ZrO_2) nanoparticles conjugated on the surface of PS as a shell using different method of nanoparticles conjugation.

- 2) Fabrication PCCA and Zirconium Oxide Thin Film via Sol-gel Process for the Detection of Chemical Nerve Agent and Organophosphate Compounds

Abstract

In this report, we have demonstrated the synthesis, fabrication, and characterization of chemical sensor thin film for the detection of organophosphate compounds (OP) and pesticides. The PCCA thin film was modified with beta-cyclodextrin (β -CD) as a capping cavity for the selectivity detection of paraoxon-ethyl, and parathion-ethyl agents. The diffraction peak of β -CD modified PCCA thin film showed red shift according to the change of paraoxon-ethyl and parathion-ethyl concentrations. Optical reflectance measurement of OP compounds on β -CD modified PCCA thin film showed fast response (10 s) and high selectivity for the detection of paraoxon-ethyl and parathion-ethyl with the detection limit of 9.4 μ g/L and 2.0 μ g/L, respectively. Secondly, we presented the synthesis and modification of zirconium- β -CD sol-gel thin film for the detection of paraoxon-ethyl and parathion-ethyl. The surface morphology of zirconium sol-gel was characterized by SEM, and EDS. Attenuated total reflectance fourier transform infrared (ATR-FTIR) spectroscopy was applied for detection OP. The results showed that the hydrolysis of paraoxon-ethyl by zirconium- β -CD sol-gel thin film give peaks shifted in the ATR-FTIR spectra with decrease transmittance percent. We suggested the hydrolysis of paraoxon-ethyl on zirconium- β -CD sol-gel involves the formation of β -CD-pesticide inclusion complexes just like the enzyme model.

- 3) Electrochemical Analysis of Parathion-ethyl using Zirconium Oxide-Laponite Nanocomposites Modified Glassy Carbon Electrode

Abstract

Parathion-ethyl is an organophosphorous compound which is widely used as a pesticide in agricultural activities and it presents serious problems in the environment, especially in surface water and in the soil. In this report, we have developed a simple electrochemical electrode by surface modification of a glassy carbon electrode (GC) with a mixture of laponite clay and zirconium oxide (ZrO₂) gel nanocomposite, using natural drop-and-dry technique. The modified electrode was used for the detection of parathion-ethyl pesticide. Different ratios of Laponite-ZrO₂ gel were used to modify the glassy carbon electrode. The fabricated electrode morphology was characterized using scanning electron microscopy (SEM) and X-ray diffraction spectroscopy (EDS) and attenuated total internal reflectance infrared spectroscopy (ATR-FTIR). The modified Laponite-ZrO₂ nanocomposite electrode was evaluated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. Also, the effect of interfering pesticides such as demeton-S and fenitrothion was investigated. The stability of the electrode and the reproducibility of the analysis were also evaluated. The results showed that the Laponite-ZrO₂ nanocomposites modified GC electrode improved the sensitivity and selectivity in the detection of parathion-ethyl when compared to bare glassy carbon electrode. The detection limit of parathion-ethyl was calculated at the oxidation potential of 0.07 V with a value as low as 1.6 ng. mL⁻¹ in the linear range from 0 to 58.3 ng.mL⁻¹ (R² = 0.994). The fabricated electrode showed fast response, is cost effective, disposable and easily portable.

4) Inclusion Complexes of Paraoxon-ethyl and Parathion-ethyl with β -Cyclodextrin Modified Zirconium Oxide Thin Film Using ATR-FTIR Spectroscopy

Abstract

We have demonstrated the synthesis and modification of zirconium dioxide with β -cyclodextrin (ZrO₂- β -CD) via sol-gel process and investigated the inclusion complexes of paraoxon-ethyl, parathion-ethyl on the ZrO₂- β -CD thin film. The formation of sol-gel thin film process has been investigated and optimized. The morphology of ZrO₂- β -CD gel was characterized using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was applied for characterization of the inclusion complexes of paraoxon-ethyl and parathion-ethyl on ZrO₂- β -CD film. The hydrolysis of paraoxon-ethyl by ZrO₂- β -CD gel thin film give peaks shifted in the ATR-FTIR spectra with increase in absorption intensity relating with the increasing paraoxon-ethyl concentration but that was not observed in the case of parathion-ethyl. The O-H vibration band of the intermolecular and intramolecular hydrogen bonds was observed to decrease with increasing paraoxon-ethyl concentration. Quantitative analysis of paraoxon-ethyl using ATR-FTIR showed good linearity in the range of 1 – 7 μ M (R² = 0.99, n = 3) with a limit of detection as low as 30 nM.

V. Student Project Report

1) Electrochemical Sensor for Pesticide and Organophosphate Compounds using Copper Nanoparticles

Trenicia Barner

Abstract:

This research experiment focused on the fabrication, development and evaluation of a chemical sensor for detection of pesticide and organophosphate compounds using copper nanoparticles. Electrochemical deposition was used to fabricate copper nanoparticles onto glassy carbon surface. The structure of copper nanoparticles was characterized by scanning electron microscopy (SEM). Sensor was evaluated using electrochemistry techniques such as cyclic voltammetry, and square wave stripping methods with demeton-S and paraoxon as sample models. Our fabricated sensor was expected to have high sensitivity, low cost, reproducibility and portability compared to enzyme-based sensors.

2) Spectral Properties of 2,4-Dinitrotoluene, 2,6-Dinitrotoluene, and 3,4-Dinitrotoluene with Fe(III) and Fe(II)

Kristopher Brown

Abstract

Some of the major objectives of analytical chemistry research include the search for quick and reliable methods to detect and analyze dangerous explosive materials, their precursors or their by-products. The work reports on the studies of the complex formation between the explosive 2,4 dinitrotoluene and iron ions in solution using absorption spectroscopy. Based on the results from spectroscopy we performed surface modification of glass carbon electrodes (GCE) by electrochemical reduction using Fe²⁺ ions at low pH and used them in the analysis of 2,4 dinitrotoluene (2,4 DNT). The electrochemical behavior of 2,4

DNT in solution was studied by square wave voltammetry (SWV) using the modified GCE. The deposited Fe solid material improved the electrochemical performance of the modified electrode. Concentrations of 2,4 DNT as low as 10 parts per billion (ppb) were detected using the Fe modified glass carbon electrode. Increasing the concentration of the 2,4 DNT resulted in the increase of the current signal strength. The increasing in the number of scans also resulted in an increase in signal strength.

3) Determination of DNA Hybridization on Gold Nanoparticle Conjugated Polystyrene Particles Thin Film using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

Juan Otano

Abstract

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to detect DNA hybridization on the polystyrene conjugated gold nanoparticles (PS-AuNPs) thin film. The AuNPs were first synthesized on the surface of poly (ethylenimine) coated polystyrene particles by citrate reduction and the single-stranded DNA with a 3'-C6-SH was then immobilized on AuNP surface via thiol bonding. UV-Vis spectrometry was used to monitor the conjugation of AuNPs on polystyrene particles and the immobilization of single-stranded DNA probe on PS-AuNPs. The morphology of PS-AuNPs thin film was characterized using scanning electron microscopy (SEM) showed successful conjugation and immobilization of our system. ATR-FTIR spectra obtained from the hybridization with complementary target DNA showed features of DNA structure and peaks shifted and changed at wave number 1657 cm^{-1} after hybridization compare to the non-complementary DNA due to the change in hydrogen bonding between N-H and C=O of complimentary bases pairs. The peaks at 1067, 975, 920, and 859 cm^{-1} , which was shifted to lower wavenumber from ones in PS-AuNPs-probe and target DNA, indicating hydrogen bonding formation between N-H and N of complimentary base pairs. The development of PS-AuNPs thin film on ATR-FTIR spectroscopy gave the way for the simple, fast, portable label-free detection of target DNA sequence on solid surface.

