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Visible-Light Activated Sensor for Detection of Chemical Warfare Agent Simulants

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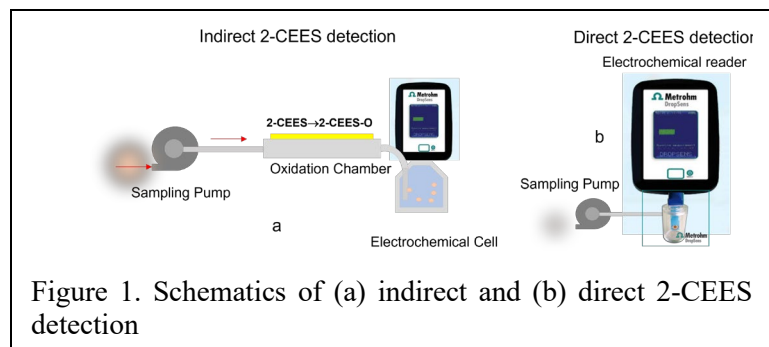
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EXECUTIVE SUMMARY

The goal of this program is to design a visible light activated sensor (VLAS) for quantitative detection of 2-chloroethyl ethyl sulfide (2-CEES), sulfur mustard (HD) simulant. In the proposed sensor design, 2-CEES is photocatalytically oxidized to 2-chloroethyl ethyl sulfoxide (2-CEES-O) on the surface of TiO_2 photocatalyst photosensitized by a plasmonic nanoparticle (NP) under visible light excitation. Subsequently, 2-CEES-O concentration is detected electrochemically from calibration curve that establishes relationship between 2-CEES-O oxidation current and concentration. Finally, 2-CEES concentration is calculated based on 2-CEES $\rightarrow$ 2-CEES-O conversion efficiency. The program has four

thrusts: (1) Materials synthesis and modeling; (2) Photocatalytic activity evaluation; (3) Sensing of CWA simulants decomposition products, and (4) Integration of materials into a VLAS prototype. Program direction undergone a significant shift in the 3rd quarter of FY20, when we discovered that 2-CEES can be directly electrochemically oxidized (and detected) in electrolyte solution. The advantages of direct vs indirect 2-



CEES detection are illustrated in Figure 1. 2-CEES direct sensing provides benefits of a more compact sensor design and higher sensitivity. Regarding other tasks and milestones, some of them have also been revised, based on the knowledge gained during the program. Our main achievements and issues that we experienced on the way to achieving the program goals are summarized below.

1. Materials synthesis and modeling

The focus of this task was on synthesis of (1) highly active open-frame TiO_2 photocatalysts and (2) plasmonic core-shell nanoparticles with a refractory plasmonic metal core (TiN or ZrN) and a 1-10 nm plasmonic metal (Au, Ag or Cu) shell that would promote photocatalytic activity of TiO_2 .

Highly efficient TiO_2 and Sm-doped TiO_2 photocatalysts were synthesized by Pajarito Powders using sacrificial support method. These materials are characterized by a highly porous structure that provides efficient light absorption, high surface area (220-250 m^2 BET surface area), and *ca* 5 nm TiO_2 crystallite size. For comparison, Degussa P25 TiO_2 which serves as a standard in photocatalysis, is characterized by *ca* 21 nm TiO_2 particle size, and 50 m^2/g BET surface area.

Although TiO_2 is wide-band semiconductor absorbing light in UV region, it can absorb light in the visible region in the presence of large number of defects on the surface. We observed significant visible light absorption by Pajarito's samples, while for commercial P25 TiO_2 it was nearly zero. Effects of multiple factors on the visible light absorption and photocatalytic activity such as annealing temperature, sacrificial support, Ti precursor, and dopants have been investigated. The most impressive improvement in photocatalytic activity and selectivity was observed for Sm-doped TiO_2 .

Synthesis of core-shell nanoparticles with TiN core and 1-10 nm Au shell by pALD turned out to be more challenging than we expected. To develop a recipe for Au pALD on TiN nanopowder, we first developed an ALD recipe for depositing Au on Si and TiN wafers. With the $\text{Me}_2\text{AuS}_2\text{CNEt}_2$ precursor, we demonstrated feasibility of formation of conformal Au films at thicknesses greater than 20 nm. Given that the $\text{Me}_2\text{AuS}_2\text{CNEt}_2$ precursor required high processing temperatures (150-200°C), we hypothesized that another precursor, $\text{Me}_3\text{AuPMe}_3$, that can be reduced to atomic Au at lower temperatures (90-110°C instead of 150°C) would enable formation of thinner 1-10 nm Au films. However, this hypothesis was not verified

by experimental observations. Instead of continuous Au films, we consistently observed isolated Au islands. Wet chemistry approaches utilized by Jonathan Boltersdorf also proved to be unsuccessful. Finally, in the 2nd quarter of FY21, a NO-GO decision was made regarding synthesis of core-shell nanoparticles with refractory transition metal core and metal shell. At this point, the effort of the pALD team was redirected towards synthesis of evenly dispersed plasmonic Au nanoparticles on high-surface-area open-frame TiO₂ support, since the pALD process offers better control over the Au particles' size and distribution on the surface in comparison to the wet chemistry method. This is also a non-trivial task, which has never been accomplished before. This goal was successfully accomplished. We developed an Au pALD process based on Me₃Au₃Me₃, O₃, and H₂O for deposition of Au NPs on ~75 mg of ARL-synthesized open-frame TiO₂ support powder (~15 m² total surface area) with an Au-coated TiO₂ nanopowder mass yield of approximately 80%. The Au-coated open-frame TiO₂ support powder exhibited plasmonic absorption peaking near 550 nm, and TEM images (along with the uniform color change of the powder) suggested spatially uniform deposition of *ca* 5 nm Au nanoparticles throughout the TiO₂ powder.

In parallel to *p-ALD*, Au, Cu, and TiN plasmonic nanoparticles were deposited on open-frame TiO₂ supports by a variety of wet chemistry methods to promote TiO₂ activity in the visible region. Plasmonic maxima were observed at 530 nm, 800 nm and 670 nm, for Au/TiO₂, Cu/TiO₂, and TiN/TiO₂, respectively. Although the strongest plasmonic response was demonstrated by Au/TiO₂, it varied depending on the synthesis method utilized for deposition of Au nanoparticles.

To utilize plasmonic properties of unexpensive refractory TiN nanoparticles, we added a new task on synthesis hybrid nanoparticles comprising TiN core, SiO₂ or TiO₂ shell, and Pt or Pd islands on the surface, as a replacement for a task on hybrid core-shell nanoparticles. Such hybrid nanoparticles combined plasmonic activity of TiN core and catalytic activity of Pt or Pd nanoparticles. SiO₂ shell was used to protect TiN core from oxidation. Such modifications led to damping plasmonic resonance, i.e. broadening and shifting in the red region of visible light.

In parallel to experimental work, optical properties of nanoparticles with TiN or ZrN core and Au shell, as well as TiN-SiO₂(TiO₂)-Pt/Pd hybrids were modeled by Ohio team led by Prof. Alexander Govorov

The Ohio Team has carried out an extended set of computational tasks for hybrid nanocrystals listed above. The simulations were done in a solution using the COMSOL software for the nano-cuboid multi-layer geometries. The computed properties included: absorption, scattering, rate of generation of high-energy electrons, and phototemperature. Overall, we conclude that the hybrid nanostructures of interest show enhanced photophysical and photochemical properties due to the combination of two metals in a single nanostructure. Our calculations described well the experiments on the photo properties of one-component nanocrystals (Au, TiN, ZrN) performed at NRL. We are also ready to compare our calculations with the experimental data for the hybrids (TiN-Pt and TiN-Pb) when the data become available after the clearance.

Some of the main conclusions from our theory on the hybrids of interest - **(1) TiN-Au hybrid:** [a] Since the TiN-Au hybrid is composed of two plasmonic materials and gold is much more optically active, the gold properties start to dominate rapidly by increasing the shell; [b] the Au shell strongly amplifies optical responses, including the absorption signal, due to the optical antenna effect; [c] thicker Au shells lead to strong scattering that is not preferable for photochemistry; [c] the core-shell TiN-Au and ZrN-Au nanocubes behave in similar ways; [d] we concluded that thin Au shells could work as optical and photochemical amplifiers due to their plasmonic antenna effect. Simultaneously, the TiN and ZrN cores can work as supports and additional absorbers made of inexpensive materials. **(2) TiN-SiO₂-Pt/Pd hybrids:** (a) Our hybrid is composed of two metallic materials (TiN/ZrN and Pt/Pd), which interact optically. However, the plasmonic metal (TiN/ZrN) dominates the optical response, while the photocatalytic metal (Pt/Pd) is less optically active; (b) we observe the effect of damping of the TiN/ZrN plasmons due to the Pt/Pd shells. This effect happens because Pt and Pd are very resistive; (c) overall, the TiN/ZrN-based cubes strongly amplify optical responses, including the absorption and electromagnetic signals, due to the optical antenna effect.

(d) TiN demonstrates lower plasmonic amplification coefficients than ZrN; (e) we show that the TiN/ZrN cubic cores can be used in photochemistry as optical amplifiers due to their strong plasmonic antenna effect. Simultaneously, these TiN and ZrN core cubes work as support materials, which hold expensive photochemical components (Pt- and Pd-shells). Notably, the above materials (TiN and ZrN) are inexpensive; **(3) TiN-SiO₂-Pt/Pd hybrids for the hot electron generation:** (a) TiN-Pt/Pd hybrids are excellent generators of hot electrons in the Pt/Pd shells, and these electrons can be used for surface photochemistry of CWAs; (b) The HE production efficiencies grow in the visible and red intervals due to the amplification of the plasmonic effects in these spectral intervals; (c) simultaneously, the Pt/Pb shells tend to create the damping of the plasmon resonances of the TiN/ZrN components; (d) the hybrids TiN/ZrN-Pt/Pb have two sources of generation of HEs: the Pt/Pb-water interface and TiN/ZrN-SiO₂ interface. The first one (i.e., Pt/Pb-water interface) is critical for our application since it provides HEs for the surface catalysis; (e) overall, the triple-material hybrids – a plasmonic core (TiN/ZrN) --- a catalytic metal - (Pt/Pd) deserve further investigations and show interesting photophysical behaviors as HE generators; (f) since the thermal conductivity of the components (TiN/ZrN, SiO₂, Pt/Pd) is high and the absorption in the TiN/ZrN-core is strong, our hybrids efficiently generate photo-temperature that should be taken into account for designing chemical sensors.

2. Photocatalytic activity evaluation

We demonstrated that some of the synthesized open-frame TiO₂ materials exhibited high photocatalytic activity towards 2-CEES photooxidation to 2-chloroethyl ethyl sulfoxide (2-CEES-O) and sulfone under visible light excitation. Nearly complete 2-CEES oxidation was observed within 4 h of exposure to visible light. The same procedure performed with commercial P25 TiO₂ resulted in very minor 2-CEES photooxidation, which highlights the effect of morphology on the photocatalyst's activity. We discovered that photooxidation occurs in parallel to hydrolysis pathway (hydrolysis of C-Cl bond resulting in formation of 2-(ethylthio)-ethanol as a major byproduct). As such, our effort was focused on suppression of hydrolysis and promotion of selective photooxidation to 2-CEES-O. Significant improvement in reaction selectivity was achieved by Sm-doping of TiO₂ support and utilizing Au plasmonic nanoparticles to further promote photocatalytic activity of Sm-doped TiO₂. To the best of our knowledge, it was the first demonstration of plasmonic effect on 2-CEES photocatalytic oxidation confirmed by analysis of reaction products by GC-MS analysis.

Incorporation of other plasmonic nanoparticles such as TiN and Cu did not result in a significant shift of the reaction pathway towards 2-CEES-O production. The reason for that is that both TiN and Cu promote 2-CEES hydrolysis due to the presence of oxide layers on the surface.

Addition of Pt and Pd nanoparticles to TiN-SiO₂/TiO₂ hybrids led to promotion of the catalysts' activity in the dark with formation of hydrolysis (2-(ethylthio)-ethanol) and oxidation (methylthiopropyl acetate) products. No visible light effect was observed. Nearly complete 2-CEES oxidation was observed within 24 h challenge for 8 synthesized catalysts.

3. Sensing of 2-CEES

In the original proposal, electrochemical sensing of 2-CEES-O was proposed for indirect detection of 2-CEES concentration in air. Feasibility of 2-CEES-O detection on glassy carbon electrodes in solutions of 20 v% CH₃CN+0.1M Britton-Robinson buffer at pH 2 was demonstrated in the program. However, while experimenting with 2-CEES, we discovered, that 2-CEES also can be detected electrochemically. Then the focus of the program was shifted to direct electrochemical detection of 2-CEES. To optimize conditions for 2-CEES detection, electrolyte solution, electrode material, and parameters of cyclic voltammetry technique were optimized. Our experiments demonstrated that 2-CEES can be detected on screen printed doped diamond electrodes (BDD SPEs, Metrohm) with sensitivity of 2 ppm and response time on the order of 2 min. In a parallel series of experiments, we proved that sufficient for electrochemical detection 2-CEES concentration can be generated in electrolyte after purging it for 2 min with 2-CEES flowing in air at 10

ml/min. 2-CEES concentration in the balance air was correlated to 2-CEES concentration in the electrolyte solution. The major issues we experienced in this part of the program is in that Metrohm discontinued production of BDD SPEs

4. Integration of individual parts into a sensor prototype: 2-CEES direct electrochemical detection

The original sensor prototype consisted of a (a) photocatalytic chamber; (2) a sampling pump that would draw 2-CEES vapors in the chamber; (3) an electrochemical cell; (3) electrochemical cell, and (4) Metrohm electrochemical reader, as illustrated in Figure 1a. 2-CEES concentration would be determined after running cyclic voltammetry (CV) curve by an electrochemical reader. The current peak on CV due to 2-CEES oxidation would be converted into concentration using built-in calibration curve.

