

REPORT DOCUMENTATION PAGE

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RPPR Final Report
as of 01-Nov-2018

Agency Code:

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INVESTIGATOR(S):

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DUNS Number: 824910376

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Final Report for Period Beginning 01-Jul-2013 and Ending 31-Mar-2018

Title: Graphene-Based Assemblies for Sensing and Degradation of Hazardous Chemical Contaminants

Begin Performance Period: 01-Jul-2013

End Performance Period: 31-Mar-2018

Report Term: 0-Other

Submitted By: Prashant Kamat

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STEM Degrees: 5

STEM Participants: 6

Major Goals: Detection and mineralization of representative hazardous chemicals such as 4-nitrobenzenethio (4-NBT) and dimethyl methylphosphonate (DMMP) are being tested using semiconductor, metal oxide and metallic nanoparticles. The overarching goal to design catalytic and photocatalytic systems for simultaneous detection and degradation of these organic contaminants was addressed during the funding period.

Accomplishments: Please refer to "Accomplishments" Document in "Upload" section.

Training Opportunities: Graduate student (Victoria L. Bridewell) successfully completed defended her PhD thesis in Spring 2018 (Semiconductor and graphene oxide nanomaterial assemblies for sensing and photocatalytic degradation of chemical contaminants) . Her work was funded through this grant.

RPPR Final Report

as of 01-Nov-2018

Results Dissemination: Meeting Presentations

Surface Sciences and Multifunctional Materials Review, 2016, Durham, NC
Bridewell, V.L.; Alam, R.; Karwacki, C.J.; Kamat, P. V. Graphene-Based Multifunctional Catalyst Mats: Simultaneous Sensing and Degradation of Model Simulants. (Oral)

PINDU Inorganic Symposium, 2016, Purdue University, West, Lafayette IN
Bridewell V.L.; Alam R.; Karwacki C.J.; Kamat P.V. Size-tunable CdSe/CdS nanorods as photocatalysts. (Oral)

Summer Undergraduate Research Symposium, 2017, Notre Dame, IN
Butler, S. K.; Bridewell, V. L.; Kamat, P. V. Degradation of Chemical Warfare Agent Proxies through ZnO Nanocrystal Assisted Photocatalysis. (Poster)

Radomsky, R. C.; Bridewell, V. L.; Kamat, P. V. ZnO and CdSe Dual-Emission Ratiometric Probe for the Detection of Organophosphonates. (Poster)

Gordon Research Conference on Environmental Nanotechnology, Stoweflake Conference Center in Stowe VT, June 18, 2017 – June 23, 2017 Prashant V. Kamat, Making Sense of Smart Sensors. A Nanotechnology Perspective for Environmental Remediation (Invited)

DTRA Surface Science/Multifunctional Materials Science, an Army Research Meeting, Raleigh, North Carolina, September 5-7, 2017 Simultaneous Sensing and Degradation of Model Simulants

ACS Publications Symposium: Innovation in Energy Conversion, in Dalian China September 24-26 "Photocatalysis to Photovoltaics: Managing Charge Transfer at Semiconductor Interface"

Undergraduate Research Symposium: Notre Dame, IN

July 26 "Degradation of Chemical Warfare Agent Proxies through ZnO Nanocrystal Assisted Photocatalysis"

Savannah Butler, V. L. Bridewell, and P. V. Kamat "ZnO and CdSe Dual-Emission Ratiometric Probe for the Detection of Organophosphonates" Rebecca Radomsky, V. L. Bridewell, and P. V. Kamat

PINDU Inorganic Symposium: Bloomington, IN, October 28

"Towards Heterogeneous CO₂ Catalysis with Reduced Graphene Oxide and Fe-porphyrin Complexes" Victoria L. Bridewell (ND Chair and Organizer), M. Robert, and P. V. Kamat

Honors and Awards: Cited as one of the most cited researchers by Clarivate Analytics

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI

Participant: Prashant V Kamat

Person Months Worked: 1.00

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Funding Support:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Shanthil Madhavan

RPPR Final Report
as of 01-Nov-2018

Person Months Worked: 7.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Victoria L. Bridewell

Person Months Worked: 12.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

ARTICLES:

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First Page #: 0

Date Submitted:

Date Published:

Publication Location:

Article Title: : Simultaneous Detection and Degradation of Low-Level Contaminants Using Graphene-Based Smart Material Assembly

Authors:

Keywords: graphene oxide; photocatalysis; SERS detection; environmental remediation; nitro compounds; TiO₂

Abstract: Smart material nanoassemblies that can simultaneously sense and shoot low level contaminants from air and water are important for overcoming the threat of hazardous chemicals. Graphene oxide (GO) sheets deposited on mesoscopic TiO₂ films that underpin the deposition of Ag nanoparticles with UV-irradiation provide the foundation for the design of a smart material. The Ag particle size is readily controlled through precursor concentration and UV irradiation time. These semiconductor - graphene oxide - metal (SGM) films are SERS active and hence capable of sensing aromatic contaminants such as nitrobenzenethiol (NBT) in nanomolar range. Increased local concentration of organic molecule achieved through interaction with 2D carbon support (GO) facilitates low-level detection of contaminants. Upon UV irradiation of the NBT loaded SGM film, one can induce photocatalytic transformations. Thus, each component of the SGM film plays a pivotal role in aiding the detection and degradation of a cont

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Date Submitted:

Date Published:

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Article Title: Taming Bipolar Membranes: Tracking Electron Flow in Photocatalytically Active Membranes.