4) Synthesis of Core Magnetic Nanoparticle and Shell Thermoresponsive Hydrogel

Kawani L. Brown

Abstract:

Magnetic nanoparticles are a class of nanoparticle which can be manipulated using magnetic field gradients. Such particles commonly consist of magnetic elements such as iron, nickel and cobalt and their chemical compounds. These particles may be used to selectively attach or transport a targeted species to a desired location by the influence of an external magnetic field. Magnetic nanoparticles are super-paramagnetic and small enough to offer great potential in a variety of applications in the bare form or by attaching other chemicals on their surface for a specific application. Hydrogels are extensively used for various biomedical applications such as: tissue engineering, wound dressing materials, molecular imprinting, drug delivery, etc. In this experiment the hydrogel, poly (N-isopropylacrylamide), was adopted as the shell for their thermoresponsive properties. Fourier transform infrared spectroscopy (FT-IR) was used to characterize them. From the FT-IR spectra there were significantly different peaks observed for both core and core-shell. The isopropyl and carbonyl functional groups peaks at 1386.814 and 1624.313 cm^{-1} were observed only in the spectra of the core-shell. This indicated that polymerization of the hydrogel has been successfully synthesized.

5) Investigation of Microgel Mediated Taxel Based Drugs for the Treatment of Breast Cancer Cell

Alycia Lewis

Abstract

Docetaxel (DTX) is a drug commonly used for its anticancer properties. It has been of use for over a decade and is used to treat a variety of cancer types. DTX is a hydrophobic drug that cannot be used alone in nature for the treatment of breast cancer. In order to increase the effectiveness of this drug, we will try to load more of this drug into a nanomaterial. Microgels of poly N-isopropylacrylamide (PNIPAM) were tested to load high amounts of DTX. It was found that the PNIPAM microgel is hydrophilic and experienced a release of the drug below the lower critical solution temperature. Because of this, PNIPAM was cross-linked with N-tert-butylacrylamide (BAM) to make a hydrophobic microgel (PNIPAM-BAM). Different ratios of PNIPAM-BAM microgels were synthesized. The synthesized hydrogels were studied using UV-Vis spectroscopy to look at their concentrations and the particle size analyzer was used to determine the particle sizes of the different hydrogel ratios. Also, the hydrogels were encapsulated with the DTX creating a hydrogel-DTX pellet. Using UV-Vis spectroscopy, the pellet was studied to measure the amount of drug being released as temperature increased.

Scanning Electron Microscopy (SEM, JEOL 6610LV)

1. Instrument description.

The scanning electron microscopy (SEM, JSM 6610LV) was purchased on 5/17/2012 from JEOL USA Inc. The JSM-6610LV is high-performance scanning electron microscopes for fast characterization and imaging of fine structures. With a large chamber and stage, it provides easily handle a wide variety of sample sizes and shapes and is widely-used in all research fields and industrial applications. It has "Low Vacuum" model provides the versatility of dealing with samples that are wet, oily, outgas excessively or are non-conductive without pretreatment.

The SEM located in the Natural Science Department, Albany State University and mainly used for the following purpose.

- Analyze and characterize samples for DoD project: "Portable sensor for chemical nerve agents and organophosphate compounds"
- Provide service for faculty member in the Natural Science Department at ASU, analyze and imaging sample
- Train undergraduate students to understand and use SEM as one of nanotechnology tools for research experiment.

2. Applications

a. SEM morphology characterization for polymer materials, metal nanoparticles, metal surface

SEM was used to characterize polystyrene nanoparticle and its assembly into CCA and PCCA network at low and high resolution.

SEM images of gold nanoparticles, zirconium sol-gel thin film, and stainless steel surface

SEM images of Laponite-Zirconium nanocomposite by electrochemical deposition

b. EDS characterization material components.

The SEM was equipped with the energy-dispersive X-ray spectroscopy (EDS) provides chemical analysis of the field of view or spot analyses of minute particles. The sample can be analyzed at spot, line or whole field of view.

- The EDS analysis of Zirconium nanoparticles in spot and whole field characterization
- The EDS analysis of Zirconium-laponite nanocomposite in whole field characterization

VII. Submitted Grant

1) A comprehensive assessment of the toxicity of organophosphate compounds and development of a high-throughput screening platform

Seong S. Seo, Ph.D. Byung-Hoon Kim, Ph.D. Co-PI; Yong J. Lee, Ph.D. Co-PI; Kenya T. Lemon, Ph.D. Senior Researcher; Shayla D. Williams, Ph.D. Senior Researcher; DOD MSI STEM, White paper, (not funded), 2015

2) Explosives Sensing by Electrochemistry and Fluorescence Spectroscopy using Carbon Quantum Dots

Seong S. Seo, Ph.D. DOD MSI STEM, White paper, (not funded), 2015

3) Gel Thin Films for the Analysis of Chemical Warfare Agents Simulants, Seong Seo PI, DOD HBCU MI (not funded), 2015

VIII. Publications and Presentations

a) Peer Reviewed Journals Selected Publications

1) Minh-Phuong Ngoc Bui and Seong S. Seo, "Zirconium oxide thin film modified β -cyclodextrin via sol-gel process for the detection of organophosphate compounds", submitted

2) Sudha Ananth, Jaya Gnana-Prakasam, KaBre'shiya, Minh-Phuong Ngoc Bui, Seong Seo, Sylvia Smith and Vadivel Ganapathy, "Mammalian and bacterial siderophores exhibit similar iron-chelation properties but elicit different biological effects

in mammalian retinal cells”, Investigative Ophthalmology & Visual Science in revision.

3) Kristopher Brown, Hyungie Doo, Honest Makamba, and Seong Seo, Spectroscopic Studies on Iron and 2,4-Dinitrotoluene Complex and Electrochemical Analysis of 2,4-Dinitrotoluen, analytical letter(in press) 2015, DOI: 10.1080/00032719.2015.1030675.

4) Minh-Phuong Ngoc Bui and Seong S. Seo*, Electrochemical Analysis of Parathion-ethyl using Zirconium Oxide-Laponite Nanocomposites Modified Glassy Carbon Electrode, Journal of Applied Electrochemistry, 2015, 45:365-373

5) Minh-Phuong Ngoc Bui and Seong S. Seo, “Fabrication of polymerized crystalline colloidal array thin film modified β -cyclodextrin for the detection of Paraoxon-ethyl and Parathion-ethyl”, Analytical Science, Vol. 30, 1-7, 2014

6) Minh-Phuong Ngoc Bui, Anil Khannal and Seong S. Seo, “Microgel encapsulated methylene blue for the treatment of breast cancer cell by photodynamic therapy”, Journal of Breast Cancer, March 17(1), 1-7, 2014

7) Determination of oligonucleotide on gold nanoparticle conjugated polystyrene particles thin film using ATR-FTIR spectroscopy, Juan Otano,[¿] Minh-Phuong N. Bui,[¿] and Seong S. Seo, (DOI:10.1080/00032719.2013.831429), Analytical Letters, Vol 47, 167-177, 2014