After discovery of feasibility of direct 2-CEES electrochemical detection, the focus was shifted to a simpler sensor design, which is shown in Figure 1b. Photocatalytic chamber in this design is eliminated. Regarding the latter design, all the necessary parts have been assembled and prepared for a final demonstration. Sampling pump was designed and calibrated to obtain flow rates in the range of 4-22 ml. A miniature electrochemical cell was custom-made by Glass Technologist, Inc. There was a couple of issues with electrochemical reader due to (1) 2-CEES incorrect concentration calculation, and (2) inability to correct for background curve (i.e. curve measured in the absence of 2-CEES in electrolyte solution), which lowered 2-CEES detection limit from 2 to 20 ppm. However, both issues were resolved by a replacement of an electrochemical reader by a more advanced miniature Sensit BT (PalmSens) potentiostat. The potentiostat can be controlled by an Android cell phone via Bluetooth or USB cable.

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INTRODUCTION

This program was inspired by discovery of (1) visible-light-driven 2-CEES photooxidation to 2-chloroethyl ethyl sulfide (2-CEES-O) on the surface of 5 nm TiO₂ nanoparticles supported on SiO₂ spheres [1] and (2) theoretical prediction of enhancement of plasmonic response of refractory transition metal TiN nanoparticles in the presence of 1-10 nm Au shell. We hypothesized that TiN-Au core-shell nanoparticles will further drive photocatalytic activity of 5 nm TiO₂ nanoparticles towards desired reaction products. For synthesis of TiN-Au core-shell nanoparticles, synthesis by particle ALD was chosen as the most feasible path.

To increase TiO₂ surface area and visible light absorption, it was proposed to use materials synthesized by sacrificial support method, which is based on removal of sacrificial support by an etching agent. Theoretical modeling was expected to provide a guidance for materials design.

2-CEES-O, produced by 2-CEES photocatalytic oxidation, was proposed to detect electrochemically, assuming that the relationship between concentration of 2-CEES-O and 2-CEES be established. Given that the literature on electrochemical properties of CWA simulants is scarce, we expected to make contribution to the field by providing insights into electrochemical properties of 2-CEES-O.

The proposed sensor prototype integrated a photooxidation chamber, in which 2-CEES photooxidation to 2-CEES-O would occur and an electrochemical cell, in which 2-CEES-O would be electrochemically detected from electrolyte solution.

The part of the program related to a sensor design has undergone a major change after discovery of direct 2-CEES electrochemical oxidation, which allowed to eliminate a photooxidation chamber from a sensor prototype design thus enabling increase in sensor sensitivity.

Below we report the results on

- 1) Materials synthesis and modeling
- 2) Catalysts' photocatalytic activity evaluation toward 2-CEES photooxidation
- 3) Electrochemical sensing of 2-CEES and 2-CEES-O
- 4) Integration of all the individual sensor parts into a sensor prototype

EXPERIMENTAL

Materials

Commercially Available Materials

50 nm TiN NPs were purchased from PlasmaChem. P25 TiO₂ (Aeroxide[®] P25, 25 nm primary particle size) was acquired from Sigma Aldrich.

Methods

UV-Vis spectroscopy

At ARL, ultraviolet-visible (UV-Vis) absorbance spectra were collected from UV to near-infrared (NIR) for colloidal nanoparticles suspended in solution with an AvaSpec-ULS2048L spectrometer fiber-coupled deuterium and halogen light source. Diffuse reflectance spectra were obtained for all powder samples with the addition of an Avasphere-30 PTFE integrating sphere. At NRL, Perkin-Elmer UV/VIS/NIR λ 1050 spectrometer, equipped with integrated sphere was utilized. Powdered samples were diluted to 3 wt% with KBr prior to collecting spectra.

XPS

(NRL) XPS was performed on a Thermo Scientific K-Alpha instrument (Al K α radiation). The samples were prepared by pressing the powders onto indium foil (thickness 1 mm, Sigma Aldrich). Flood gun was used to avoid charging of insulating powders. Survey and high resolution core level spectra were collected. All peaks were referenced to the C1s peak at 285 eV. Peak fitting was performed with CASA software, after background correction by Tougaard [2] or Shirley methods. The line shapes of core level spectra were constructed using Gaussian/Lorentzian profiles.

(ARL) X-ray photoelectron spectroscopy (XPS) was carried out on a Physical Electronics VersaProbe III (East Chanhassen, MN) with a monochromated Al K α source with a 100 μ m diameter 25 W beam, 55 eV pass energy, and a take-off angle of 45°. Surface charging was neutralized by a low-voltage Ar-ion beam and a barium oxide neutralizer. Spectra were energetically corrected to a 284.8 eV C 1s line and baseline corrected to a Shirley model.

PXRD

(ARL) High-resolution powder X-ray diffraction (PXRD) was collected on a Rigaku MiniFlex 600 diffractometer using Cu K α_1 (λ = 1.540593 Å) radiation from a sealed-tube X-ray source (40 kV and 15 mA) equipped with a D/teX Ultra detector.

TEM

Samples for TEM imaging were prepared by drop casting a suspension of TiN and ZrN samples dispersed in 1:1 water:methanol mixtures onto a carbon film-coated copper mesh TEM grid. Bright-field transmission electron microscopy (TEM) and high-angle annular dark-field imaging scanning TEM (HAADF-STEM) were performed in JEOL 2100F (Peabody, MA) at 200 kV equipped with an EDAX Octane T Optima system (Mahwah, NJ, USA) energy dispersive X-ray spectrometer (EDXS) to map the elemental distribution. Principal component analysis differentiated raw EDXS spectra.

TGA

Thermogravimetric analysis (TGA) was performed on a TA Instruments' TGA 5500 with a Tru-Mass balance and a quadrupole mass spectrometer (MS) optimized for evolved gas analysis with a closed ion source, a triple mass filter and a dual (Faraday and Secondary Electron Multiplier) detector system. All

samples were analyzed under a nitrogen gas atmosphere in the temperature range from room temperature to 700 °C.

ALD and p-ALD

Atomic layer deposition (ALD) and particle atomic layer deposition (pALD) of Au, Al₂O₃, and Pt were performed using a Forge Nano (formerly ALD NanoSolutions) RX-series rotary reactor equipped with a titanium alloy rotary drum. The precursors for these processes were trimethyl(trimethylphosphine)gold (Me₃AuPMe₃), O₃, and H₂O; trimethylaluminum and H₂O; and trimethyl(methylcyclopentadienyl)platinum (MeCpPtMe₃) and O₃; respectively. Additionally, Au ALD experiments were carried out using Me₂Au(S₂CNEt₂) and O₃ in Veeco Savannah conventional thermal ALD reactor (see Supplemental Information).

Electrochemical Characterization

Electrochemical characterization was performed in (1) a three-electrode electrochemical cell, (2) in a 20 ml vial using commercial screen-printed electrodes (SPEs) and (3) a custom-made cell which was equipped with a gas-dispensing tube for introduction of 2-CEES in balance N₂/air into the cell. When carrying out electrochemical measurements in the three-electrode electrochemical cell, mirror-polished glassy carbon electrode served as a working electrode, while a Pt mesh and an Ag/AgCl served as a counter and reference electrodes, respectively. Autolab potentiostat (Metrohm, μ -III) was used for performing potentiostatic and cyclic voltammetry measurements. Electrochemical reader equipped by built-in 2-CEES calibration curve and Sensit BT miniature potentiostat were acquired from Metrohm and BASi, respectively. Boron-doped diamond and carbon SPEs were purchased from Metrohm, Pine Research, and Conductive Technologies.

Materials Decontamination Challenge

Reactivity challenges were performed on powdered samples in the bottom of the 2 mL clear GC-MS vials to enable the use of visible light excitation [1, 3]. Typical simulant decontamination experiments are run using approximately 7 mg of the solid materials in the bottom of clear glass GC vials.

Dose extraction: a stock solution of 2-CEES (19.25 μ L, 1.65×10^{-4} mol) was prepared in 2 mL of CH₂Cl₂. The 2-CEES is measured with a 50 μ L syringe and the CH₂Cl₂ is measured based upon mass ($d = 1.33$ g/mL). TiO₂ materials (~7 mg) are challenged with 2-CEES via deposition of 25 μ L of the 2-CEES stock solution followed by evaporation of the solvent CH₂Cl₂ for 10 minutes after which the vials were sealed and exposed to light or stored in the dark. A broad band visible light source, Lumina FO-150 (Chiu Technical Corporation, Kings Park, NY, USA), was 12 cm from the vials and utilized at full power with a 3-74 UV cut-off filter to eliminate wavelengths below 400 nm.

Extractions are performed by adding 1 mL of ACN via a Gilson P1000 pipette and the samples were vortex mixed to ensure the best extraction. The 1 mL solutions are then transferred to Eppendorf plastic centrifuge tubes and then centrifuged for 2 minutes at 15000 rpm. After which the Gilson P1000 pipette is used to transfer 800 μ L of solution to a clean GC-vial for analysis with GC-MS with PEST7-CEES method.

A calibration curve for 2-CEES concentration assessment is constructed from gas chromatography coupled with a mass spectrometer (GC-MS) analysis of solutions with known volumes of the contaminant stock solution (1 μ L to 30 μ L) measured with a 50- μ L syringe diluted with 1 mL of ACN.

Headspace analysis (This is not standard to run on all samples): following the same dosing and exposure above the vials remain sealed and the gas phase in the headspace of the vial is analyzed using PEST8 method. Following injection of the headspace, the catalysts are extracted using the same protocol as above. The biggest issue with this is that if samples are not immediately solvent extracted after the headspace injection the hole in the septa allows 2-CEES to adsorb into the rubber and thus 2-CEES is not detected in the extraction.

The visible light source used was a broadband Lumina FO-150 (Chiu Technical Corporation, Kings Park, NY, USA) utilized at full power with a 3-74 UV cut-off filter to eliminate wavelengths below 400 nm. Initial challenges were performed over a 24-hour period to test the viability of the materials for their reactivity toward 2-CEES. Subsequent time trials were performed for the highly active materials to assess reactivity with exposure times of 1, 4 and 8 hours. Samples for each simulant challenge were extracted with 1 mL of acetonitrile and analyzed by GC-MS for residual 2-CEES and reaction byproducts. All challenges were run in duplicate in order to assess variability and to conserve materials.

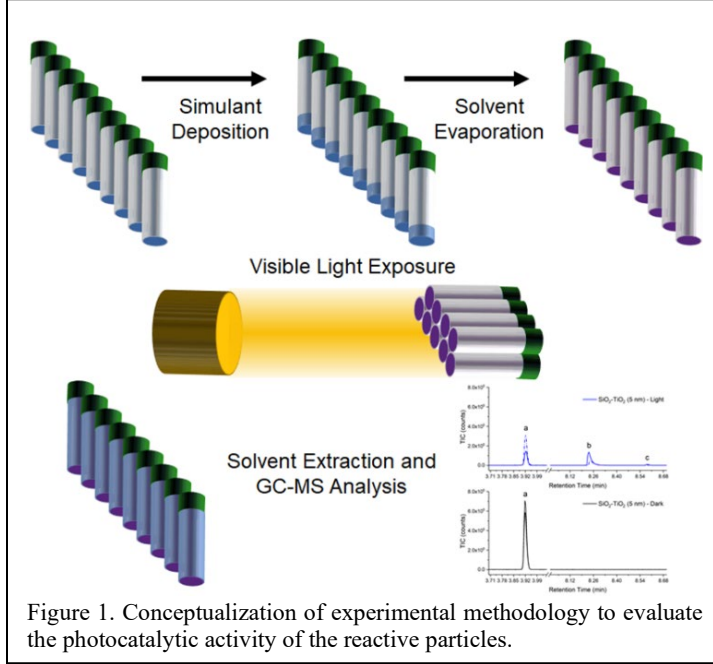


Figure 1. Conceptualization of experimental methodology to evaluate the photocatalytic activity of the reactive particles.

GC-MS analysis was performed using an Agilent 7890B gas chromatograph coupled with an Agilent 5977B mass spectrometer (MS) detector operating in electron ionization mode and an Agilent 7693A autoinjector (Agilent Technologies, Santa Clara, CA, USA). The column was a Restek Rxi®-5HT with a Crossbond® 5% diphenyl 95% dimethylpolysiloxane film (Restek Corporation, Bellefonte, PA, USA). The carrier gas was helium, with a constant flow rate of 1.636 mL min⁻¹. The injection volume was 1 µL, with a split injection ratio of 10:1. The temperature program has an initial temperature of 65 °C for two minutes, then 10 °C·min⁻¹ ramp to 130 °C, followed by a 20 °C·min⁻¹ ramp to 280 °C, with a two minute post-run hold at 300 °C. The injection inlet temperature, auxiliary temperature, MS quad temperature, and MS source temperature

were 275, 280, 150 and 230 °C, respectively. The solvent delay was set at 2.00 minutes and the detector scanned from 34 to 350 m/z.