Authors: Bridewell, V.L.; Karwacki, C. J.; Kamat, P. V.

Keywords: bipolar membrane, photocatalysis, electron transfer

Abstract: Oxidation/reduction reactions employing metal nanoparticles play an important role in emerging energy technologies as well as photocatalytic remediation of wastewater and air. The effective removal of toxic industrial chemicals as well as chemical warfare agents such as organophosphates, sulfur mustards, and nitroaromatics, from wastewater runoff or accidental discharge, is of vital importance.^{1–4} Because of their deleterious health hazards at very low levels (ppb – ppm), efficient and rapid removal remains difficult. Photocatalytic remediation of these low-level contaminants has already been shown to be effective from both air and water with metal oxides and nanoparticles; however, colloidal stability of catalytically active nanoparticles and thus long-term use of these systems is limited. We were able to carry out catalytic reduction of undesired chemicals such as nitroaromatics.

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Acknowledged Federal Support: Y

Research Progress:

Sense and Shoot: Simultaneous Detection and Degradation of Low Level Contaminants using Graphene Based Smart Material Assembly

Smart material nanoassemblies that can simultaneously *sense and shoot* low-level contaminants from air and water are important for overcoming the threat of hazardous chemicals. Graphene oxide (GO) sheets deposited on mesoscopic TiO₂ films that underpin the deposition of Ag nanoparticles with UV-irradiation provide the foundation for the design of a *smart material* (Figure 1). The Ag particle size is readily controlled through precursor concentration and UV irradiation time. These semiconductor – graphene oxide – metal (SGM) films are SERS active and hence capable of sensing aromatic contaminants such as 4-nitrobenzenethiol (4-NBT) in nanomolar range. Increased local concentration of organic molecule achieved through interaction with 2D carbon support (GO) facilitates low-level detection of contaminants. Upon UV irradiation of 4-NBT loaded SGM film, one can induce photocatalytic transformations. Thus, each component of the SGM film plays a pivotal role in aiding the detection and degradation of a contaminant dispersed in aqueous solutions. The advantage of using SGM films as multipurpose “detect and destroy” systems for nitroaromatic molecule is discussed.

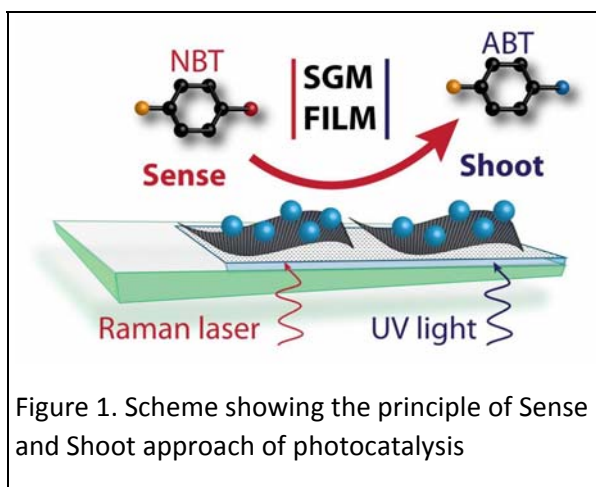


Figure 1. Scheme showing the principle of Sense and Shoot approach of photocatalysis

Modulation of Cu_{2-x}S Nanocrystal Plasmon Resonance through Reversible Photoinduced Electron Transfer

Copper sulfide (Cu_{2-x}S) nanocrystals with nonstoichiometric composition exhibit plasmon resonance in the near-infrared region. Compositional changes and varying electron density markedly affects the position and intensity of the plasmon resonance (Figure 2). We report a photochemically induced phenomenon of modulating the plasmon resonance in a controlled fashion. As photogenerated reduced methyl viologen radicals transfer electrons to Cu_{2-x}S in inert solutions, we observe a decrease in localized surface plasmon resonance (LSPR) absorbance at 1160 nm. Upon exposure to air the plasmon resonance band recovers as stored electrons are scavenged away by oxygen. This cycle of electron charge and discharge of Cu_{2-x}S nanocrystals is reversible and can be repeated through photoirradiation in N₂ saturated solution and then exposing the suspension to air. The spectroscopic study that provides mechanistic insights into the reversible charging and discharging of plasmonic Cu_{2-x}S are discussed.