8) Hafnium Polystyrene Composite Particles for the Detection of Organophosphate Compound, Brittany Souder, Pandya Prashant, and Seong S. Seo, Soft Materials, Vol. 11, Number 1, 40-44, 2013

b) Selected Presentations

1) Hyungie Doo, Alycia Lewis, Lilya Heggs, and Seong Seo, Novel Hydrophobic Hydrogel to deliver Anti-cancer Drugs into targeted Cancer, UKC 2015 Conference, July 29-August 1, 2015, Hyatt Regency Atlanta, Atlanta, GA

2) Kristopher Brown, Minh-Phuong Ngoc Bui, Honest Makamba and Seong S. Seo, “Spectral Properties and Determination of 2, 4-Dinitrotuene by Using Modified Glassy Carbon Electrode”, 2014 CBD S&T Conference 17-21 November, 2014, St. Louis, MO

3) Charlene N. Middlebrooks, Minh-Phuong Ngoc Bui, Honest Makamba and Seong S. Seo “Determination of Dinitrotuene isomers by Using Silver Modified Glassy Carbon Electrode”, 2014 CBD S&T Conference 17-21 November, 2014, St. Louis, MO

4) Hyungie Doo, Anil Khanal and Seong Seo, “Investigation of microgel mediated taxel based drugs for the treatment of breast cancer”, The 66th Southeastern Regional Meeting of the American Chemical Society 2014, Nashville TN, Oct. 18th, 2014.

5) Minh-Phuong Ngoc Bui, and Seong Seo, “Electrochemical Analysis of Parathion-ethyl Pesticide by Zirconium Oxide-Laponite Composite Modified Glassy Carbon Electrode” (Oral) SERMACS 2013, Atlanta, GA, USA.

6) Minh-Phuong Ngoc Bui, and Seong Seo, “Sol-gel Thin Film of Zirconium Oxide for Detection of Organophosphate Compounds and Pesticides” (Poster) SERMACS 2013, Atlanta, GA, USA.

7) Minh-Phuong Ngoc Bui, and Seong Seo, “Gold Nanoparticle Conjugated Polystyrene Particles Thin Film For DNA Hybridization Detection Using ATR-FTIR Spectroscopy”, (Poster) SERMACS 2013, Atlanta, GA, USA.

8) Minh-Phuong Ngoc Bui, and Seong Seo, “Fabrication of polymer colloidal crystal array thin film for chemical nerve agent detection”, (Poster) 90th Georgia Academy of Science Conferencce, Valdosta, GA, USA. 2013

9) Minh-Phuong Ngoc Bui, and Seong Seo, “Polymer colloidal crystal array thin film for detection chemical nerve agent using optical reflectance measurement”, (Oral) 2013 Korean-American Scientists and Engineers Association Southeastern Regional Conference, Atlanta, GA, USA. Feb 23, 2013

10) Kristopher M. Brown, Minh-Phuong Ngoc Bui, and Seong Seo”Spectral Analysis of Iron Complex Formation to Different Derivatives of Dinitrotulene isomer compounds” (Oral) 2013 Korean-American Scientists and Engineers Association Southeastern Regional Conference, Atlanta, GA, USA. Feb 23, 2013

VI. Graduate Schools

a) Graduate School Information

1) Randy Lane: University of Alabama, Medical School

2) Juan C. Ontano, Pharmacy School at Charleston, SC

VII) Research Recognitions

- 1) ASU professor gets \$573,000 research grant from Defense Department, Fox 31, WFXL.com
- 2) ASU gets half million grant for research on national security, WALB News 10

VIII) Student Research Assistant and Presentations

- 2011-2012: Randy Lane, Kristopher M. Brown, Juan C. Ontano, Kimberly Gaines
- 2013-2014: Kristopher M. Brown, Juan C. Ontano, Kimberly Gaines, Trenicia Barner, Greer Williams, Ana Maldonado
- 2015-Present: Kristopher M. Brown, Lilya Heggs, Kawani Brown

IX) Bibliography

Seong S. Seo, Ph.D
Department of Natural Science,
Albany State University, Albany, GA 31705
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Education

Degree Year	Institution	Major
Post Doc, 2000-2002	University of Arkansas	Bioanalytical Chemistry
Ph. D, 1995-2000	University of Arkansas	Analytical Chemistry
M. S., 1993-1995	Polytechnic University at NY	Physical Chemistry
M.S., 1985-1987	Chonnam Nat., University, Korea	Analytical Chemistry
B. S., 1981-1985	Chonnam Nat., University, Korea	Chemistry

Research Experiences

2005 Summer, NIH-RIMI, summer research at Georgia Tech
2004 Summer, Mentor, NSF-HBCU-UP summer research at ASU
2003 Summer, Participating NSF-RSEC summer research at U of Tennessee, Knoxville, TN
2000-2002, Post Doctoral Research Associate, University of Arkansas

Teaching Experiences

2009-Present, Chemistry Program Coordinator, Albany State University, GA
2008-Present, Associate Professor, Albany State University, GA
2002 - 2008, Assistant Professor, Albany State University, GA
1995-2000, Teaching Assistant and Research Assistant, University of Arkansas
1993 – 1995, Teaching Assistant, Polytechnic University, New York
1985 – 1988, Instructor and Teaching Assistant, Chonnam Nat. University, Korea

Area of Certification

Teacher Certification, 1985, South Korea

Academic Awards:

- 1) Research of the Year 2010, April 2010, Albany State University
- 2) Grant Writing Award, Office of Research & Sponsored Programs, ASU, 2007
- 3) Who's Who Among America's Teachers, 2006, Who's Who ID#: 40469939-6

Funding

- 1) Portable Sensor for Chemical Nerve Agents and Organophosphorus compounds, Seong S. Seo, FY10 DoD Research and Educational Program for HBCUs/MIs. Role: PI, \$562,510.00
- 2) Ashok Jain (PI), Seong S. Seo (CO-PI), Arun Saha (CO-PI), DOD CDMRP Training Grant, "nanomaterial for the increased

detection, targeted drug delivery”, Role: Co-PI, \$1, 232, 015.00

3) Portable Sensor for Chemical Nerve Agents and Organophosphorus compounds, Seong S. Seo, FY08 DoD Infrastructure Support Program for HBCU/MI. \$426,460.00. (Awarded but not funded)

Technology Transfer

Portable Sensor for Chemical Nerve Agents and Organophosphorus

Compounds: contract Number: W911NF-11-1-0181

Seong S. Seo, Ph.D.

Department of Natural Sciences,
Albany State University
Albany, GA 31705

I. Summary of the most important result

We have developed an alternative approach for GC electrode modification using Laponite clay and ZrO₂ gel nanocomposites. This facile one-step fabrication using drop-and-dry techniques provides affordable, low cost electrode for OP compound detection. The fabrication process was optimized with 1:1 ratio of Laponite 2%:ZrO₂ gel, and the modified electrodes were successfully used for electrochemical detection of parathion-ethyl in acetate buffer, pH 4.0 using DPV technique. The sensors showed good linearity over a wide range of parathion-ethyl from 0 to 58.3 ng.mL⁻¹ ($R^2 = 0.994$) with a detection limit of 1.6 ng.mL⁻¹. The electrode exhibited high selectivity of parathion-ethyl detection in the presence of fenitrothion and demeton-S-methyl and showed good repeatability and reasonable stability. Although further investigation is needed for improving the reproducibility and stability, this work has expanded the scope of utilizing low cost Laponite clay-ZrO₂ gel nanocomposite for OP compound detection.