Electromagnetic modeling

The theoretical modeling was performed with COSMOL Multiphysics, which solves Maxwell's equations using the finite element method and the absorbing boundary conditions at large distances. The system consists of a single NP which may have or two shells. The incident light intensity was fixed at 10⁵ W/m². The surrounding medium is water with a dielectric constant equal to 1.8. To begin the computation, the considered electric field inside and outside of a nanostructure has the following form:

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_\omega e^{-i\omega t} + \mathbf{E}_\omega^* e^{+i\omega t}$$

The absorption power is then given by

$$Q_{abs} = \langle \int_{NP} \mathbf{j} \cdot \mathbf{E} dV \rangle_{time}$$

where $\mathbf{j}$ is the current inside the NPs. Then, given the light intensity I_0 , the absorption cross section is expressed as

$$\sigma_{abs} = \frac{P_{abs}}{I_0}$$

Additionally, we assume that the optical extinction cross-section of our NPs is a combination of absorbed and scattered light. Therefore, the extinction cross-section becomes a sum, as shown below:

$$\sigma_{ext}(\omega) = \sigma_{abs}(\omega) + \sigma_{scat}(\omega)$$

As part of the light absorption process, there is a generation of hot electrons, which occurs near the NP surface. The rate of this generation is then expressed as

$$\text{rate}_{\text{HE}} = \frac{2}{\pi^2} \frac{e^2 E_F^2}{\hbar} \frac{1}{(\hbar\omega)^3} \int_{S_{\text{NC}}} |E_{\omega, \text{normal}}(\theta, \phi)|^2 ds,$$

where e is the electron charge, E_F is the Fermi energy (5.5 eV for Au) and $E_{\omega, \text{normal}}$ is the normal electric field. However, in many cases we are more interested in the hot electrons that possess a high enough energy to overcome an energy potential (ΔE_{bar}) and therefore, be transferred to another material or to an adsorbed molecule. The rate of generation of these types of hot electrons is given by,

$$\text{rate}_{\text{HE, over-barrier}} = \frac{2}{\pi^2} \frac{e^2 E_F^2}{\hbar} \frac{(\hbar\omega - \Delta E_{\text{bar}})}{(\hbar\omega)^4} \int_{S_{\text{NC}}} |E_{\omega, \text{normal}}(\theta, \phi)|^2 ds,$$

where the energy barrier is typically ~ 1 eV.

Moreover, the dielectric function used in the computation of the generation rates of hot electrons incorporates a quantum surface-scattering effect that must be considered in the description of the process of light dissipation. With this approach, the local dielectric function is given by

$$\varepsilon_{\text{metal}}(\omega) = \varepsilon_{\text{metal, bulk}}(\omega) + \frac{\omega_p^2}{\omega(\omega + i\gamma_D)} - \frac{\omega_p^2}{\omega(\omega + i(\gamma_D + \gamma_s))}$$

where $\varepsilon_{\text{metal, bulk}}$ is the empirical dielectric constant, ω_p is the plasmon frequency, γ_D is the Drude broadening, and γ_s is the quantum plasmonic broadening. The last parameter is the one responsible for the incorporation of the scattering of electrons at the NP surface, which is size-dependent.

Finally, the surface charge distribution maps were also computed with COMSOL Multiphysics with the following expression:

$$\sigma = E\varepsilon_0$$

Overall, our approaches to compute photophysical responses have shown their reliability in many studies describing various experimental systems.

RESULTS AND DISCUSSION

Task 1. Materials Synthesis and Modeling

Subtask 1.1 Synthesis of (1) core-shell nanoparticles with TiN or ZrN core and Au shell and (2) hybrid TiO₂-SiO₂-Pt/Pd nanostructures by p-ALD and wet chemistry methods

Development of Me₃AuPMe₃ and O₃ dosing for Au ALD and pALD (Benjamin Greenberg, Boris Feygelson. And Virginia Wheeler, NRL)

To do pALD of Au on large batches of TiN NPs, we need to expose all NPs to sufficient O₃ during pALD. This is not trivial because of the high NP powder surface area, unique pALD reactor geometry, and tendency of O₃ to decay to O₂. The optimal dose time, flow dynamics, and pressure of O₂/O₃ in the pALD chamber are not obvious. To develop a general O₃ dosing procedure for pALD, we tested various O₃ dosing methods using a prototypical ALD chemistry: the deposition of Al₂O₃ from TMA and O₃ at 150 °C. For a test substrate we used 1 g of YSZ NP powder. The dosing methods tested were high-pressure static microdoses, low-pressure static microdoses, and continuous flow doses (Fig. 1.1.1a). In high-pressure static microdoses, the chamber is filled to ~100 Torr with an O₂/O₃ mixture, the pressure is held constant (inlet and outlet valves closed) for 20–30 s, and then the gas is pumped out; this cycle is repeated 10–20 times for a total dose time of 5 to 25 min. Low-pressure static microdoses are the same except the O₂/O₃ pressure is ~20 Torr and the cycle is repeated up to 40 times for a total dose time up to 32 min. In continuous flow dosing, the system is held at steady state for 8–32 min: the inlet and outlet valves remain open, and an O₂/O₃ mixture flows through the chamber, producing a constant pressure of ~2 Torr. We found that high-pressure static microdoses yield the best Al₂O₃ growth rate: an ~8 min O₃ dose yields an ALD GPC of ~0.9 Å/cyc (Fig. 1.1.1b). We can use this method to do the necessary hundreds of Au pALD cycles on large batches of TiN NPs with a reasonable total process time.

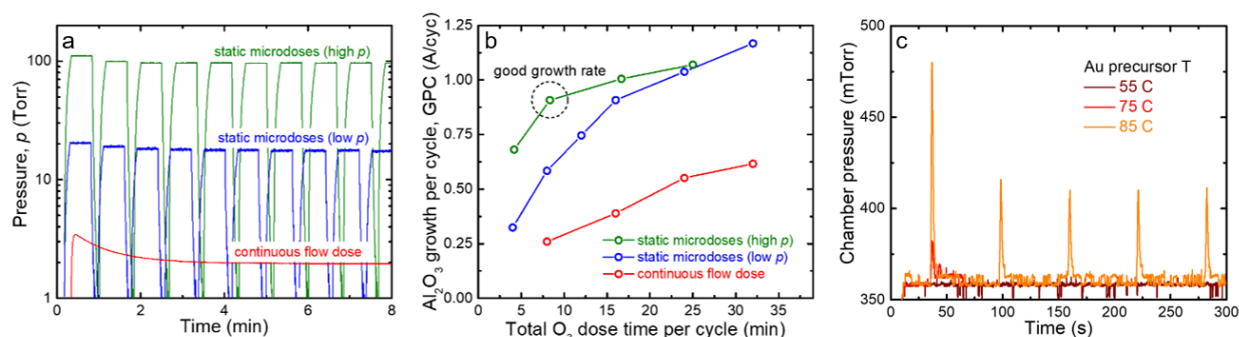


Fig. 2.1.1. (a) Total pressure in the pALD chamber during various O₃ doses. (b) Al₂O₃ pALD growth per cycle on YSZ NP test powder as a function of the total O₃ dose time. (c) Total chamber pressure during Me₃AuPMe₃ dosing at various Me₃AuPMe₃ temperatures.

Deposition of thin conformal Au shells on TiN NPs by pALD requires low deposition temperature; therefore we need to keep the Au precursor temperature low, ideally below 90 °C. However, Au precursors generally have low vapor pressure below 90 °C, which may hinder delivery of precursor to the chamber. To develop a Me₃AuPMe₃ dosing procedure, we maintained a deposition temperature of 115 °C and varied the Me₃AuPMe₃ temperature from 55 to 85 °C, and we analyzed the chamber pressure during Me₃AuPMe₃ pulses with a 1 s pulse time (Fig. 1.1.1c). Me₃AuPMe₃ delivery looks suitable at a Me₃AuPMe₃ temperature of 85 °C: the rate of pressure increase is 52 mTorr/s, equivalent to 1.5 μmol/s of Au. This is within an order of magnitude of typical delivery rates of common ALD precursors (e.g., ~5 μmol/s of Zr for TDMAZ) and can allow Au deposition on a reasonable timescale.

Au ALD on Si and TiN wafers

To prepare for Au pALD on TiN nanopowder, we first developed an ALD recipe for depositing Au on Si and TiN wafers. From literature there are two promising Au precursors available for film growth. The first is an expensive, sulfur-based precursor, $\text{Me}_2\text{Au}(\text{S}_2\text{CNEt}_2)$, that can be reduced in a single step using ozone. The second is a cheaper precursor based on a trimethylphosphine ($\text{Me}_3\text{AuPMe}_3$) which requires a two-step reduction process using oxygen plasma or ozone followed by water pulses to volatilize any remaining phosphorus pentoxide contaminants. The precursors and the routes to produce Au metal are shown in Figure S1. We focused our initial attention on the sulfur-based precursor due to its simplicity. Our main results with sulfur-based precursor are provided in the SI (Figures S2-S6 and corresponding text). We demonstrated that it is not feasible to grow 1-10 nm Au thin films even on a flat substrate. We hypothesized that temperature is a key for conformal growth of thin Au films by ALD. Because a trimethylphosphine precursor requires lower temperatures, we shifted attention to this precursor.

An Au ALD cycle with trimethylphosphine precursor consists of $\text{Me}_3\text{AuPMe}_3$, O_3 , and H_2O doses, and each doses can consist of multiple microdoses. Holding the number of cycles at 50 and deposition temperature at 105 C and positioning a Si wafer in the front of the rotary drum (which contains the TiN powder in pALD experiments), we varied the number of microdoses from 1 to 3 and measured the quantity of Au deposited by ellipsometry (Fig. 1.1.2a,b). The spectral line shape of psi (peaked rather than sigmoidal) indicated that we deposited Au islands rather than a continuous thin film, which is generally expected for a 50 cycle deposition and was observed in our earlier work on Au ALD using $\text{Me}_2\text{AuS}_2\text{CNEt}_2$ in the conventional ALD reactor. Using a B-spline fitting of psi and delta to quantify the deposited Au in terms an effective film thickness, we found that 3 microdoses produced a reasonable growth per cycle (GPC) of ~ 0.08 Å/cyc on the Si wafer. We then used this recipe to deposit 50 cycles of Au on Si and TiN wafers placed in the front and back of the drum; GPC in the back of the drum is particularly important, because this is where TiN powder is located for pALD. We found that while GPC on Si wafers is 50% lower in the back of the drum, this effect is cancelled out by the generally higher GPC on TiN wafers, so that the GPC on a TiN wafer in the back of the drum is still ~ 0.08 Å/cyc (Fig. 1.1.2c).

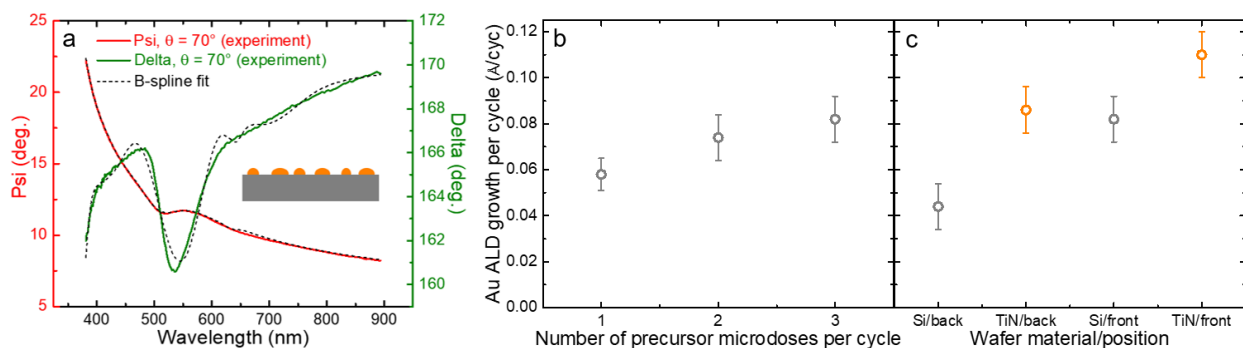


Fig. 1.1.2. (a) Representative ellipsometry spectra for Au islands deposited on a Si wafer. (b) Au ALD growth per cycle as a function of the number of $\text{Me}_3\text{AuPMe}_3$ microdoses per cycle. (c) Au ALD growth per cycle for various substrate materials and positions within the pALD drum.