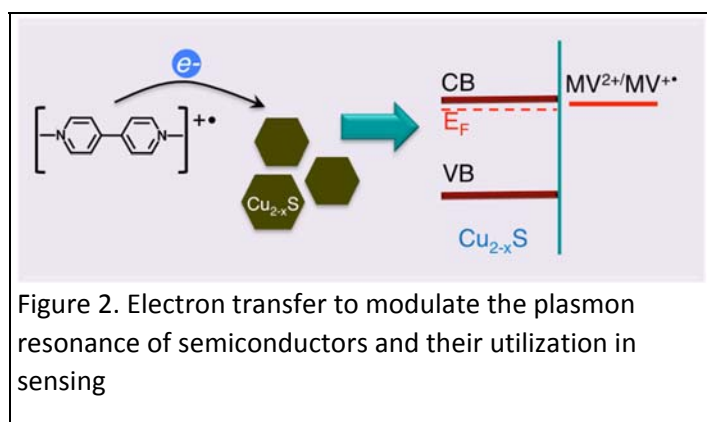


Figure 2. Electron transfer to modulate the plasmon resonance of semiconductors and their utilization in sensing

CdSe/CdS Nanorod Photocatalysts: Tuning the Interfacial Charge Transfer Process through Shell Length

CdSe/CdS core/shell semiconductor nanorods (NR) with rod-in-rod morphology offer new strategies for designing highly emissive nanostructures. The interplay between energetically matched semiconductors results in enhanced emission from the CdSe core. In order to further evaluate the cooperative role of these two semiconductors in a core/shell geometry, we have probed the photoinduced charge transfer between CdSe/CdS core/shell semiconductor NR and methyl viologen (MV^{2+}) (Figure 3). The quenching of the emission by the electron acceptor, MV^{2+} , as well as the production of electron transfer product $MV^{\bullet+}$ depends on the aspect ratio (l/w) of the NR thus pointing out the role of CdS shell in determining the overall photocatalytic efficiency.

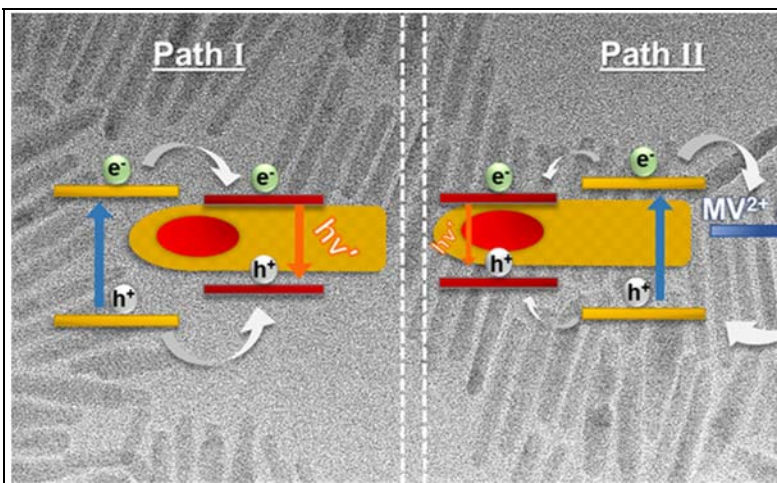


Figure 3. Photoinduced charge transfer between CdSe/CdS core/shell semiconductor NR and methyl viologen (MV^{2+})

Transient absorption measurements show that the presence of MV^{2+} influences only the bleaching recovery of the CdS shell and not of the CdSe core recovery. Thus, optimization of shell aspect ratio plays a crucial role in maximizing the efficiency of this photocatalytic system.

Electrocatalysis with Reduced Graphene Oxide. Electron Shuttling between Redox Couples Anchored on a 2-D Surface

The electron storage and shuttling capabilities of reduced graphene oxide (RGO) have been explored by anchoring two redox couples, methyl viologen (MV^{2+}) and ferrocene (Fc) (Figure 4). When an RGO modified glassy carbon electrode (RGO/GCE) was subjected to a cathodic scan, a quasi-reversible reduction of MV^{2+} was seen indicating a loss of electrons contributed to “charging” of RGO. These stored electrons can then be transported to oxidized Fc during the anodic scan through the C-C network of RGO.