The DoD project has significantly benefited to establish a research laboratory of nanomaterial and microgels to develop sensors for chemical nerve agents and it has benefited the Natural Science department of Albany State University. The research laboratory is equipped with a Scanning Electron Microscopy (SEM). This equipment has enabled us to maintain student presence and interest in our laboratory. There is usually an average three undergraduates working in my laboratory, with 3 students at present for spring 2015. The typical student's experience includes research experience in my lab, conferences travel, numerous presentation opportunities, journal writing and publications. Furthermore, these students have found great success in their continuing education goals.

We published 6 papers in peer reviewed journals and presented 10 papers in regional and national conferences. There is one paper in the press and another one paper is submitted. The research efforts that the DOD project has supported have also incited much recognition from my peers, the community and the press. Our laboratory has been featured in numerous news articles, both internal and external, and upon faculty recommendations. There is excellent result to show that the DoD project has been instrumental in the Natural Science Department and our laboratory's research focus to advance and enhanced scientific knowledge in the areas of nanomaterial science and microgels.

II) Statement of the Problem Studied

Parathion-ethyl is an organophosphorous compound which is widely used as a pesticide in agricultural activities and it presents serious problems in the environment, especially in surface water and in the soil. The pesticides are meant to kill pests, but they are also dangerous to human beings if they are exposed regularly to such chemicals. Organophosphorus compounds

act by inhibiting an enzyme called acetylcholinesterase, which regulates nerve function. Because of their poisonous effects, these organophosphorus compounds are also used as nerve agents by rogue governments and terrorist organizations. Therefore it is important to develop analytical methods that can be applied to detect and analyze these dangerous compounds. This report is meant to develop methods that can be used to detect an organophosphorus compound electrochemically but the method can be modified for use in detecting similar organophosphorus compounds. In this report, we have developed a simple electrochemical electrode by surface modification of a glassy carbon electrode (GC) with a mixture of laponite clay and zirconium oxide (ZrO_2) gel nanocomposite, using a natural drop-and-dry technique. The modified Laponite- ZrO_2 nanocomposite electrode was evaluated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. Also, the effect of interfering pesticides such as demeton-S and fenitrothion was investigated. The stability of the electrode and the reproducibility of the analysis were also evaluated. The results showed that the Laponite- ZrO_2 nanocomposites modified GC electrode improved the sensitivity and selectivity in the detection of parathion-ethyl when compared to bare glassy carbon electrode. The fabricated electrode showed fast response, is cost effective, disposable and easily portable. The fabricated electrode has a potential for use in the detection of dangerous organophosphorus compounds in the environment.

III. Research Highlights

A) Fabrication of Polymerized Crystalline Colloidal Array Thin Film Modified β -Cyclodextrin Polymer for Paraoxon-ethyl and Parathion-ethyl Detection

Highlights

- 1) The PCCA thin film was modified with β -cyclodextrin (β -CD) polymer as capping cavity for the selectivity detection of paraoxon-ethyl, and parathion-ethyl chemical agents.
- 2) The PCCA thin film was characterized using scanning electron microscopy (SEM).
- 3) The diffraction peak of β -CD modified PCCA thin film showed red shift according to the change of paraoxon-ethyl and parathion-ethyl concentrations.

B) Inclusion Complexes of Paraoxon-ethyl and Parathion-ethyl with β -Cyclodextrin modified Zirconium Oxide Thin Film Using ATR-FTIR Spectroscopy

Highlights

- 1) The synthesis and modification of zirconium gel with β -cyclodextrin (ZrO_2 - β -CD) via sol-gel process have been established.
- 2) The surface morphology of ZrO_2 - β -CD gel was characterized by SEM and EDS and ATR-FTIR
- 3) The inclusion complexes of paraoxon-ethyl, parathion-ethyl on the ZrO_2 - β -CD gel thin film have been studied.

4) The hydrolysis of paraoxon-ethyl by ZrO_2 - β -CD gel thin film give peaks shifted in the ATR-FTIR spectra but that was not observed in case of parathion-ethyl with limit of detection as low as 0.03 μM .

C) Electrochemical Analysis of Parathion-ethyl using Zirconium Oxide-Laponite Nanocomposites Modified Glassy Carbon Electrode

Highlights

- 1) The simple electrochemical electrode was developed by surface modification of a glassy carbon electrode (GC) with a mixture of laponite clay and zirconium oxide (ZrO_2) gel nanocomposite, using natural drop-and-dry technique.
- 2) The surface morphology of modified glass carbon electrode was characterized by SEM, EDS and ATR-FTIR.
- 3) The detection limit of parathion-ethyl was calculated at the oxidation potential of 0.07 V with a value as low as 1.6 ng.mL^{-1} in the linear range from 0 to 58.3 ng.mL^{-1} ($R^2 = 0.994$).
- 4) The modified Laponite- ZrO_2 nanocomposite electrode was evaluated using cyclic voltammetry (CV) and different pulse voltammetry (DPV) techniques.

IV. Research Focus

1) Core/Shell (PS- ZrO_2) Portable Sensor for Chemical Nerve Agents Detection

Abstract

Synthetic chemical nerve agents or organophosphorous compounds such as demeton-S, parathion and paraoxon-ethyl, are widely used in agricultural as pesticides in the US and worldwide. These compounds are neurotoxins which can breakdown neurotransmitter acetylcholine at the neural synapse, resulting in a loss of muscular function, paralysis or death. Because of their high neurotoxicity, chemical nerve agents have been exploited for use as pesticides in crop, livestock, and poultry products and as chemical and biological warfare agents.

As a result of the high toxicity and the important for national security, fast and effective detection of chemical nerve agents in the environment and public place are needed. In recent years, organophosphorous pesticide kits have become commercial that offer advantages, including portability, rapid turnaround time, and cost effectiveness. However, these still involve complicated handling procedures and often lack sensitivity and precision in detecting low concentration at ppm level. Thus, the detection and identification of newly-introduced, OP neurotoxins in air, water and soil remains an extremely difficult challenge. To meet the requirements of rapid warning and field deployment, more-compact low-cost instruments, are highly desirable for facilitating the task of on-site monitoring of organophosphorous compounds. Recent research have become focusing of on the developing of sensor using nanomaterials for fast, high sensitivity and selectivity to detect chemical nerve agent. In this study, we fabricated polystyrene (PS) core with zirconium oxide (ZrO_2) nanoparticles conjugated on the surface of PS as a shell using different method of nanoparticles conjugation.

2) Fabrication PCCA and Zirconium Oxide Thin Film via Sol-gel Process for the Detection of Chemical Nerve Agent and Organophosphate Compounds

Abstract

In this report, we have demonstrated the synthesis, fabrication, and characterization of chemical sensor thin film for the detection of organophosphate compounds (OP) and pesticides. The PCCA thin film was modified with beta-cyclodextrin (β -CD) as a capping cavity for the selectivity detection of paraoxon-ethyl, and parathion-ethyl agents. The diffraction peak of β -CD modified PCCA thin film showed red shift according to the change of paraoxon-ethyl and parathion-ethyl concentrations. Optical reflectance measurement of OP compounds on β -CD modified PCCA thin film showed fast response (10 s) and high selectivity for the detection of paraoxon-ethyl and parathion-ethyl with the detection limit of 9.4 $\mu\text{g/L}$ and 2.0 $\mu\text{g/L}$, respectively. Secondly, we presented the synthesis and modification of zirconium- β -CD sol-gel thin film for the detection of paraoxon-ethyl and parathion-ethyl. The surface morphology of zirconium sol-gel was characterized by SEM, and EDS. Attenuated total reflectance fourier transform infrared (ATR-FTIR) spectroscopy was applied for detection OP. The results showed that the hydrolysis of paraoxon-ethyl by zirconium- β -CD sol-gel thin film give peaks shifted in the ATR-FTIR spectra with decrease transmittance percent. We suggested the hydrolysis of paraoxon-ethyl on zirconium- β -CD sol-gel involves the formation of β -CD-pesticide inclusion complexes just like the enzyme model.