Au pALD on TiN nanoparticles: effect of powder position within the pALD chamber

Based on the encouraging results of these Au ALD experiments, we proceeded to develop a ALD on particles (pALD) recipe for coating TiN NPs with Au. To deposit Au on a substrate with a much larger surface area, we increased the number of microdoses from 3 to 4 and we increased the microdose hold times (the time that the precursor is held in the chamber after the pulse to allow the reaction to continue): from 8 to 30 s for $\text{Me}_3\text{AuPMe}_3$, from 0 to 30 s so for O_3 , and from 16 to 60 s for H_2O . For O_3 and H_2O , we also increased the pulse times (from 16 to 40 s and from 2 to 3 s, respectively), while for $\text{Me}_3\text{AuPMe}_3$, we did not increase the pulse time, because no additional vapor could be obtained from a longer pulse ($\text{Me}_3\text{AuPMe}_3$

delivery is evaporation-rate-limited). The Au deposition temperature was 105 or 110 C depending on the location of the substrate. The conditions and TEM results of four Au pALD experiments, numbered P162-165, are shown in Fig. 1.1.3. In P162, 20 mg of TiN NP powder was placed in the typical position in the back of the rotary drum, and the drum was rotated to agitate the powder. As shown in Fig. 1.1.3a, this procedure resulted in very little Au deposition on the TiN powder. In P163, to determine whether Au deposition could be increased via decreasing substrate surface area, Au was deposited directly on a TEM grid containing TiN NPs; this resulted in slightly more Au on the TiN NPs but still not enough to form the basis of a procedure for depositing continuous Au shells (Fig. 1.1.3b). Therefore, to understand better peculiarities of Au deposition on TiN powder, we tried a new approach in which the powder was positioned in a boat directly in front of the chamber inlet in order to maximize $\text{Me}_3\text{AuPMe}_3$ exposure (although powder agitation was not possible, because the powder was not inside the rotary drum), and we increased the number of Au ALD cycles to 100 and 200 (P164 and P165, respectively). These runs resulted in significantly more Au deposition in some regions of the TiN powder, but the deposition was nonuniform (some regions contained no Au), and the Au formed particles/island rather than continuous films (Fig. 1.1.3c,d).

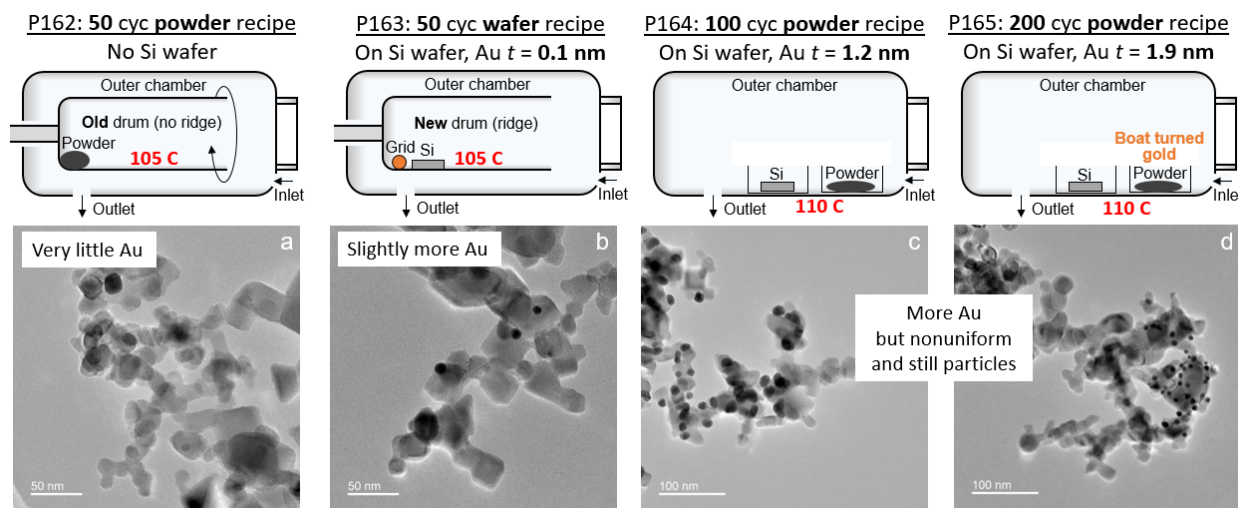


Fig. 1.1.3. Schematics of Au pALD trials and TEM of resultant Au-coated TiN NPs. (a) P162. (b) P163. (c) P164. (d) P165.

As shown in Fig. 1.1.4, further characterization of the samples produced by the inlet-adjacent boat method (P164 and P165) confirmed that these samples do not have the targeted morphology and optical properties. STEM/EDS elemental mapping of the P164 sample (Fig. 1.1.4a) showed Au particles without any signs of coalescence or thin Au shell formation. UV-vis spectra of aqueous suspensions of the two samples revealed slightly redshifted absorption without enhancement, which is consistent with the formation of Au particles rather than continuous Au shells.

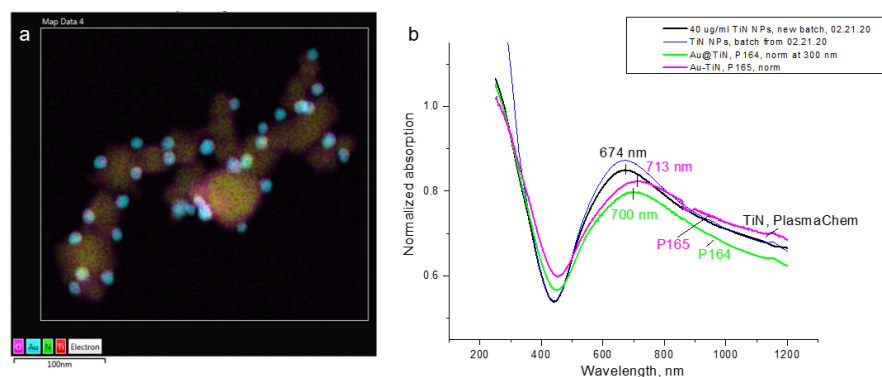


Fig. 1.1.4. (a) STEM/EDS elemental mapping of P164: 100 cycles Au pALD on TiN NPs. (b) UV-vis spectra of P164 and P165: 200 cycles Au pALD on TiN NPs with spectra of uncoated TiN NPs for comparison.

Au pALD on TiN nanoparticles: increasing the quantity of Au deposited

As shown above, the quantity of Au deposited was greatly enhanced by removing the TiN powder from the rotary drum and moving it closer to the pALD chamber inlet. In this position however, the powder can no longer be agitated by rotary motion, and the deposited Au was found to be nonuniform with high quantities of Au nanoparticles deposited in some regions of the TiN powder and virtually no Au in other regions. In an effort to obtain a combination of high Au quantity and high uniformity, we modified the pALD reactor: we added an inlet extension tube within the pALD chamber that injects the Au precursor directly into the back of the rotary drum, so that the TiN can be near the Au precursor injection point and still be agitated via rotary motion. Fig. 1.1.5a shows the original pALD reactor configuration, and Fig. 1.1.5b shows the modified reactor with inlet extension. We used a standard Al_2O_3 pALD procedure to test the Fig. 1.1.5b configuration, and we found that pALD precursor delivery was in fact too direct: over the course of the pALD run, the gas flow blew all of the powder out of the drum, preventing consistent powder agitation and defeating the purpose of the modification. To address this challenge, we added a gas diffuser to the end of the precursor injection tube, as shown in Fig. 1.1.5c. This improved the retention of powder in the drum, but still >30% of the powder was blown out of the drum over the course of an Al_2O_3 pALD test run. We tested multiple diffuser designs, stand-off distances, and precursor flow rates, and we experimented with an additional injection point outside of the drum to reduce the pressure difference between the drum interior and the outer chamber; despite these additional modifications, the powder loss remained above 30%. This loss rate is not acceptable, because it is expected to lead to loss of nearly all powder over the course of a typical Au ALD run, which is ~ 10 times longer in duration than an Al_2O_3 test run. We concluded that the powder loss challenge can be overcome only through completely eliminating the pressure difference between drum and outer chamber, which will require adding a more sophisticated exterior injection point with flow control. We prepared a design for this modification, but in the interest of time we first tried another approach to obtaining high Au quantity and uniformity.

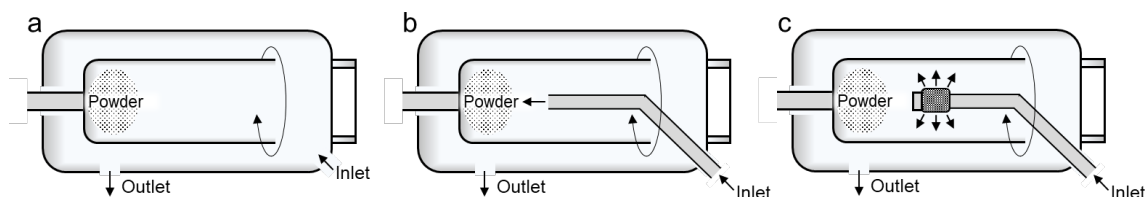


Fig. 1.1.5. Schematics showing different precursor injection strategies. (a) Typical pALD reactor configuration. (b) Modified pALD reactor with precursor injection near the powder. (c) Modified pALD reactor with gas diffuser.

In principle, the amount of Au precursor delivered to the powder can also be enhanced by increasing the overall quantity of Au precursor in the chamber. In the Au precursor delivery strategy used so far, we

already maximized the quantity of Au precursor delivered per dose by using up all of the vapor in the Au precursor cylinder headspace. The overall Au precursor delivery rate thus was limited by the rate at which this headspace vapor pressure was regenerated by evaporation from the Au precursor liquid between pulses. Therefore, in order to increase the Au precursor quantity significantly without unreasonably increasing pALD run time, we developed a new Au precursor delivery method based on the introduction of an inert carrier gas feed. Fig. 1.1.6 compares this new method (“approach 2”) to our previous method of simply moving the powder closer to the pALD reactor inlet (“approach 1”). In approach 2, the number of Au precursor microdoses per cycle was increased from 4 to 6, and in each microdose the Au pulse time was increased from 4 s to 30 s; also, during each pulse a 120 SCCM N₂ flow was added over the open Au precursor cylinder, which pushed Au precursor away from the cylinder and into the pALD chamber, boosting the Au precursor evaporation rate and enabling the delivery of a greater Au precursor quantity in each pulse. TEM reveals that approach 2 significantly increased the quantity of Au deposited on the TiN powder; however, the deposition was nonuniform, and large regions of the TiN powder remain virtually uncoated (Fig. 1.1.6c). These results are very similar to the results of approach 1 (Fig. 1.1.6a); note that 100 Au pALD cycles were used to test approach 1 vs. 50 cycles used to test approach 2. Given that the powder is agitated in approach 2, the nonuniformity is likely due not to uneven exposure of nanoparticle surfaces to the precursor but rather to the overall precursor quantity still being insufficient, despite the large improvement achieved by modifying the dosing procedure. Overall our results suggest that reasonably high Au deposition rates are obtainable via further development of the precursor dosing procedure; however, continuous and reasonably thin (~5 nm) Au shells on TiN nanoparticles remain elusive.

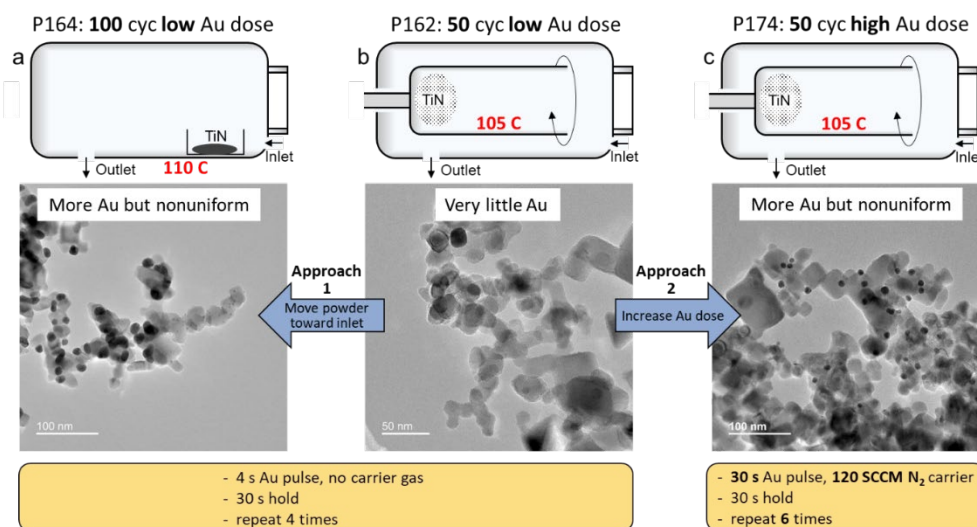


Fig. 1.1.6. Schematics of Au pALD trials and TEM of resultant Au-coated TiN NPs. (a) P164. (b) P162. (c) P174.

Development of wet chemistry approaches for synthesis of core-shell nanoparticles with TiN or ZrN core and Au shell (Jonathan Boltersdorf, ARL)

Synthesis of plasmonic ZrN NPs

Synthesis of the plasmonic metal nitride, ZrN, was performed by a gelation and carbothermic nitridation method in-house at ARL for visible-light photosensitization of TiO₂ supports. Nitridation of zirconium precursors in the absence of an oxygen scavenger necessitates unsuitable high temperatures up to 2000+ °C. The preparation method utilizes a nitrogen-rich gel precursor that contains a zirconium and carbon source. Carbon black acts as an oxide scavenger to enable the conversion of zirconia and zirconium metal salts to zirconium nitride. Careful control of the zirconium to carbon molar ratio controls the phase composition and was optimized to yield pure ZrN. The reactions take place at high reaction temperatures

to facilitate full nitride conversion under a nitrogen atmosphere to prevent oxidation.[4] The crystalline ZrN phase was identified by PXRD and no residual bulk zirconium oxy-nitrides or oxides were observed, as shown in Figure 1.1.7a with the miller indices indicated above each prominent diffraction peak. The oxynitride phase, $\text{Zr}_7\text{O}_{11}\text{N}_2$, was produced in the early nitridation process, then decreased with further nitridation. Therefore, increasing the reaction temperature and time eliminated the presence of diffraction peaks associated with zirconium oxynitrides and carbides.