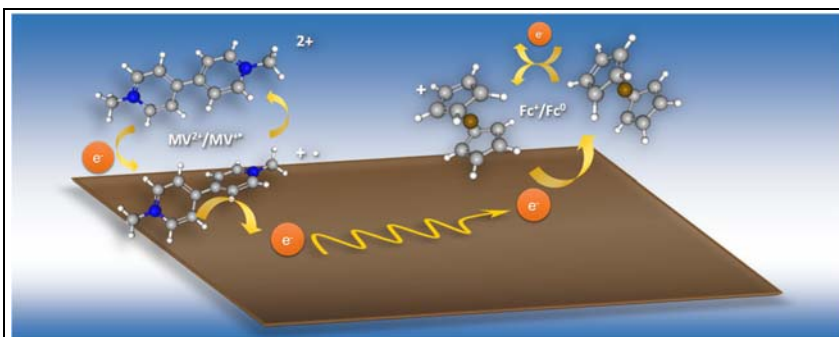


Figure 4. Electron shuttling properties of graphene oxide

The recycling and peak current magnitude of oxidized and reduced forms of Fc during the anodic scan is strongly dependent on the scan rate, concentration and extent of MV^{2+} reduction,

either complete or partial, during the cathodic scan. This electrocatalytic property of RGO film enables the design of sensors and catalysts with the capacity to capture, store and shuttle electrons and corroborate a boost in sensitivity for the electrochemical detection and conversion of low level analytes.

TiO₂ and silver nanoparticle functionalized carbon fibers for detection and degradation of DMMP

Incorporation of TiO₂ and silver nanoparticles (AgNP) on PTFE treated carbon fabric (CF) have

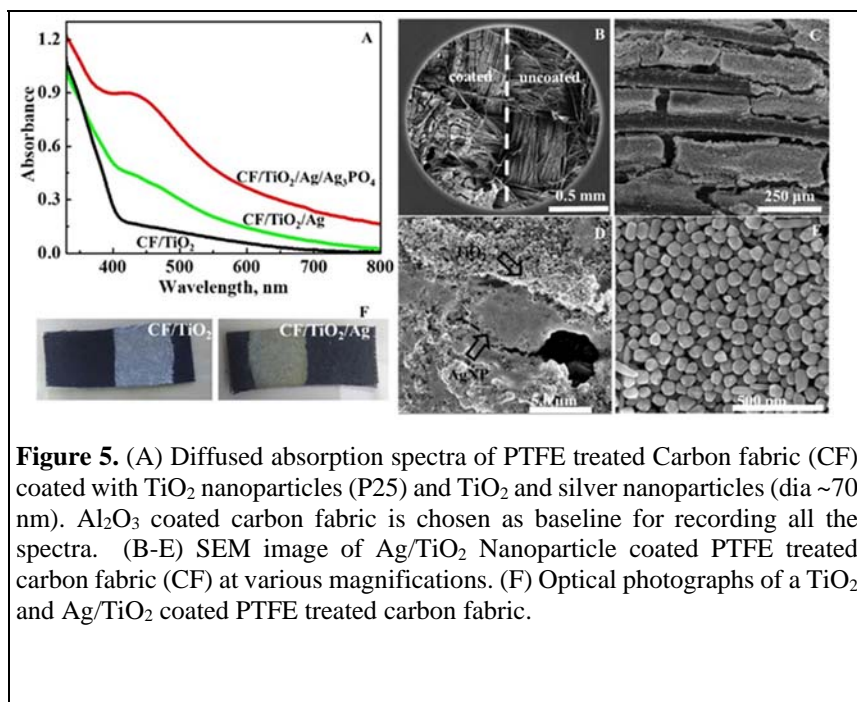


Figure 5. (A) Diffused absorption spectra of PTFE treated Carbon fabric (CF) coated with TiO₂ nanoparticles (P25) and TiO₂ and silver nanoparticles (dia ~70 nm). Al₂O₃ coated carbon fabric is chosen as baseline for recording all the spectra. (B-E) SEM image of Ag/TiO₂ Nanoparticle coated PTFE treated carbon fabric (CF) at various magnifications. (F) Optical photographs of a TiO₂ and Ag/TiO₂ coated PTFE treated carbon fabric.

been developed to sense and degrade phosphonated derivatives. The porosity of carbon fabric allows the penetration of small molecules and provide rooms for photodegradation. On the other hand, hydrophobicity of PTFE coating prevents the self-degradation of fabric during photodegradation process. Combining these three materials synchronically provides a material with interesting properties for real kind of applications.

The as prepared CF/TiO₂/Ag were initially characterized by diffused reflectance spectroscopy as shown in the Figure 5A. Surface plasmon resonance of citrate capped silver nanoparticles was observed at 440 nm on Ag/TiO₂ coated carbon fabric. Scanning Electron Microscope (SEM) images of Ag/TiO₂/CF were recorded at various magnifications are presented in the Figure 5 B-E. TiO₂ nanoparticles were distributed on the surface and in between the fibers of the fabric. The drop casted AgNPs (dia – 70 nm) forms islands on the surface of TiO₂ nanoparticles (dia 21 nm) and it is evident from the SEM image. The Ag/TiO₂ assemblies make carbon fabric can be used as detection and degradation substrate for chemical contaminants.

Photocatalysis of 4-nitrobenzenethiol via electron shuttling using AuNP decorated bipolar membranes.