3) Electrochemical Analysis of Parathion-ethyl using Zirconium Oxide-Laponite Nanocomposites Modified Glassy Carbon Electrode

Abstract

Parathion-ethyl is an organophosphorous compound which is widely used as a pesticide in agricultural activities and it presents serious problems in the environment, especially in surface water and in the soil. In this report, we have developed a simple electrochemical electrode by surface modification of a glassy carbon electrode (GC) with a mixture of laponite clay and zirconium oxide (ZrO_2) gel nanocomposite, using natural drop-and-dry technique. The modified electrode was used for the detection of parathion-ethyl pesticide. Different ratios of Laponite- ZrO_2 gel were used to modify the glassy carbon electrode. The fabricated electrode morphology was characterized using scanning electron microscopy (SEM) and X-ray diffraction spectroscopy (EDS) and attenuated total internal reflectance infrared spectroscopy (ATR-FTIR). The modified Laponite- ZrO_2 nanocomposite electrode was evaluated using cyclic voltammetry (CV) and different pulse voltammetry (DPV) techniques. Also, the effect of interfering pesticides such as demeton-S and fenitrothion was investigated. The stability of the electrode and the reproducibility of the analysis were also evaluated. The results showed that the Laponite- ZrO_2 nanocomposites modified GC electrode improved the sensitivity and selectivity in the detection of parathion-ethyl when compared to bare glassy carbon electrode. The detection limit of parathion-ethyl was calculated at the oxidation potential of 0.07 V with a value as low as 1.6

ng.mL⁻¹ in the linear range from 0 to 58.3 ng.mL⁻¹ ($R^2 = 0.994$). The fabricated electrode showed fast response, is cost effective, disposable and easily portable.

4) Inclusion Complexes of Paraoxon-ethyl and Parathion-ethyl with β -Cyclodextrin Modified Zirconium Oxide Thin Film Using ATR-FTIR Spectroscopy

Abstract

We have demonstrated the synthesis and modification of zirconium dioxide with β -cyclodextrin (ZrO_2 - β -CD) via sol-gel process and investigated the inclusion complexes of paraoxon-ethyl, parathion-ethyl on the ZrO_2 - β -CD thin film. The formation of sol-gel thin film process has been investigated and optimized. The morphology of ZrO_2 - β -CD gel was characterized using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was applied for characterization of the inclusion complexes of paraoxon-ethyl and parathion-ethyl on ZrO_2 - β -CD film. The hydrolysis of paraoxon-ethyl by ZrO_2 - β -CD gel thin film give peaks shifted in the ATR-FTIR spectra with increase in absorption intensity relating with the increasing paraoxon-ethyl concentration but that was not observed in the case of parathion-ethyl. The O-H vibration band of the intermolecular and intramolecular hydrogen bonds was observed to decrease with increasing paraoxon-ethyl concentration. Quantitative analysis of paraoxon-ethyl using ATR-FTIR showed good linearity in the range of 1 – 7 μ M ($R^2 = 0.99$, $n = 3$) with a limit of detection as low as 30 nM.

V. Student Project Report

1) Electrochemical Sensor for Pesticide and Organophosphate Compounds using Copper Nanoparticles

Trenicia Barner

Abstract:

This research experiment focused on the fabrication, development and evaluation of a chemical sensor for detection of pesticide and organophosphate compounds using copper nanoparticles. Electrochemical deposition was used to fabricate copper nanoparticles onto glassy carbon surface. The structure of copper nanoparticles was characterized by scanning electron microscopy (SEM). Sensor was evaluated using electrochemistry techniques such as cyclic voltammetry, and square wave stripping methods with demeton-S and paraoxon as sample models. Our fabricated sensor was expected to have high sensitivity, low cost, reproducibility and portability compared to enzyme-based sensors.

2) Spectral Properties of 2,4-Dinitrotoluene, 2,6-Dinitrotoluene, and 3,4-Dinitrotoluene with Fe(III) and Fe(II)

Kristopher Brown

Abstract

Some of the major objectives of analytical chemistry research include the search for quick and reliable methods to detect and analyze dangerous explosive materials, their precursors or their by-products. The work reports on the studies of the complex formation between the explosive 2,4 dinitrotoluene and iron ions in solution using absorption spectroscopy. Based on the results from spectroscopy we performed surface modification of glass carbon electrodes (GCE) by electrochemical reduction using Fe^{2+} ions at low pH and used them in the analysis of 2,4 dinitrotoluene (2,4 DNT). The electrochemical behavior of 2,4 DNT in solution was studied by square wave voltammetry (SWV) using the modified GCE. The deposited Fe solid material improved the electrochemical performance of the modified electrode. Concentrations of 2,4 DNT as low as 10 parts per billion (ppb) were detected using the Fe modified glass carbon electrode. Increasing the concentration of the 2,4 DNT resulted in the increase of the current signal strength. The increasing in the number of scans also resulted in an increase in signal strength.

3) Determination of DNA Hybridization on Gold Nanoparticle Conjugated Polystyrene Particles Thin Film using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

Juan Otano

Abstract

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to detect DNA hybridization on the polystyrene conjugated gold nanoparticles (PS-AuNPs) thin film. The AuNPs were first synthesized on the surface of poly(ethylenimine) coated polystyrene particles by citrate reduction and the single-stranded DNA with a 3'-C6-SH was then immobilized on AuNP surface via thiol bonding. UV-Vis spectrometry was used to monitor the conjugation of AuNPs on polystyrene particles and the immobilization of single-stranded DNA probe on PS-AuNPs. The morphology of PS-AuNPs thin film was characterized using scanning electron microscopy (SEM) showed successful conjugation and immobilization of our system. ATR-FTIR spectra obtained from the hybridization with complementary target DNA showed features of DNA structure and peaks shifted and changed at wave number 1657 cm^{-1} after hybridization compare to the non-complementary DNA due to the change in hydrogen bonding between N-H and C=O of complimentary bases pairs. The peaks at 1067 , 975 , 920 , and 859 cm^{-1} , which was shifted to lower wavenumber from ones in PS-AuNPs-probe and target DNA, indicating hydrogen bonding formation between N-H and N of complimentary base pairs. The development of PS-AuNPs thin film on ATR-FTIR spectroscopy gave the way for the simple, fast, portable label-free detection of target DNA sequence on solid surface.

4) Synthesis of Core Magnetic Nanoparticle and Shell Thermoresponsive Hydrogel

Kawani L. Brown

Abstract:

Magnetic nanoparticles are a class of nanoparticle which can be manipulated using magnetic field gradients. Such particles commonly consist of magnetic elements such as iron, nickel and cobalt and their chemical compounds. These particles may be used to selectively attach or transport a targeted species to a desired location by the influence of an external magnetic field. Magnetic nanoparticles are super-paramagnetic and small enough to offer great potential in a variety of applications in the bare form or by attaching other chemicals on their surface for a specific application. Hydrogels are extensively used for various biomedical applications such as: tissue engineering, wound dressing materials, molecular imprinting, drug delivery, etc. In this experiment the hydrogel, poly (N-isopropylacrylamide), was adopted as the shell for their thermoresponsive properties. Fourier transform infrared spectroscopy (FT-IR) was used to characterize them. From the FT-IR spectra there were significantly different peaks observed for both core and core-shell. The isopropyl and carbonyl functional groups peaks at 1386.814 and 1624.313 cm^{-1} were observed only in the spectra of the core-shell. This indicated that polymerization of the hydrogel has been successfully synthesized.