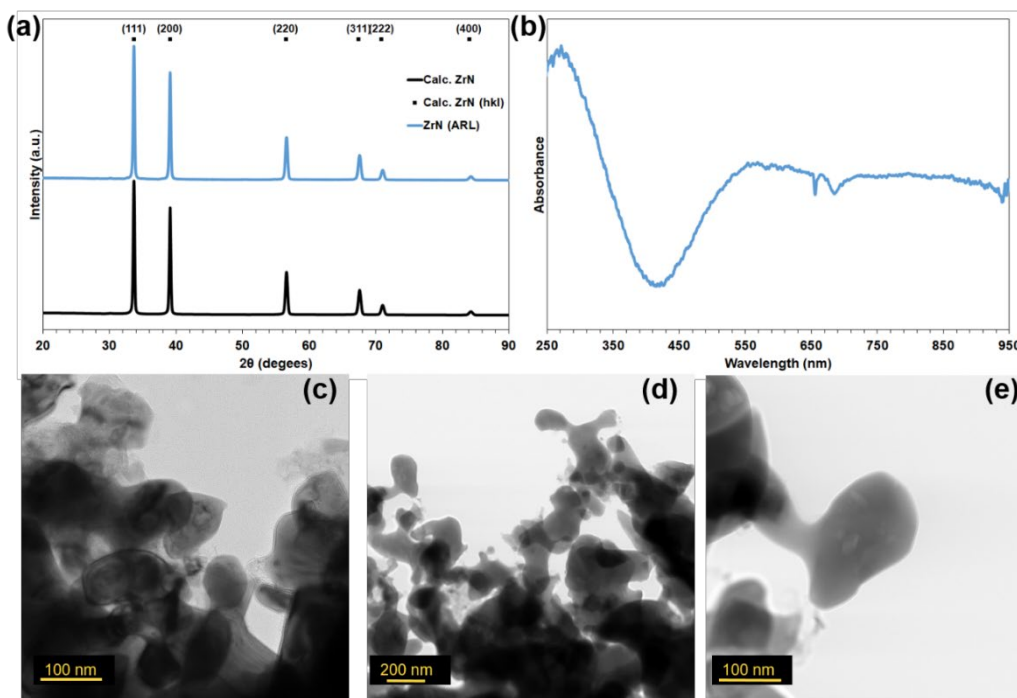


Figure 1.1.7 (a) PXRD pattern, (b) UV-vis spectra of ZrN in 20% methanol solution, (c) TEM image, and (d-e) HAADF-STEM images of ZrN NPs

TEM images of the ZrN sample in Figure 1.1.7 c-e show that the particle morphologies are irregular with smooth surfaces and coated in a thin native oxide layer. No residual amorphous carbon was observed, which indicates complete reaction of the carbon black as an oxygen scavenger. XPS in Figure 1.1.8 confirms the thin layer on ZrN observed in TEM images corresponds to an oxide layer on top of the ZrN phase, which may be due to exposure to atmosphere that resulted in surface oxidation. The Zr 3d region detail scan was examined with curve fitting and exhibited two prominent sets of Zr 3d peaks that correspond to Zr-O and Zr-N species. However, since XPS is a surface-sensitive technique, this is not representative of the bulk of the nanoparticles (NPs). Absorbance spectra collected from UV to near-infrared (NIR) for the ZrN NPs suspended in 20% methanol solution were obtained. ZrN NPs were suspended in a 20% methanol in water solution to ensure particle suspension and prevent aggregation, which revealed a broad plasmonic absorption from ~450-950 nm in Figure 1.1.7 b, similar to previously reported ZrN samples.

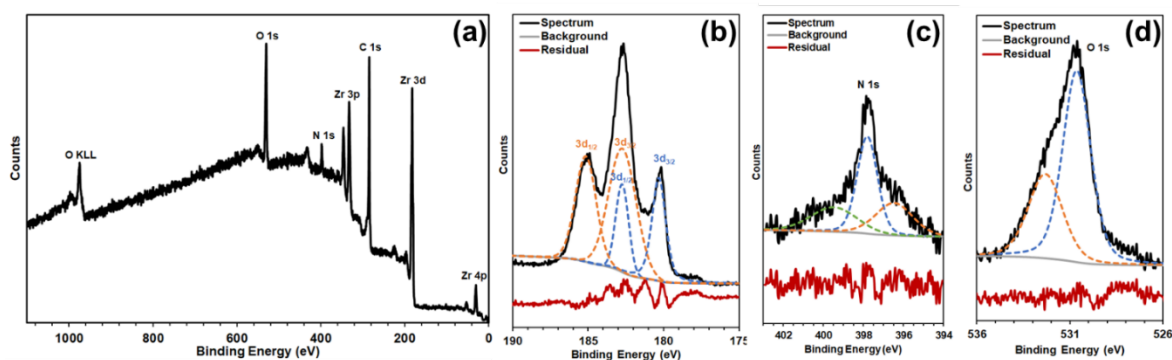


Figure 1.1.8. XPS (a) survey scan showing all chemical species present in ZrN sample, as well as (b) Zr 3d, (c) N 1s, and (d) O 1s regions with curve fitting

An attempt to synthesize ZrN nanoparticles was also made by Pajarito Powders. They used magnesiothermal/carbothermal reduction of ZrO_2 to Zr followed by nitridation in flowing N_2 at 1100°C . Because of the strong affinity of Zr to oxygen, ZrO_2 was formed instead of ZrN, as indicated by X-Ray diffraction. Surface analysis by XPS confirmed the presence of ZrO_2 (see surface composition in Table S2).

Synthesis of Plasmonic Core-Shell NPs with TiN core Au shell

Synthetic procedures for the growth of a conformal Au shell on TiN cores to form core-shell NPs as plasmonic photocatalysts for the photosensitization of titania substrates were investigated. Preparation and surface modification of gold coated magnetic iron oxide has been previously reported, which requires surface functionalization and seeding growth with small NPs.[5, 6] Gold-coated metal nitride and metal oxide materials were prepared using various wet chemistry methods, surfactants, surface functionalizing linkers, reducing agents, dark vs light reaction conditions, and temperature conditions. Microscopy and energy dispersive X-ray spectroscopy (EDXS) were the primary techniques employed to confirm the formation of Au NPs, the growth mechanism, and verify the conformality of Au on TiN and TiO_2 cores.

Literature procedures reported for the growth of Au shell on magnetic Fe_3O_4 NPs were adapted for the coating of a Au on TiN.¹⁻² TEM imaging and elemental mapping using EDXS of each sequential step in the following synthesis procedure are shown in Figures 1.1.9-1.1.12 The TiN nanocubes were coated in oppositely charged polymeric coatings, alternating between poly(acrylic acid) (PAA) and branched poly(ethyleneimine) (BPEI), shown in Figure 1.1.9. Au nanoseeds were formed separately and combined with the BPEI-PAA-TiN (BT) NPs, which electrostatically attracted the small Au nanospheres (1-5 nm), shown in Figure 1.1.10. A subsequent Au growth solution was added to the BPEI-PAA-AuNS-BPEI-PAA-TiN (BAPT) NPs in order to grow a secondary Au layer (ABAPT), shown in Figure 1.1.12 The final gold deposition resulted in clusters of Au nanospheres of larger (ripened nanoseeds) and smaller diameter. The method shows promise for controllably depositing conformal Au nanoseeds and nanospheres, as well as adhering the Au NPs to the TiN nanocubes.

In Figure 1.1.13, BPEI was used as the polymeric coating and Au nanoseeds were grown directly on the BPEI functionalized TiN, with subsequent addition of a Au growth solution to form AAPT that showed greater Au NP coverage and good dispersion. The PAA was eliminated for simplicity as the BPEI was sufficient to aid in coordination and attachment of Au NPs to the surface of TiN. In Figure 1.1.13 c, the TiN surface is covered in larger Au nanospheres and Au nanoseeds. Further experimentation is necessary to grow a conformal shell of Au on the TiN or TiO_2 , which may be accomplished by increasing the Au growth solution concentration or combining with other growth techniques described below.

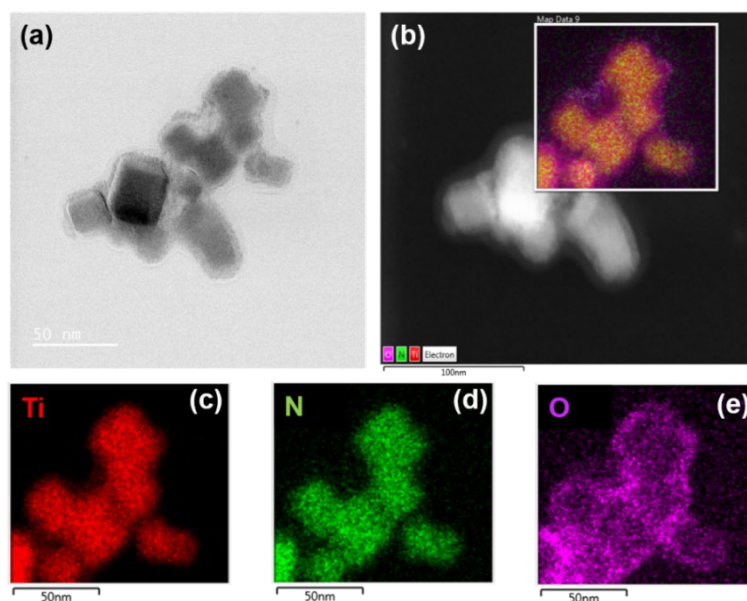


Figure 1.1.9. (a) STEM image of TiN nanocubes coated in PAA and BPEI, with (b) elemental mapping using EDXS for (c) Ti, (d) N, and (e) O species in the sample

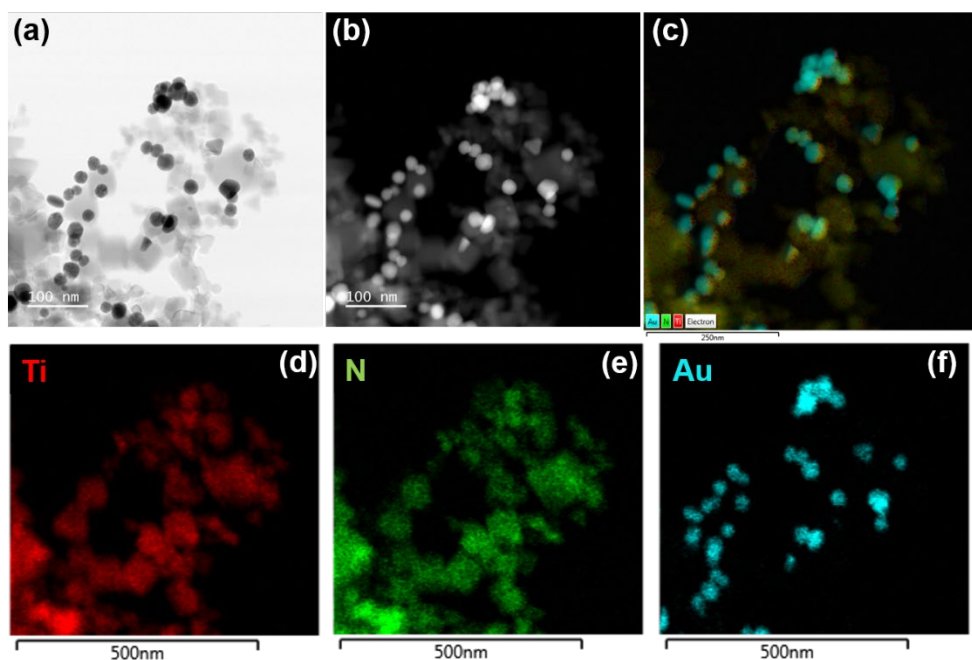


Figure 1.1.10. (a) Bright field STEM image of TiN nanocubes coated in PAA-BPEI and Au nanoseeds (ABT), with (b) HAADF-STEM images of (c) elemental mapping using EDXS for (d) Ti, (e) N, and (f) Au species in the sample

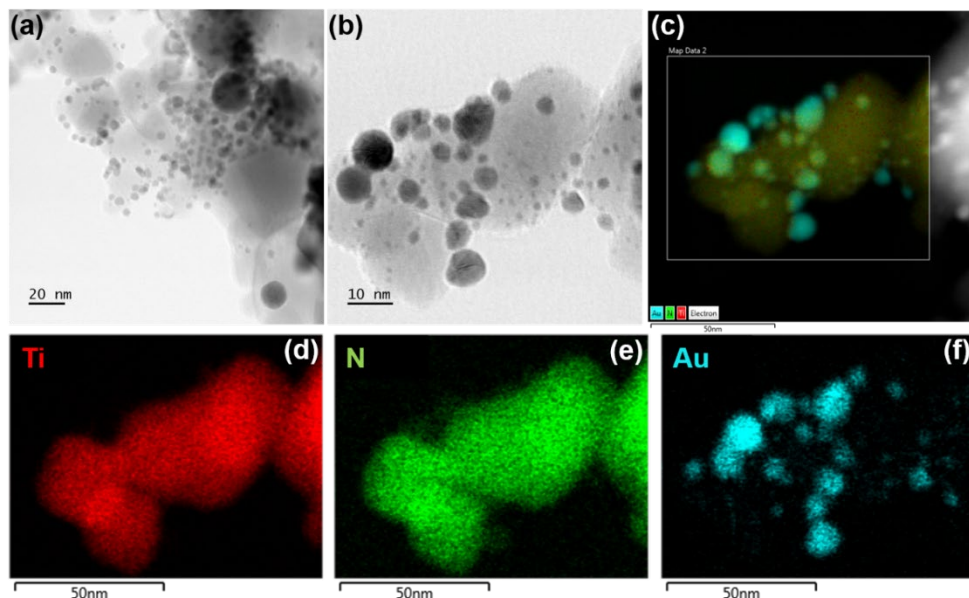


Figure 1.1.12. (a-b) Bright field STEM images of TiN nanocubes coated in PAA-BPEI, Au nanoseeds, PAA-BPEI, and Au nanospheres (ABABT), with (c) HAADF-STEM images of elemental mapping using EDXS for (d) Ti, (e) N, and (f) Au species in the sample

UV-vis spectroscopy can typically be used to observe absorption due to plasmon resonance from Au NPs in solution, while UV-vis diffuse reflectance spectroscopy (DRS) can be used to distinguish plasmon absorption on a solid substrate (i.e., TiO_2). The formation of a Au shell on a core has been shown in the literature to result in a red-shifting of the plasmon absorption to longer wavelengths. However, it is difficult to distinguish the red-shifted Au shell plasmon absorption on TiN owing to the broad plasmonic absorption of TiN in that region. The native oxide layer observed on all metal nitride samples should make the chemistry for functionalization of the surface and gold deposition similar to that of titania. Therefore, analogous experiments should be able to be performed on TiO_2 for Au shell growth. Growth of a Au shell can then be confirmed using UV-vis spectroscopy to observe the red-shifted plasmon absorbance, and the developed procedure for TiO_2 can then be subsequently applied to TiN.