Oxidation/reduction reactions employing metal nanoparticles play an important role in emerging energy technologies as well as photocatalytic remediation of wastewater and air. The effective removal of toxic industrial chemicals as well as chemical warfare agents such as

organophosphates, sulfur mustards, and nitroaromatics, from wastewater runoff or accidental discharge, is of vital importance.¹⁻⁴ Because of their deleterious health hazards at very low levels (ppb – ppm), efficient and rapid removal remains difficult. Photocatalytic remediation of these low-level contaminants has already been shown to be effective from both air and water with metal oxides and nanoparticles; however, colloidal stability of catalytically active nanoparticles and thus long-term use of these systems is limited. By incorporating catalytic particles in a membrane we should be able to carry out catalytic reduction of undesired chemicals such as nitroaromatics.

As discussed in the previous report a bipolar membrane (BPM) with cation exchange layer (CEL) and anion exchange layer (AEL) attached back to back allows manipulation of nanoparticle (NP) loading for desired applications. By loading the BPM directly with an electron donor (methyl viologen) and catalyst (gold) particles, we have been able to carry out heterogeneous catalysis (Figure 6). A concerted electron transfer cascade with methyl viologen (MV^{2+}) in the CEL and AuNP in the AEL we prepared BPM for photocatalysis. This BPM enabled us to undertake photocatalytic degradation of 4-Nitrobenzenethiol (4-NBT) to 4-aminobenzenethiol (4-ABT) via a light-induced electron transfer cascade across the CEL/AEL junction.

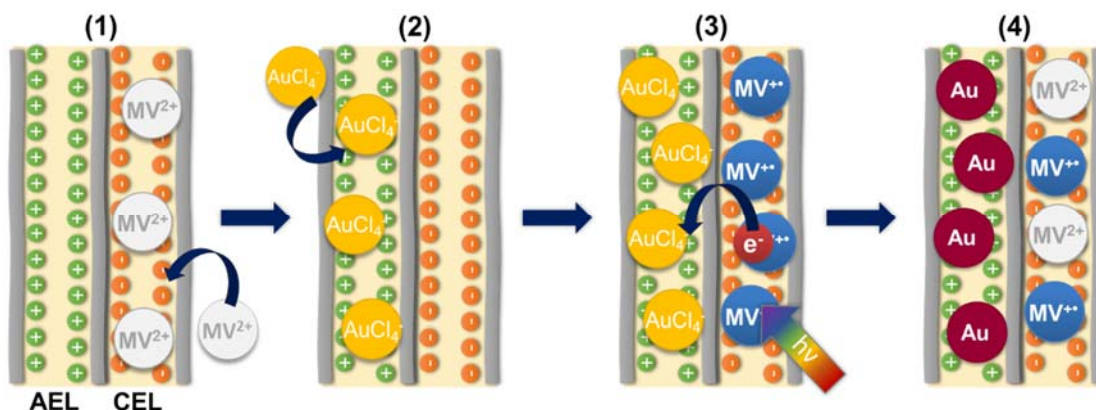


Figure 6. Schematic representation of BPM (1 - 2) electrostatic loading with MV^{2+} and $AuCl_4^-$ in the anion and cation exchange layers, respectively. (3) Visible light-induced production of $MV^{\bullet+}$ and subsequent electron transfer across the membrane for (4) AuNP nucleation and growth under continuous visible light illumination.

Figure 7 depicts the experimental design in which the BPM membrane separates the two compartments. In a typical experiment, both halves of the H-cell are filled with 3:1 water to ethanol in an inert atmosphere with 10 μ M 4-NBT then added to the AuNP loaded AEL half-cell for catalysis. The full cell is then exposed to xenon white light source with a long band pass cutoff filter of 350 nm with the MV^{2+} loaded CEL half-cell facing the source.

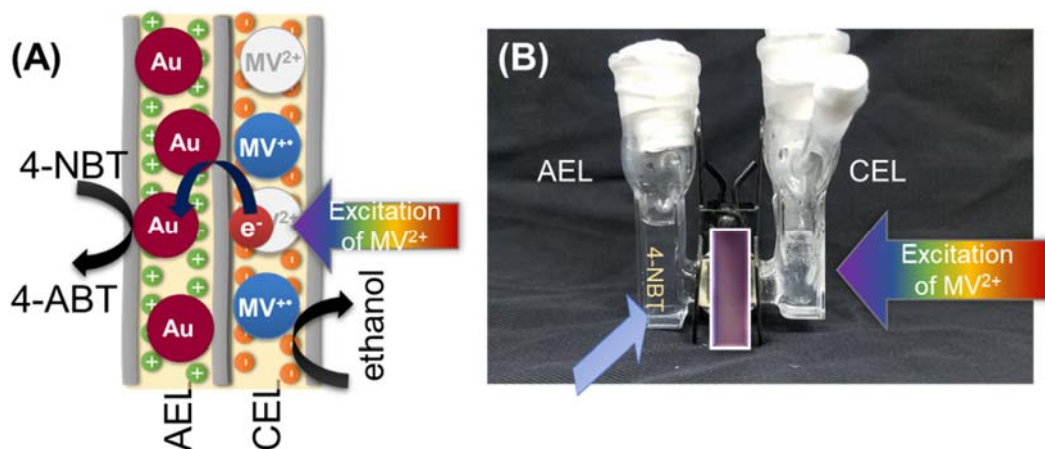


Figure 7. (A) Schematic representation of the electron transfer cascade for the reduction of 4-NBT to 4-ABT from the CEL to the AEL. (B) Photograph of H-Cell setup used to do Au/MV²⁺ -BPM photocatalysis of 10 μM 4-NBT in 3:1 water to ethanol solution.