5) Investigation of Microgel Mediated Taxel Based Drugs for the Treatment of Breast Cancer Cell

Alycia Lewis

Abstract

Docetaxel (DTX) is a drug commonly used for its anticancer properties. It has been of use for over a decade and is used to treat a variety of cancer types. DTX is a hydrophobic drug that cannot be used alone in nature for the treatment of breast cancer. In order to increase the effectiveness of this drug, we will try to load more of this drug into a nanomaterial. Microgels of poly N-isopropylacrylamide (PNIPAM) were tested to load high amounts of DTX. It was found that the PNIPAM microgel is hydrophilic and experienced a release of the drug below the lower critical solution temperature. Because of this, PNIPAM was cross-linked with N-butylacrylamide (BAM) to make a hydrophobic microgel (PNIPAM-BAM). Different ratios of PNIPAM-BAM microgels were synthesized. The synthesized hydrogels were studied using UV-Vis spectroscopy to look at their concentrations and the particle size analyzer was used to determine the particle sizes of the different hydrogel ratios. Also, the hydrogels were encapsulated with the DTX creating a hydrogel-DTX pellet. Using UV-Vis spectroscopy, the pellet was studied to measure the amount of drug being released as temperature increased.

VI. Instrument Project Report

Scanning Electron Microscopy (SEM, JEOL 6610LV)

1. Instrument description.

The scanning electron microscopy (SEM, JSM 6610LV) was purchased on 5/17/2012 from JEOL USA Inc. The JSM-6610LV is high-performance scanning electron microscopes for fast characterization and imaging of fine structures. With a large chamber and stage, it provides easily handle a wide variety of sample sizes and shapes and is widely-used in all research fields and industrial applications. It has “Low Vacuum” model provides the versatility of dealing with samples that are wet, oily, outgas excessively or are non-conductive without pretreatment.

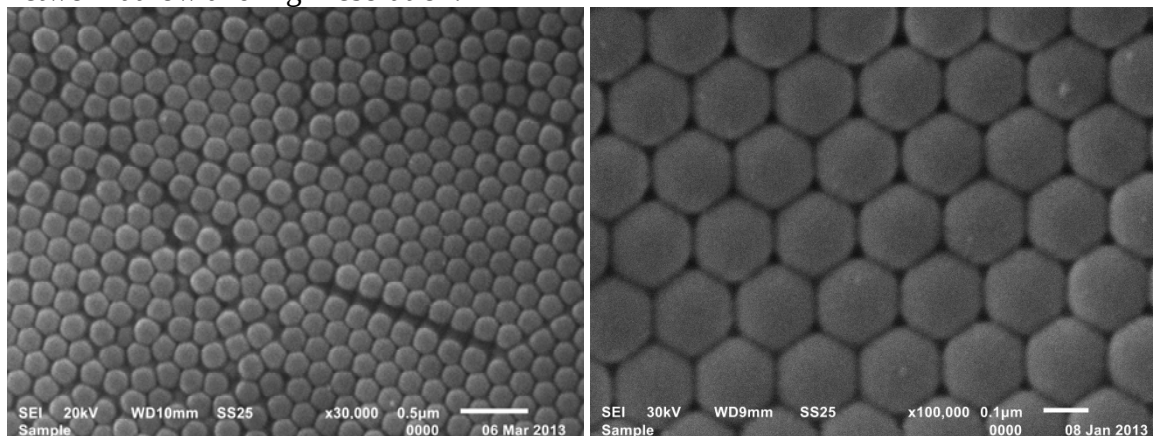
The SEM located in the Natural Science Department, Albany State University and mainly used for the following purpose.

- Analyze and characterize samples for DoD project: "Portable sensor for chemical nerve agents and organophosphate compounds"
- Provide service for faculty member in the Natural Science Department at ASU, analyze and imaging sample
- Train undergraduate students to understand and use SEM as one of nanotechnology tools for research experiment.

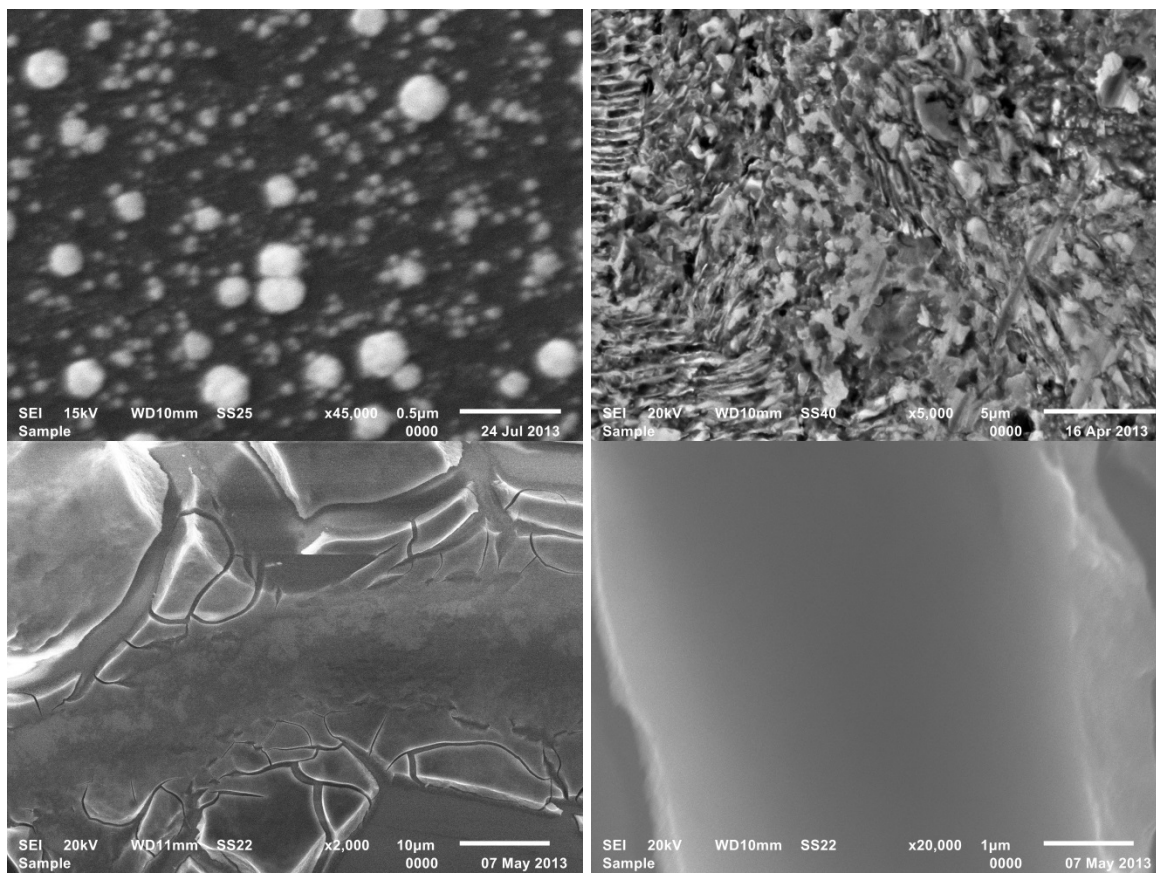
2. Applications

a. SEM morphology characterization for polymer materials, metal nanoparticles, metal surface