Other methods were attempted for the growth of Au shell on TiN nanocubes:

1. Seed mediated silver-assisted AuNR growth procedure altered to grow conformal Au on TiN nanocubes.[7-9] No gold seed solution was prepared, but instead the TiN was used as the nucleation site to initiate Au growth under dark and UV-visible light irradiation.
2. The TiN nanocubes were coated in mercaptopropionic acid (MPA) to functionalize the surface for coordination with gold via self-assembled monolayer (SAM) growth under UV-visible light irradiation. Thiol functionalities have strong binding affinity for Au and have been shown to displace other surfactants or functional groups.[10]
3. The TiN nanocubes were coated in a thin layer of hexadecyltrimethylammonium bromide (CTAB), a quaternary ammonium surfactant, bromide ions via KBr salts was added to initiate direct Au growth.[8] The addition of CTAB and bromide ions was postulated to aid nucleation and growth of a Au shell under UV-visible light irradiation.
4. Electroless gold plating was employed to deposit a gold on TiN nanocubes in combination with previous methods. The electroless gold plating solution method is typically used for deposition on other metals at high temperatures ($\sim 90\text{-}110^\circ\text{C}$), so modification of the method was developed to deposit on metal oxide/nitride surfaces. Seeding the surface with Au and Ag nanoseeds and surface functionalization with CTAB, sodium citrate, and MPA were used to initiate electroless Au deposition in dark and UV-visible light irradiation conditions.

5. Combination of different methods indicated above in #1-4.

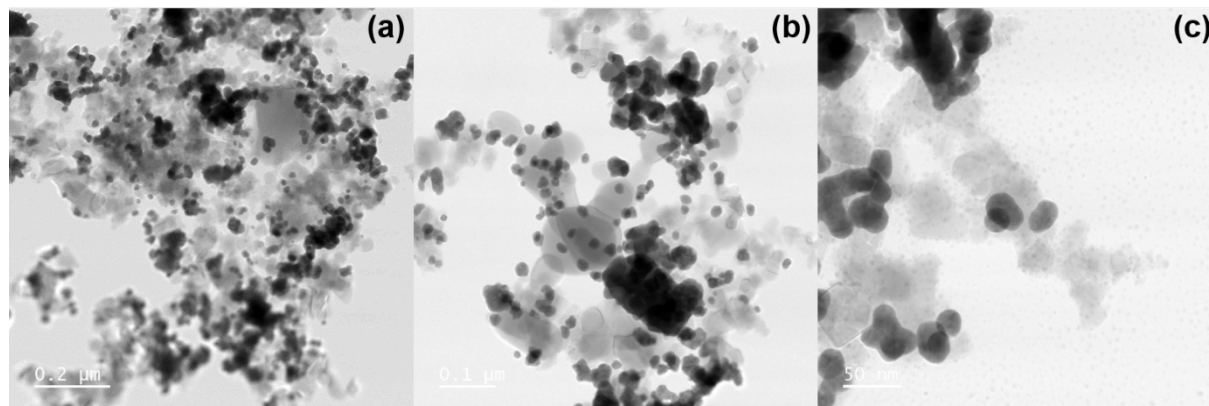


Figure 1.1.13. (a-c) HAADF-STEM images of TiN nanocubes coated in BPEI, Au nanoseeds, and Au nanospheres (AABT)

Synthesis of hybrid plasmonic NPs with TiN core and metal nanoclusters by wet chemistry methods

In previous synthesis experiments, the TiN-Au core-shell hybrid plasmonic NPs were targeted to preferentially grow conformal gold shells on TiN and TiO₂ nanoparticles but yielded a nonuniform distribution of large Au nanoparticles. A variety of wet chemical synthetic parameters were investigated that included surfactants (CTAB, PVP, etc), surface functionalized linkers (thiols, amines, etc), dark vs light reaction conditions, and high temperature conditions. The results of these studies informed our pivot to alternative hybrid core-shell/nanocluster systems and to pursue the synthetic modification of the surface of TiN to preferentially deposit cocatalysts to drive the photo-oxidation of 2-CEES.

Plasmonic TiN (plasmachem; 50 nm nanocubes) with a naturally occurring thin native oxide (TiO₂) layer on the surface was utilized as the core of the hybrid plasmonic nanoparticles. The proposed hybrid plasmonic nanostructures were: (1) TiN-core – SiO₂-thin shell – Au/Pd/Pt shells or nanoclusters and (2) TiN-core – TiO₂-thin shell – Au/Pd/Pt shells or nanoclusters. Deposition of Au was performed in parallel for comparison to the deposition properties of Pd. The deposition reactions were primarily investigated utilizing Pd owing to our extensive experience with Pd NPs and the similarity in properties (e.g., growth modality, chemical reduction, lattice compatibility, and fermi level) with Pt should make the procedures for growth analogous. The main objective was to develop a wet chemical synthesis methodology for depositing intermediate thin shell layers (i.e., SiO₂ and TiO₂) to enhance metal nanocluster growth (i.e., Pd and Pt) on the plasmonic TiN cores. Two promising wet chemical synthetic methods were investigated: (1) aminosilane functionalization with seeding and plating (SSP) and (2) incipient wetness impregnation (IWI) methods. The SSP method requires three sequential steps: (1) functionalization of the core nanostructure with a thin aminosilane layer to grow a thin SiO₂ layer, (2) subsequent metal nanoseeding of the SiO₂ surface, (3) growth of metal cocatalyst nanoshells or nanoclusters from the nanoseeds using a metal salt plating solution. The IWI method is a low temperature (<100 °C) simple approach performed in excess solvent with metal salts that is repeated over several cycles, but with no need for additional reducing agent, ligands, pH modification, etc.

To form a TiN-core – SiO₂-thin shell structure, first the native oxide layer on TiN was removed for the subsequent deposition of a thin aminosilane layer or SiO₂ intermediate layer for metal shell deposition. Removal of the oxide layer on TiN was performed with HCl at 65 °C while stirring, washed with ethanol, dried at 80 °C overnight, and stored in an Argon atmosphere glovebox to prevent surface oxidation. The clean TiN surface was functionalized with (3-Aminopropyl)triethoxysilane (APTES). APTES molecules are required to be adsorbed on the TiN-core surface to grow a thin SiO₂ layer for the metal nanoseeds to attach and grow. Firstly, 4.5 mg of cleaned TiN nanoparticles and 5 mL of ethanol were stirred for 10 min at 900 rpm, then 10 μL of APTES was added and stirred at 100 rpm for 24 hours. Afterwards, the stirred solution was heated at 90 °C for 1 h. Finally, the nanoparticles were washed and centrifuged three times in

ethanol for 15 min at 8500 rpm and redispersed in 2 mL of ethanol to yield TiN-core – SiO₂-thin shell nanoparticles.

The Au and Pd nanoseed suspensions were prepared by reacting the corresponding metal salts with tetrakis(hydroxymethyl)phosphonium chloride (THPC) in an alkaline aqueous environment to form colloidal suspension of spherical nanoseeds with diameters of 1–5 nm. First, 500 μ L of 1 M NaOH was added into 45 mL of DI water under vigorous stirring, followed by 1 mL of 68 mM THPC aqueous solution. After 5 min of stirring, 2 mL of a 1 wt% HAuCl₄ or H₂PdCl₄ solution was added, immediately turned dark brown, which indicated the formation of Au/Pd nanoseeds. The metal nanoseeds were stirred in the dark for 15 min and then stored in a refrigerator at 4 °C until needed. The THPC capping of the Au/Pd nanoseeds results in a negative surface charge, which prevents particle aggregation and provides colloidal stability.

The Au and Pd plating solutions enable the growth of the nanoseeds into larger particles and potentially merge into a shell coating. The plating solutions were prepared by adding 12.42 mg of K₂CO₃ into 50 mL of DI water, followed by 750 μ L of 1 wt% HAuCl₄ or H₂PdCl₄ solution, stirred in the dark at 900 rpm for 30 min, and stored in a refrigerator at 4 °C until needed.

The seeding step of the SSP method for depositing Au/Pd onto TiN-core – SiO₂-thin shell nanoparticles required adjusting 3 mL of Au or Pd nanoseeds to pH = 3 with HCl to ensure the favorable electrostatic interaction of positively charged cores and negatively charged metal nanoseeds. First, 60 μ L of 1 M NaCl and 200 μ L of cores were sonicated for 5 min and stirred overnight. The resulting TiN-core – SiO₂-thin shell with 1– 5 nm metal nanoseeds were centrifuged three times at 7500 rpm for 15 min and redispersed in 1 mL of DI water. The Au nanoseeds did not deposit on the surface of the core nanoparticles, and instead remained suspended in solution; therefore, no TiN-core – SiO₂-thin shell – Au-shell/nanoclusters were obtained.

The metal plating solutions were used to increase the amount of metal loading on the surface of the core nanoparticles, with the nanoseeds used as the nucleation sites for the deposition. The plating step of the SSP method included, 750 μ L of metal plating solution was added to 1 mL of seeded core nanoparticles, followed 12.5 μ L of formaldehyde, the reducing agent, while stirring. The SSP nanoparticles were centrifuged at 3000 rpm for 15 min to remove the formaldehyde and redispersed in 2 mL of DI water to yield TiN-core – SiO₂-shell – Pd nanoparticles.

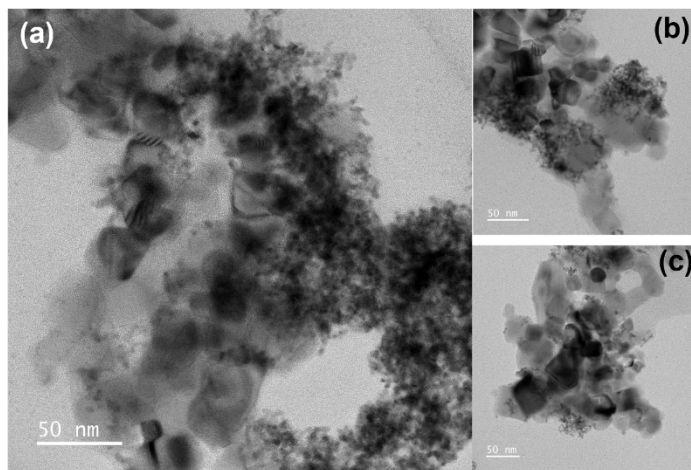


Figure 1.1.14. (a-c) TEM images of TiN-core – TiO₂-shell – Pd prepared using the SSP method

TEM, Bright-field TEM, and high-angle annular dark-field imaging scanning TEM (HAADF-STEM) were performed on the TiN-core – SiO₂-shell – Pd-nanocluster samples in Figure 1.1.14, which show the nanocube particle morphologies coated in a nonuniform distribution of Pd nanoparticles. No uniform metal shells were observed. Ultraviolet-visible (UV-vis) absorption spectroscopy was performed using 5 vol.% of TiN with a native oxide layer, clean TiN, TiN-core – SiO₂-shell, and TiN-core – SiO₂-

shell – Pd prepared using the SSP method dispersed in ethanol in 95 vol.% water. In Figure 1.1.15, the UV-vis absorption spectra were performed. The plasmonic absorption peak of TiN was slightly dampened in absorption intensity after the HCl washing step to remove the native oxide layer. The plasmonic absorption of TiN was red-shifted and dampened after depositing a SiO₂-shell, with further red-shifting after the Pd cocatalysts were deposited. The red-shifting and dampening of the plasmonic absorption of TiN is in good agreement with the COMSOL models performed by Prof. Govorov.