Figure 8A shows the real-time absorption spectra for the conversion of 4-NBT corresponding to the decrease in absorbance at 413 nm to 4-ABT as a function of exposure time using the Au/MV²⁺ BPM architecture. Figure 2C shows the performance of all iterations of the BPM system for the photodegradation of 4-NBT by tracking the loss in absorbance at 413 nm. Clearly, the composite Au/MV²⁺ BPM far outperforms the rest with complete conversion of 4-NBT to 4-ABT after just 15 minutes of illumination time.

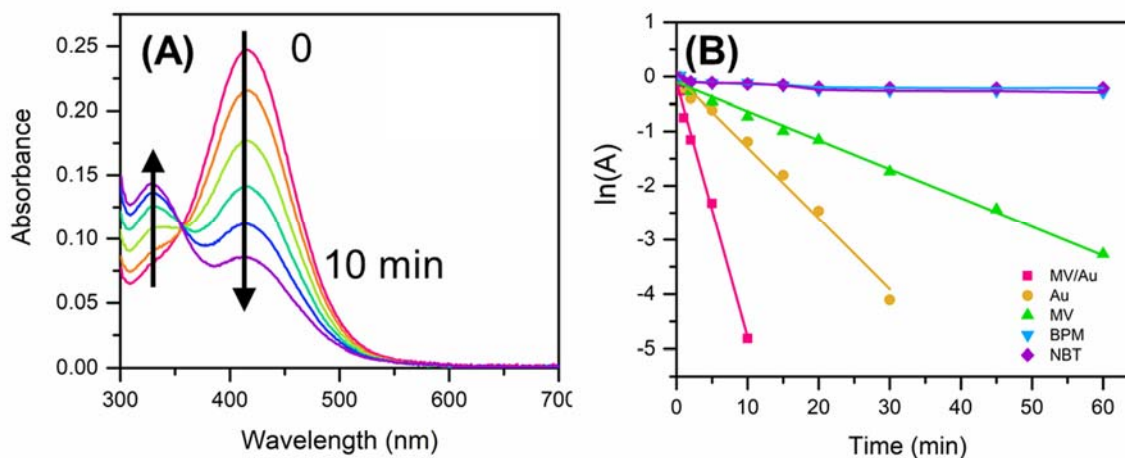
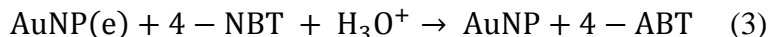


Figure 8. Photocatalytic reduction and conversion of 10 μM 4-NBT to 4-ABT via Au/MV²⁺ -BPM system (a) and (B) first order kinetic analysis of 4-NBT reduction to 4-ABT via BPM iterations.

The sequence of reactions that lead to the reduction of NBT can be summarized as follows





By tracking the loss in absorbance at 413 nm corresponding to 4-NBT and performing a first-order kinetic analysis Figure 8B compares the performance of all iterations of the BPM system for the photodegradation of 4-NBT by tracking the loss in absorbance at 413 nm. Clearly, the composite Au/MV²⁺-BPM far outperforms the rest with complete conversion of 4-NBT to 4-ABT after just 15 minutes of illumination time.

To further validate the interdependence of the MV⁺•-induced electron transfer cascade across the CEL/AEL interface for reduction of 4-NBT to 4-ABT, electron titration studies were performed in the dark. A composite Au/MV²⁺-BPM in the H-cell apparatus with 3:1 water to ethanol was purged under nitrogen for 45 minutes. The concentration of MV⁺• produced was then directly controlled and calculated through variable exposure times to the xenon light source and tracked using UV-Vis. The electrons of the stabilized MV⁺• can then be preferentially discharged across the membrane to AuNP for catalysis of 4-NBT. An injection of 4-NBT (25 μM) in the AEL cuvette was allowed to react under dark conditions to completion (1 hour). Figure 9A shows difference absorbance spectra for the degradation of 4-NBT to 4-ABT via AuNP catalysis with the highest MV⁺• (36 μM) previously generated via xenon lamp. Indeed, the electrons are transferred across the interface to AuNP for catalytic turnover of 4-NBT without continuous illumination.