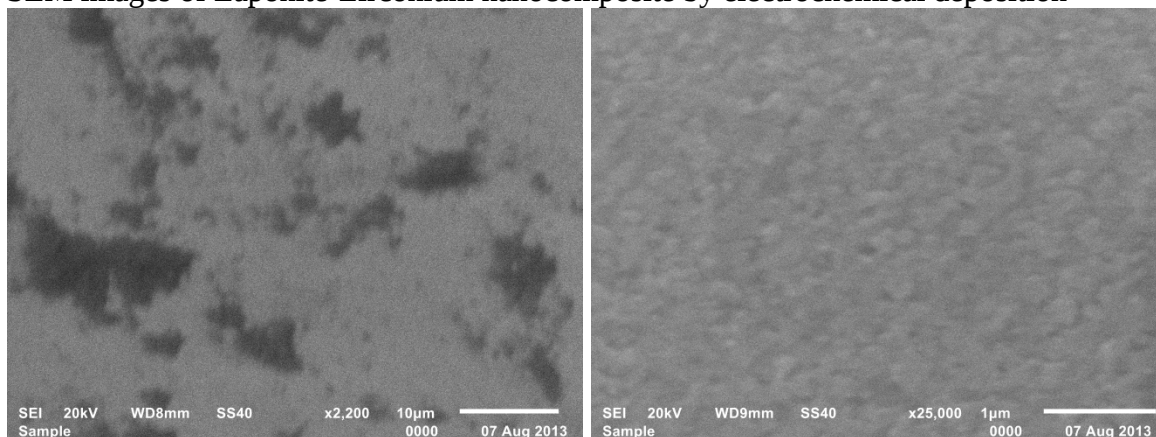
SEM was used to characterize polystyrene nanoparticle and its assembly into CCA and PCCA network at low and high resolution.



SEM images of gold nanoparticles, zirconium sol-gel thin film, and stainless steel surface



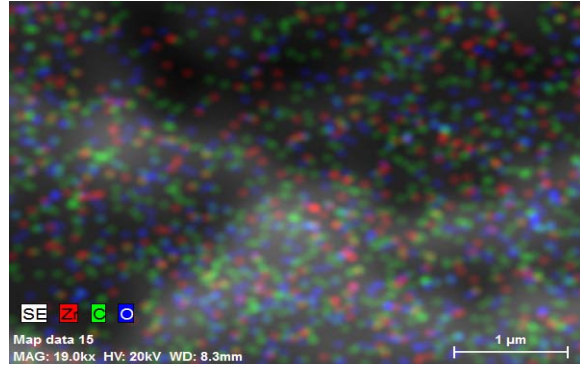
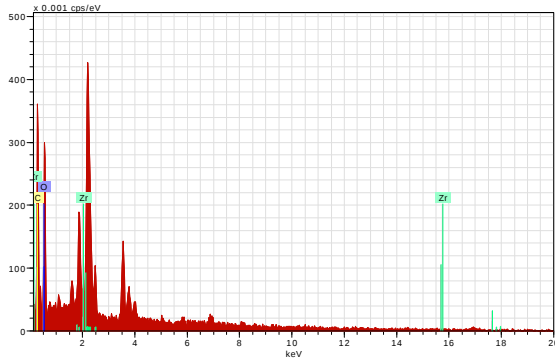
SEM images of Laponite-Zirconium nanocomposite by electrochemical deposition



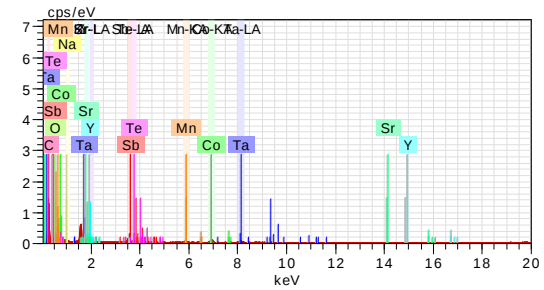
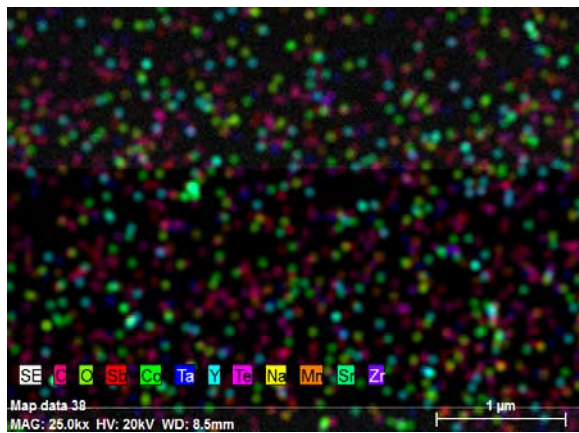
b. EDS characterization material components.

The SEM was equipped with the energy-dispersive X-ray spectroscopy (EDS) provides chemical analysis of the field of view or spot analyses of minute particles. The sample can be analyzed at spot, line or whole field of view.

- The EDS analysis of Zirconium nanoparticles in spot and whole field characterization



- The EDS analysis of Zirconium-laponite nanocomposite in whole field characterization



VII. Submitted Grant

- 1) A comprehensive assessment of the toxicity of organophosphate compounds and development of a high-throughput screening platform
Seong S. Seo, Ph.D. Byung-Hoon Kim, Ph.D. Co-PI; Yong J. Lee, Ph.D. Co-PI; Kenya T. Lemon, Ph.D. Senior Researcher; Shayla D. Williams, Ph.D. Senior Researcher; DOD MSI STEM, White paper, (not funded), 2015
- 2) Explosives Sensing by Electrochemistry and Fluorescence Spectroscopy using Carbon Quantum Dots
Seong S. Seo, Ph.D. DOD MSI STEM, White paper, (not funded), 2015
- 3) Gel Thin Films for the Analysis of Chemical Warfare Agents Simulants, Seong Seo PI, DOD HBCU MI (not funded), 2015