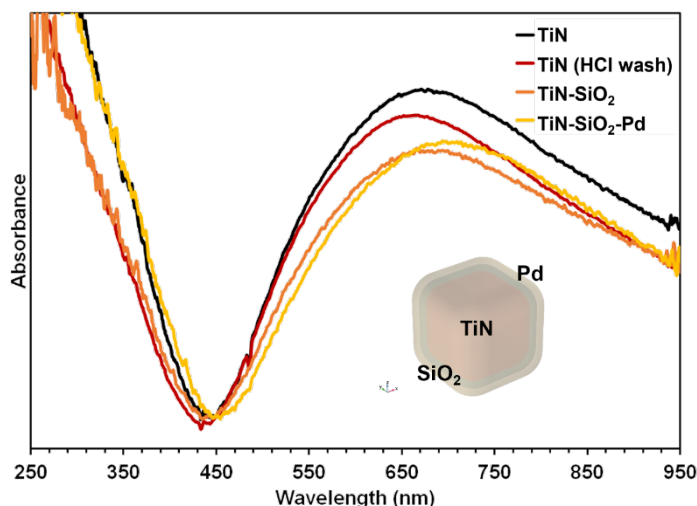


Figure 1.1.15. UV-visible absorption spectra of TiN with a native oxide layer, clean TiN, TiN-core – SiO₂-shell, and TiN-core – SiO₂-shell – Pd prepared using the SSP method with an inset schematic of the hybrid nanoparticle

The IWI method was performed using TiN nanocubes with the native oxide layer (i.e., TiN-core – TiO₂-shell) and 10 mM metal salt precursors (HAuCl₄ and H₂PdCl₄) in ethanol. The metal cocatalyst loading was controlled by the molar ratio of metal salt to TiN and subsequent deposition cycles (i.e., 1 to 4). Metal nanoparticle formation was achieved by simply drying the metal-salt-impregnated TiN-core – TiO₂-shell nanocubes at 80 °C while stirring. Metal nanoparticle formation at low temperature on an oxide support was accomplished without an external reducing agent or media. TEM images of the TiN-core – TiO₂-shell – Au/Pd-nanocluster nanocubes samples in Figure 1.1.16 and Figure 1.1.17 show that the nanocube particle morphologies exhibit smooth surfaces with the native oxide layer, and are coated in a uniform distribution of Au and Pd nanoparticles after two IWI deposition cycles. No uniform metal shells were observed to form on the TiN-core – TiO₂-shell nanocubes for 1-4 IWI deposition cycles. However, increasing the IWI deposition to 4 cycles resulted in the Au nanoseeds to ripen to significantly larger Au NPs (~200 nm), detach from the TiN, and nonuniformly distribute across the sample, as shown in the BF-TEM in Figure 1.1.16 d. Similarly, increasing the IWI deposition to 4 cycles resulted in a nonuniform distribution of Pd nanoseeds and some larger Pd NPs (~50-90 nm) across the TiN, as shown in the BF-TEM in Figure 1.1.17 c. In Figure 1.1.18, the UV-vis absorption spectra were performed using 5 vol.% of TiN and the TiN-core – TiO₂-shell – Au/Pd samples dispersed in ethanol in 95 vol.% water. The plasmonic absorption peak of TiN was red-shifted and dampened after Au and Pd cocatalysts were deposited. TiN plasmonic absorption continued to decrease in intensity with increasing Au deposition cycles; however, there was not a significant difference in absorption for 2x and 4x Pd deposition. The experimental absorbance spectra agreed with COMSOL models of TiN, TiN-core – TiO₂-shell, and TiN-core – TiO₂-shell – Pd/Pt-shell. Interestingly, similar optical effects for small discrete nanoparticles on TiN were observed experimentally to the models of uniform shell coverage with metal cocatalysts.

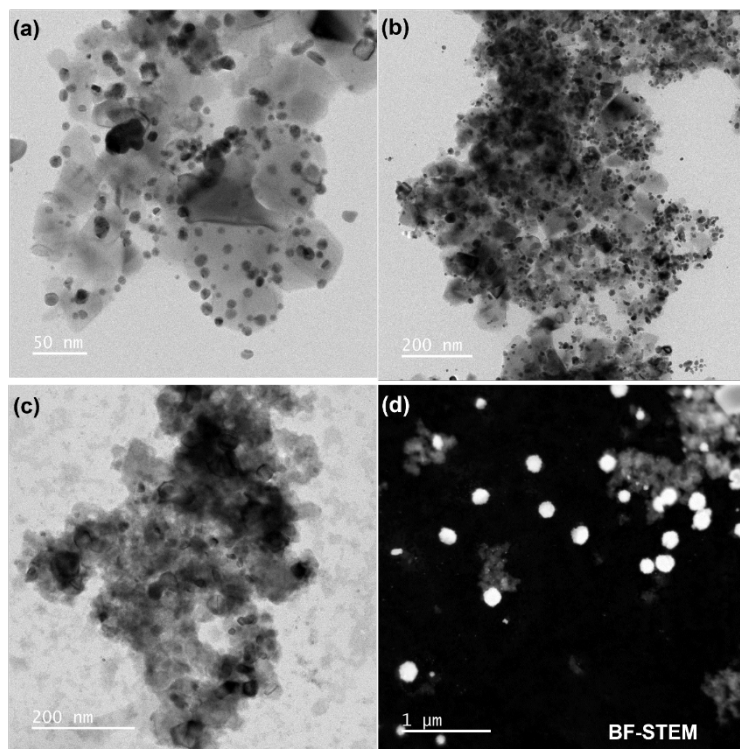


Figure 1.1.16. TEM images of the IWI deposited Au NPs on TiN-core – TiO₂-shell nanocube samples prepared after (a-b) two IWI deposition cycles and (c-d) four IWI deposition cycles, with large Au NPs shown in the BF-TEM in (d)

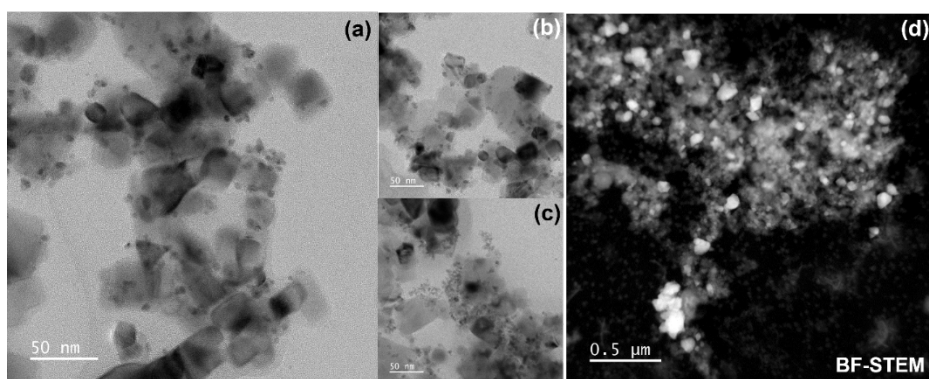


Figure 1.1.17. TEM images of the IWI deposited Pd NPs on TiN-core – TiO₂-shell nanocube samples prepared after (a-c) two IWI deposition cycles and (c) four IWI deposition cycles, with large Au NPs shown in the BF-TEM in (d)

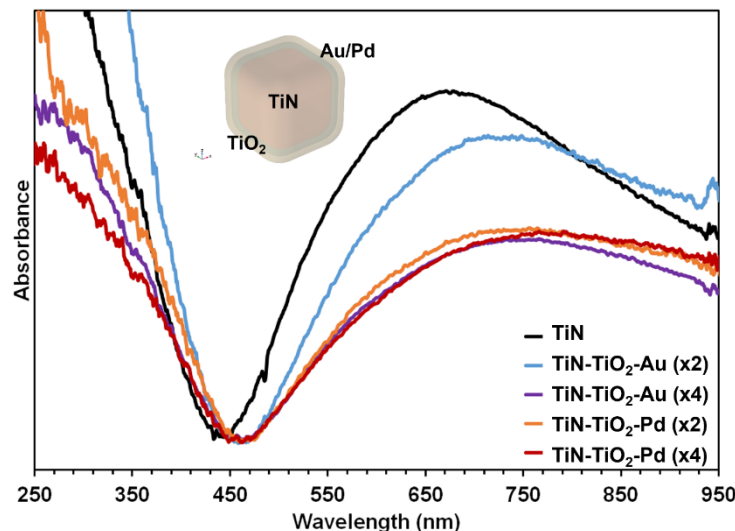


Figure 1.1.18. UV-visible absorption spectra of TiN and the IWI deposited Au and Pd NPs on TiN-core – TiO₂-shell with an inset schematic of the hybrid nanoparticle

The wet chemical synthesis methodology was further refined for enhance metal cocatalyst nanocluster growth (i.e., Pd and Pt) on the plasmonic TiN cores utilizing the (1) photochemical deposition (PCD) and (2) incipient wetness impregnation (IWI) methods. The PCD method utilizes a sacrificial reagent that is preferentially oxidized by photogenerated holes from TiN cores in the presence of a metal salt that is reduced by photogenerated electrons. The IWI method is a low temperature (<100 °C) simple approach performed in excess solvent with metal salts that is repeated over several cycles, but with no need for additional reducing agent, ligands, pH modification, etc.

Table 1. Hybrid plasmonic nanostructures composition for all 8 samples

Nanoporous Titania Substrate	Plasmonic Core	Metal Cocatalyst
TiO ₂	TiN-TiO ₂	Pd
TiO ₂	TiN-TiO ₂	Pt
3% Sm-TiO ₂	TiN-TiO ₂	Pd
3% Sm-TiO ₂	TiN-TiO ₂	Pt
TiO ₂	TiN-SiO ₂	Pd
TiO ₂	TiN-SiO ₂	Pt
3% Sm-TiO ₂	TiN-SiO ₂	Pd
3% Sm-TiO ₂	TiN-SiO ₂	Pt

The hybrid plasmonic TiN-core – TiO₂-thin shell – Pd/Pt samples were prepared by PCD and IWI methods with untreated TiN with the native oxide layer (i.e., TiN-core – TiO₂-shell) for a 20 mol% Pd/Pt loading on TiN, as listed in Table 1. For the PCD method, 5 mg of TiN was stirred in solution with 1616 µL of 10 mM H₂PdCl₄ or H₂PtCl₆ solution and 20 vol% methanol in DI water. The unreacted samples are sonicated in the dark for 1 hour before irradiating with a UV-visible light source for 2 hours while stirring to photoreduce Pd(II)/Pt(IV) to Pd(0)/Pt(0) nanoparticles on the surface of TiN. The IWI method was performed using TiN nanocubes and 10 mM metal salt precursors (H₂PdCl₄ or H₂PtCl₆) in ethanol. The metal cocatalyst loading was controlled by the molar ratio of metal salt to TiN and two subsequent deposition cycles of 808 µL of 10 mM H₂PdCl₄ or H₂PtCl₆ solution. Metal nanoparticle formation was achieved by simply drying the metal-salt-impregnated TiN-core – TiO₂-shell nanocubes at 80 °C while stirring. Metal nanoparticle formation at low temperature on an oxide support was accomplished without an external reducing agent or media. Finally, all the nanoparticles synthesized using PCD and IWI methods

were washed and centrifuged three times in ethanol for 15 min at 8500 rpm and redispersed in 1 mL of ethanol to yield TiN-core – TiO₂-thin shell – Pd/Pt samples, which were stored at 4 °C.

To form a TiN-core – SiO₂-thin shell structure, first the native oxide layer on TiN was removed for the subsequent deposition of a thin aminosilane layer or SiO₂ intermediate layer for metal shell deposition. Removal of the oxide layer on TiN was performed with HCl at 65 °C while stirring, washed with ethanol, dried at 80 °C overnight, and stored in an Argon atmosphere glovebox to prevent surface oxidation. The clean TiN surface was functionalized with (3-Aminopropyl)triethoxysilane (APTES). APTES molecules are required to be adsorbed on the TiN-core surface to grow a thin SiO₂ layer for the metal nanoseeds to attach and grow. Firstly, 20 mg of cleaned TiN nanoparticles and 5 mL of ethanol were stirred for 10 min at 900 rpm, then 45 μ L of APTES was added and stirred at 100 rpm for 24 hours. Afterwards, the stirred solution was heated at 90 °C for 1 h. Finally, the nanoparticles were washed and centrifuged three times in ethanol for 15 min at 8500 rpm and redispersed in 2 mL of ethanol to yield TiN-core – SiO₂-thin shell nanoparticles. The hybrid plasmonic TiN-core – SiO₂-thin shell – Pd/Pt samples were prepared by PCD and IWI methods with the HCl cleaned TiN functionalized with an SiO₂ layer (i.e., TiN-core – SiO₂-thin shell) using the same procedure as the TiN-core – TiO₂-thin shell – Pd/Pt samples outlined above.