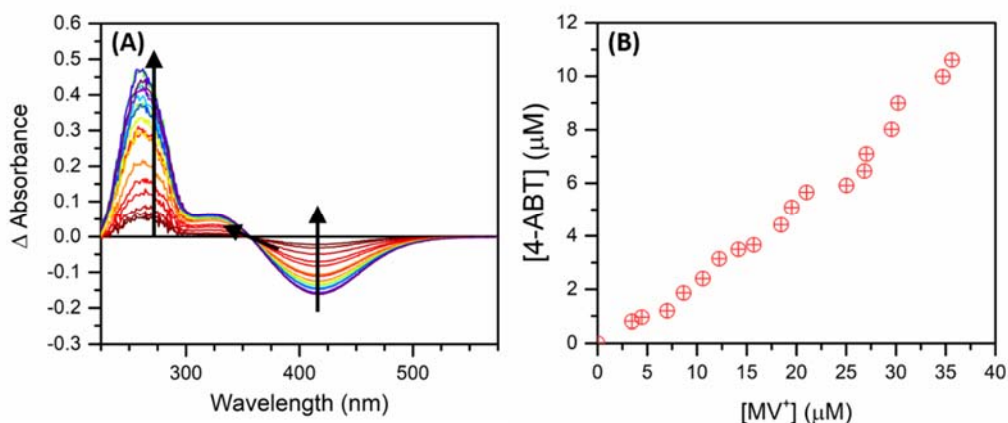


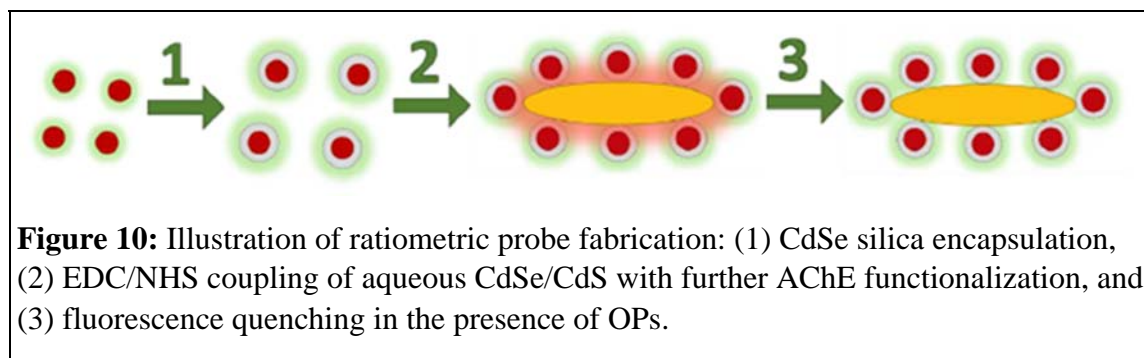
Figure 9. Electron titration across AEL/CEL interface in the dark. (A) Difference absorbance spectra for the photocatalytic turnover from 4-NBT (430 nm) to 4-ABT (260 nm) using Au/MV²⁺-BPM photocatalysis of 25 μM 4-NBT in 3:1 water to ethanol solution with maximum MV⁺• concentration (36 μM) for 60 minutes in the dark. (B) Confirmation of electron transfer across the membrane following the discharge of MV⁺• to AuNP for conversion of 4-NBT to 4-ABT by linear correlation.

This suggests a direct correlation to the amount of MV²⁺ reduced and the amount of 4-ABT produced further supported by Figure 9B. It confirms the direct, linear correlation between the concentration of MV⁺• and the amount of 4-ABT produced during dark catalysis. This proves the concerted electron transfer cascade through the BPM for indirect catalysis of 4-NBT. Similar

control studies under dark conditions without light-soaking were performed and show no autocatalytic characterizations verifying all turnover is indeed as result of electron transfer.

Water Soluble, Biofunctionalized Semiconductor Ratiometric Probes Toward Organophosphonate Detection

A ratiometric fluorescence probe based on semiconductor nanoparticles has been designed to sense Organophosphonates (Ops), such as dimethyl methylphosphonate (DMMP) and methyl parathion (MP), and visibly change emission color to indicate their presence. These probes can then be used for real-time, on-site determination of low levels of OPs via an observed excited-state color change by eye as well as for concentration determination via ratiometric calibration. The system developed in our laboratory is comprised of a CdSe quantum dot (QD) encapsulated in silica (CdSe@SiO₂) as a nonresponder probe (NRP), bound to a CdSe/CdS quantum rod (QR) responder probe (RP). Upon detection of OP, the CdSe@SiO₂ fluorescence shall remain unperturbed, whereas the fluorescence of the CdSe/CdS QR will be quenched inducing an observed change in fluorescence color. In this way, the change of fluorescence emission due to the quenching will be visible to the naked eye serving as a threshold sensor for exposure to OPs via color change. Analysis and calibration with known OP concentrations and the ratio of the RP to NRP fluorescence intensities concentration determination can also be achieved. Furthermore, additional surface modification and functionalization with acetylcholinesterase (AChE) can yield higher sensitivity and boast increased selectivity toward OP detection over other contaminants. Likewise due to the previously established photocatalytic properties of CdSe/CdS QRs, visible light photocatalysis can be performed to degrade the detected OPs.¹¹ Research efforts focused on the development and improvement of a fluorescent ratiometric probe employing CdSe@SiO₂ as the NRP with a CdSe/CdS RP following the design presented in Figure 10.