VIII. Publications and Presentations

a) Peer Reviewed Journals Selected Publications

- 1) Minh-Phuong Ngoc Bui and Seong S. Seo, “Zirconium oxide thin film modified β -cyclodextrin via sol-gel process for the detection of organophosphate compounds”, *submitted*
- 2) Sudha Ananth, Jaya Gnana-Prakasam, KaBre'shiya, Minh-Phuong Ngoc Bui, Seong Seo, Sylvia Smith and Vadivel Ganapathy, “Mammalian and bacterial siderophores exhibit similar iron-chelation properties but elicit different biological effects in mammalian retinal cells”, *Investigative Ophthalmology & Visual Science* in revision.
- 3) Kristopher Brown, Hyungie Doo, Honest Makamba, and Seong Seo, Spectroscopic Studies on Iron and 2,4-Dinitrotoluene Complex and Electrochemical Analysis of 2,4-Dinitrotoluen, *analytical letter(in press) 2015*, DOI: [10.1080/00032719.2015.1030675](https://doi.org/10.1080/00032719.2015.1030675).
- 4) Minh-Phuong Ngoc Bui and Seong S. Seo*, Electrochemical Analysis of Parathion-ethyl using Zirconium Oxide-Laponite Nanocomposites Modified Glassy Carbon Electrode, *Journal of Applied Electrochemistry*, 2015, 45:365-373
- 5) Minh-Phuong Ngoc Bui and Seong S. Seo, “Fabrication of polymerized crystalline colloidal array thin film modified β -cyclodextrin for the detection of Paraoxon-ethyl and Parathion-ethyl”, *Analytical Science*, Vol. 30, 1-7, 2014
- 6) Minh-Phuong Ngoc Bui, Anil Khannal and Seong S. Seo, “Microgel encapsulated methylene blue for the treatment of breast cancer cell by photodynamic therapy”, *Journal of Breast Cancer*, March 17(1), 1-7, 2014
- 7) Determination of oligonucleotide on gold nanoparticle conjugated polystyrene particles thin film using ATR-FTIR spectroscopy, Juan Otano,[†] Minh-Phuong N. Bui,[†] and Seong S. Seo, (DOI:10.1080/00032719.2013.831429), *Analytical Letters*, Vol 47, 167-177, 2014

8) Hafnium Polystyrene Composite Particles for the Detection of Organophosphate Compound, Brittany Souder, Pandya Prashant, and Seong S. Seo, *Soft Materials*, Vol. 11, Number 1, 40-44, 2013

b) Selected Presentations

1) Hyungie Doo, Alycia Lewis, Lilya Heggs, and Seong Seo, Novel Hydrophobic Hydrogel to deliver Anti-cancer Drugs into targeted Cancer, UKC 2015 Conference, July 29-August 1, 2015, Hyatt Regency Atlanta, Atlanta, GA

2) Kristopher Brown, Minh-Phuong Ngoc Bui, Honest Makamba and Seong S. Seo, "Spectral Properties and Determination of 2, 4-Dinitrotuene by Using Modified Glassy Carbon Electrode", 2014 CBD S&T Conference 17-21 November, 2014, St. Louis, MO

3) Charlene N. Middlebrooks, Minh-Phuong Ngoc Bui, Honest Makamba and Seong S. Seo "Determination of Dinitrotuene isomers by Using Silver Modified Glassy Carbon Electrode", 2014 CBD S&T Conference 17-21 November, 2014, St. Louis, MO

4) Hyungie Doo, Anil Khanal and Seong Seo, "Investigation of microgel mediated taxel based drugs for the treatment of breast cancer", The 66th Southeastern Regional Meeting of the American Chemical Society 2014, Nashville TN, Oct. 18th, 2014.

5) Minh-Phuong Ngoc Bui, and Seong Seo, "Electrochemical Analysis of Parathion-ethyl Pesticide by Zirconium Oxide-Laponite Composite Modified Glassy Carbon Electrode" (Oral) SERMACS 2013, Atlanta, GA, USA.

6) Minh-Phuong Ngoc Bui, and Seong Seo, "Sol-gel Thin Film of Zirconium Oxide for Detection of Organophosphate Compounds and Pesticides" (Poster) SERMACS 2013, Atlanta, GA, USA.

7) Minh-Phuong Ngoc Bui, and Seong Seo, "Gold Nanoparticle Conjugated Polystyrene Particles Thin Film For DNA Hybridization Detection Using ATR-FTIR Spectroscopy", (Poster) SERMACS 2013, Atlanta, GA, USA.

8) Minh-Phuong Ngoc Bui, and Seong Seo, "Fabrication of polymer colloidal crystal array thin film for chemical nerve agent detection", (Poster) 90th Georgia Academy of Science Conference, Valdosta, GA, USA. 2013

9) Minh-Phuong Ngoc Bui, and Seong Seo, "Polymer colloidal crystal array thin film for detection chemical nerve agent using optical reflectance measurement", (Oral) 2013 Korean-American Scientists and Engineers Association Southeastern Regional Conference, Atlanta, GA, USA. Feb 23, 2013

10) Kristopher M. Brown, Minh-Phuong Ngoc Bui, and Seong Seo "Spectral Analysis of Iron Complex Formation to Different Derivatives of Dinitrotulene isomer compounds" (Oral) 2013

Korean-American Scientists and Engineers Association Southeastern Regional Conference,
Atlanta, GA, USA. Feb 23, 2013

VI. Graduate Schools

a) Graduate School Information

- 1) Randy Lane: University of Alabama, Medical School
- 2) Juan C. Ontano, Pharmacy School at Charleston, SC

VII) Research Recognitions

- 1) ASU professor gets \$573,000 research grant from Defense Department, Fox 31, WFXL.com
- 2) ASU gets half million grant for research on national security, WALB News 10

VIII) Student Research Assistant and Presentations

- 2011-2012: Randy Lane, Kristopher M. Brown, Juan C. Ontano, Kimberly Gaines
- 2013-2014: Kristopher M. Brown, Juan C. Ontano, Kimberly Gaines, Trenicia Barner, Greer Williams, Ana Maldonado
- 2015-Present: Kristopher M. Brown, Lilya Heggs, Kawani Brown

IX) Bibliography

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Albany State University, Albany, GA 31705

seong.seo@asurams.edu, (229) 430-4825(O)

Education

<u>Degree Year</u>	<u>Institution</u>	<u>Major</u>
Post Doc, 2000-2002	University of Arkansas	Bioanalytical Chemistry
Ph. D, 1995-2000	University of Arkansas	Analytical Chemistry
M. S., 1993-1995	Polytechnic University at NY	Physical Chemistry
M.S., 1985-1987	Chonnam Nat., University, Korea	Analytical Chemistry
B. S., 1981-1985	Chonnam Nat., University, Korea	Chemistry

Research Experiences

2005 Summer, NIH-RIMI, summer research at Georgia Tech
2004 Summer, Mentor, NSF-HBCU-UP summer research at ASU
2003 Summer, Participating NSF-RSEC summer research at U of Tennessee, Knoxville, TN
2000-2002, Post Doctoral Research Associate, University of Arkansas

Teaching Experiences

2009-Present, Chemistry Program Coordinator, Albany State University, GA
2008-Present, Associate Professor, Albany State University, GA
2002 - 2008, Assistant Professor, Albany State University, GA
1995-2000, Teaching Assistant and Research Assistant, University of Arkansas
1993 – 1995, Teaching Assistant, Polytechnic University, New York
1985 – 1988, Instructor and Teaching Assistant, Chonnam Nat. University, Korea

Area of Certification

Teacher Certification, 1985, South Korea

Academic Awards:

- 1) Research of the Year 2010, April 2010, Albany State University
- 2) Grant Writing Award, Office of Research & Sponsored Programs, ASU, 2007
- 3) Who's Who Among America's Teachers, 2006, Who's Who ID#: 40469939-6

Funding

- 1) Portable Sensor for Chemical Nerve Agents and Organophosphorus compounds, Seong S. Seo, FY10 DoD Research and Educational Program for HBCUs/MIs. *Role: PI, \$562,510.00*
- 2) Ashok Jain (PI), Seong S. Seo (CO-PI), Arun Saha (CO-PI), DOD CDMRP Training Grant, “nanomaterial for the increased detection, targeted drug delivery”, *Role: Co-PI, \$1, 232, 015.00*
- 3) Portable Sensor for Chemical Nerve Agents and Organophosphorus compounds, Seong S. Seo, FY08 DoD Infrastructure Support Program for HBCU/MI. *\$426,460.00.* (Awarded but not funded)