The fully constructed ratiometric probe was subjected to the same excited-state quenching experiments as its individual counterparts prior. Figure 11A and B shows the systematic quenching

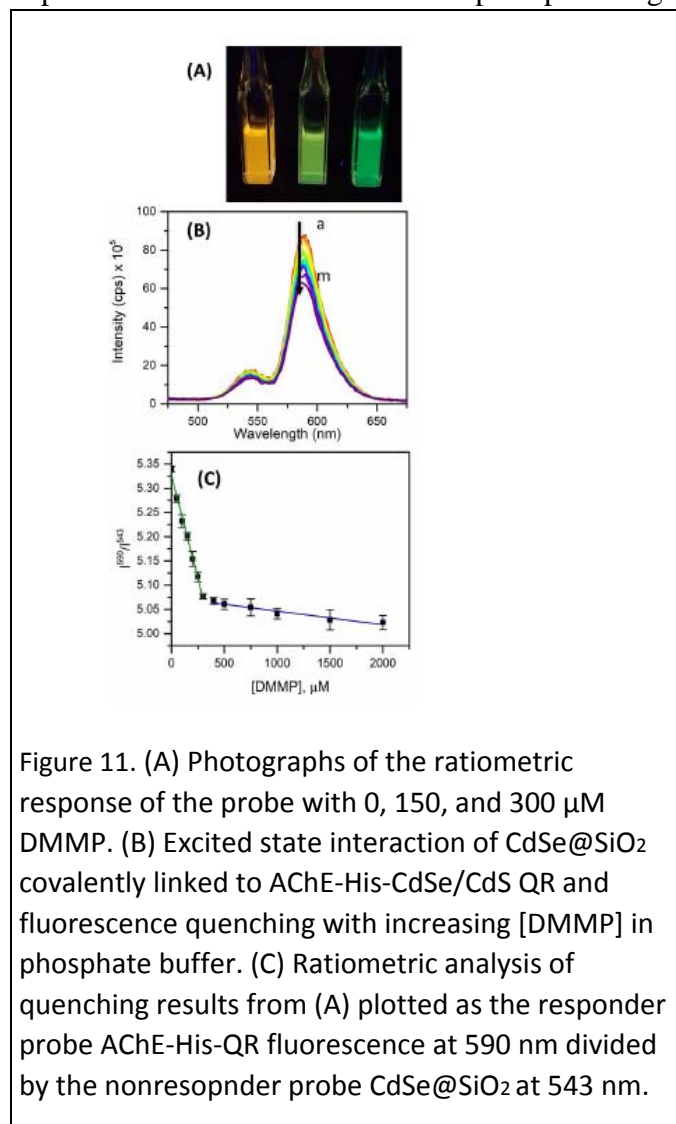


Figure 11. (A) Photographs of the ratiometric response of the probe with 0, 150, and 300 μM DMMP. (B) Excited state interaction of CdSe@SiO₂ covalently linked to AChE-His-CdSe/CdS QR and fluorescence quenching with increasing [DMMP] in phosphate buffer. (C) Ratiometric analysis of quenching results from (A) plotted as the responder probe AChE-His-QR fluorescence at 590 nm divided by the nonresopnder probe CdSe@SiO₂ at 543 nm.

detection selectivity and sensitivity with AChE functionalization towards OPs as compared with single QF-based probes.

In summary, several semiconductor and metal nanoparticles, and graphene oxide based assemblies were designed to sense and degrade target molecules. The electron transfer processes involved in the photocatalytic degradation have been elucidated. These studies should further aid in designing wearable devices capable of detecting warfare agents.

of the 590 nm peak corresponding to the AChE-His-QR RP with nominal change in the 543 nm peak of the CdSe@SiO₂ nonresponder probe (NRP). Figure 11B shows the emission spectra recorded with increasing concentration of DMMP. Figure 11C shows the change in the responder probe (at 590 nm) over that of the NRP (at 543 nm) resulting in two, distinct linear regions with increasing DMMP concentrations. These experiments demonstrate that a ratiometric probe comprised of CdSe@SiO₂ as a nonresponder and CdSe/CdS dot-in-rod responder probe is viable as a chemical sensor for the threshold detection and calibration of OPs.

This work has demonstrated a new concept and utility for visual and quantitative detection of organophosphonates, such as DMMP and MP, in aqueous solutions. The concept takes advantage of the fluorescence optical properties of QDs and QRs for the visual signal output via ratiometric fluorescence of the dual-emission probe. This method exhibits significantly enhanced visual