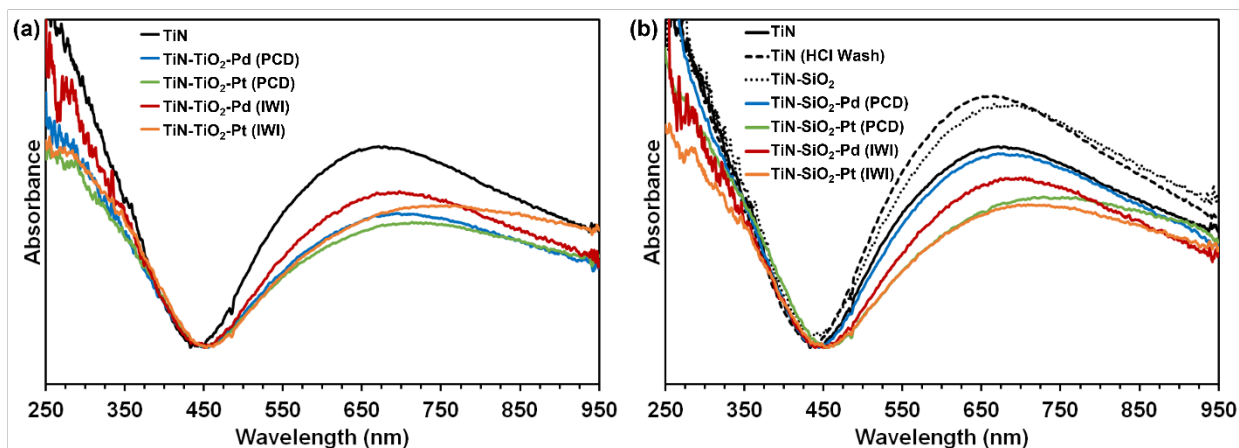


Figure 1.1.19. UV-visible absorption spectra of (a) TiN-core – TiO₂-shell – Pd/Pt and (b) TiN-core – SiO₂-shell – Pd/Pt hybrid nanoparticles synthesized using PCD and IWI methods, as well as TiN with a native oxide layer, HCl clean TiN, TiN-core – SiO₂-shell for comparison

Ultraviolet-visible (UV-vis) absorption spectroscopy was performed on 5 vol.% of plasmonic nanoparticles samples dispersed by sonication in ethanol in 95 vol.% water. In Figure 1.1.19, the UV-visible absorption spectra of TiN-core – TiO₂-shell – Pd/Pt (Figure 1.1.19 a) and TiN-core – SiO₂-shell – Pd/Pt (Figure 12b) hybrid nanoparticles synthesized using PCD and IWI methods are shown. Table 2 outlines the peak wavelength of maximum absorbance for plasmonic TiN after surface treatment and deposition of Pd/Pt nanoparticles determined, with the difference in peak wavelength given in relation to untreated TiN-core – TiO₂-shell. The plasmonic absorption peak of TiN-core – TiO₂-shell was dampened by ~7-13% in absorption intensity after PCD (~11-13%) and IWI (~7-10%) deposition of Pd and Pt. The wavelength for peak plasmonic absorption (λ_{MAX} (nm)) was red-shifted by ~23-85 nm after deposition of Pd/Pt nanoparticles. In Figure 1.1.19 b, the absorption of the TiN plasmon peak increased in intensity by ~6% after removal of the native oxide layer. The plasmonic absorption of TiN was slightly dampened by ~2% and red-shifted by ~3 nm after depositing a thin SiO₂-shell on clean TiN. Further dampening of the intensity by ~5-12% and red-shifting by ~0-58 nm of the plasmon resonance was observed after the Pd/Pt cocatalysts were deposited on the TiN-core – SiO₂-shell nanoparticles. The intensity of the TiN plasmon peak was observed to be greater for hybrid plasmonic nanoparticulate samples with SiO₂-shell layers compared to analogues with a native oxide layer. The red-shifting and dampening of the plasmonic absorption of TiN is in good agreement with the COMSOL models performed by Prof. Govorov. Interestingly, changes in

plasmonic absorption with the addition of a thin SiO₂ layer and small discrete Pd/Pt nanoparticles on TiN exhibited similar optical trends as the COMSOL models of uniform shell coverage with metal cocatalysts.

Table 2. Peak wavelength of maximum absorbance for plasmonic TiN (λ_{MAX} (nm)) after surface treatment and deposition of Pd/Pt nanoparticles determined from UV-vis absorption spectra, with the difference in peak wavelength given in relation to untreated TiN-TiO₂ ($\Delta\lambda_{\text{MAX}}$ (nm)). The difference in absorbance intensity ($\Delta\text{Abs. Int. (\%)}$) was compared to untreated TiN-TiO₂ at λ_{MAX} .

Material	Deposition Method	λ_{MAX} (nm)	$\Delta\lambda_{\text{MAX}}$ (nm)	$\Delta\text{Abs. Int. (\%)}$
TiN-TiO ₂	-	671	0	0
TiN	-	663	-8	+6
TiN-SiO ₂	APTES	666	-5	+4
TiN-TiO ₂ -Pd	PCD	694	+23	-11
TiN-TiO ₂ -Pt	PCD	714	+43	-13
TiN-TiO ₂ -Pd	IWI	697	+27	-7
TiN-TiO ₂ -Pt	IWI	756	+85	-10
TiN-SiO ₂ -Pd	PCD	671	0	-1
TiN-SiO ₂ -Pt	PCD	729	+58	-8
TiN-SiO ₂ -Pd	IWI	706	+35	-5
TiN-SiO ₂ -Pt	IWI	709	+38	-8

Bright-field STEM and HAADF-STEM were performed, with energy dispersive X-ray spectrometry (EDXS) used to map the elemental distribution. Representative STEM images of TiN-TiO₂ and TiN-SiO₂ with Pd nanoparticles deposited using PCD and IWI methods are shown in Figure 1.1.20 and Figure 1.1.21, respectively. No uniform metal shells were observed. The TiN nanocube particle morphologies exhibit smooth surfaces with a thin native oxide layer and are coated in a uniform distribution of Pd nanoparticles. In some cases, large Pd nanoparticles were observed on TiN-TiO₂ samples prepared using the PCD method due to Ostwald ripening of smaller Pd nanoparticles. HAADF-STEM images show the elemental distribution of Ti, N, and Pd species in TiN-TiO₂ (Figure 1.1.20) and TiN-SiO₂ (Figure 1.1.21) samples prepared using PCD and IWI methods, which confirm the formation of discrete Pd nanoparticles on TiN surfaces. In Figure 1.1.22, the HAADF-STEM images show the elemental distribution of SiO₂ on the TiN-SiO₂-Pd samples (Figure 1.1.21), which shows a coating of SiO₂ on the TiN nanocubes.

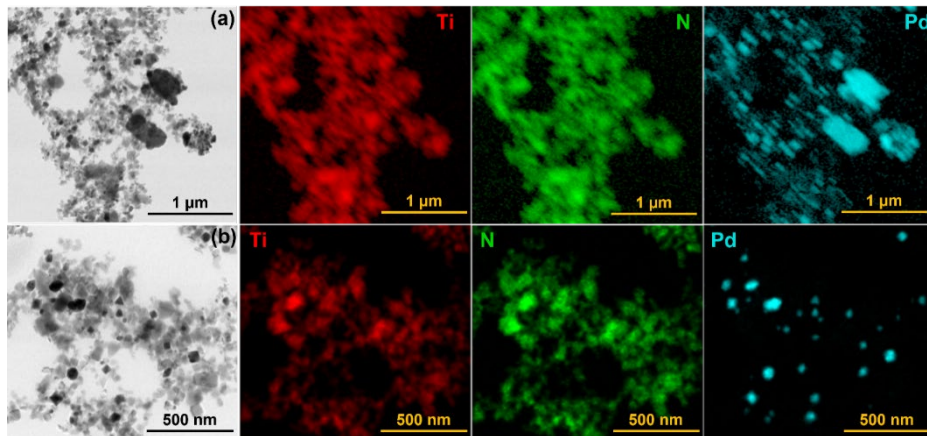


Figure 1.1.20. Bright field STEM images of TiN-TiO₂ nanocubes coated in Pd nanoparticles deposited using (a) PCD and (b) IWI methods, with HAADF-STEM images of elemental mapping using EDXS for Ti, N, and Pd species in the sample.

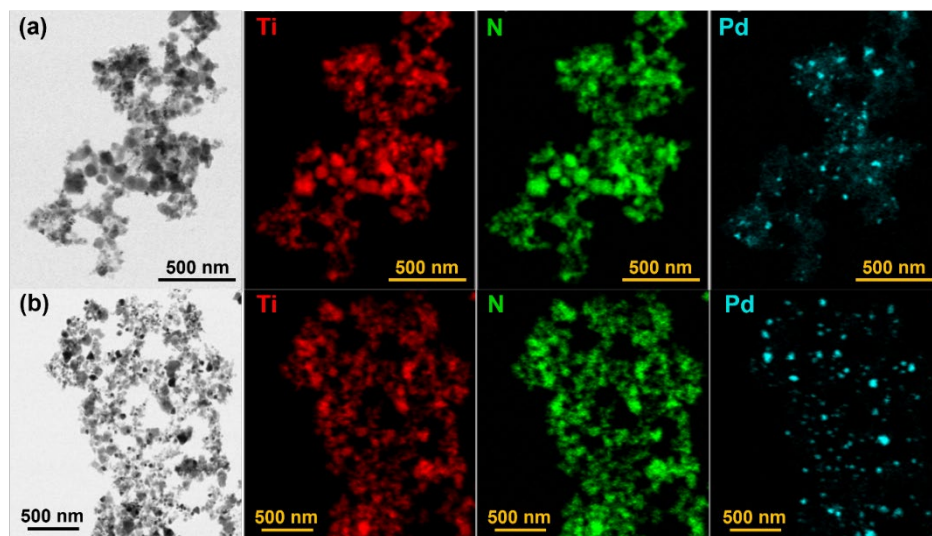


Figure 1.1.21. Bright field STEM images of TiN-SiO₂ nanocubes coated in Pd nanoparticles deposited using (a) PCD and (b) IWI methods, with HAADF-STEM images of elemental mapping using EDXS for Ti, N, and Pd species in the sample

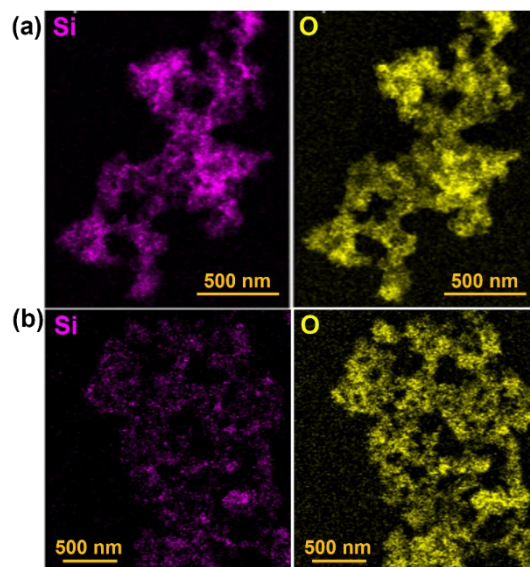


Figure 1.1.22. HAADF-STEM images of TiN-SiO₂ nanocubes elemental mapping using EDXS for Si and O species in the sample

Subtask 1.2 Synthesis of open-frame TiO₂ structures

Open-frame TiO₂ materials were synthesized by sacrificial support method. In the beginning of the program (October 2019 – December 2020), materials' synthesis was carried out by Geoff McCool from Pajarito Powder. In the sacrificial support method, Ti precursor is first mixed with an aqueous slurry of fumed SiO₂. Then the mixture is allowed to dry until all the liquids are evaporated. Following that, the mixture is baked at elevated temperature under flow of air or nitrogen. Finally, SiO₂ is etched, yielding a highly porous network of TiO₂. Details of synthesis of the particular materials can be found in the Supplemental Information. Materials were characterized by XRD, BET, XPS and UV-Vis in order to obtain information on the TiO₂ crystallite size, surface area, surface speciation and visible light absorption. All materials were synthesized in 300 mg batches.

Table 3 below summarizes physico-chemical properties and heat-treatment conditions of the materials, synthesized by Pajarito.

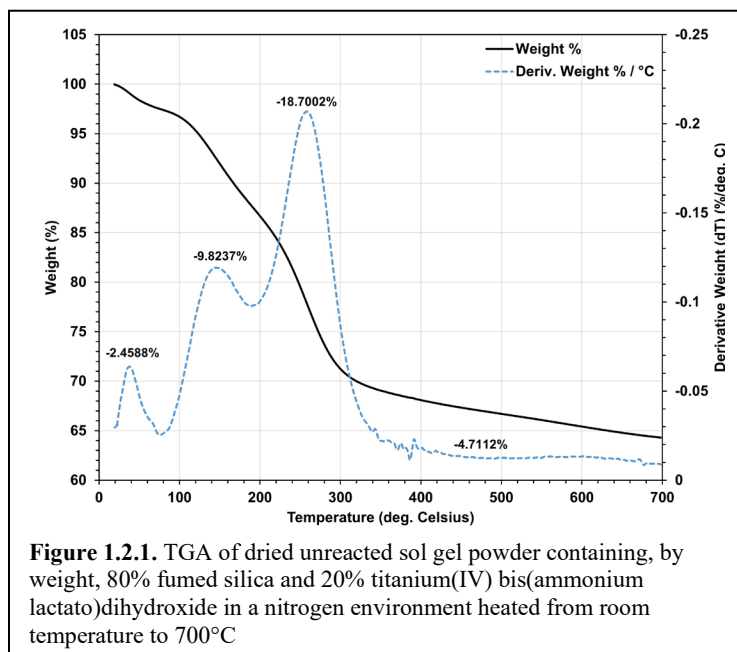
Table 3. Surface area and crystallite size of the materials synthesized by Pajarito Powders

Sample composition	Sample number	BET, m ² /g	Crystallite size, nm	Heat treatment t-re, °C
5 nm TiO ₂ /SiO ₂	NRL-1	-	-	
5 nm TiO ₂ /SiO ₂	NRL-5	30	4.1-12.9	
TiO ₂	NRL-3	252	3-4.5	450, air
TiO ₂	NRL-4	6	amorphous	450, air
TiO ₂	NRL-6A	223	4.1-6.1	
TiO ₂	NRL-6B	222	3.5-4.5	
TiO ₂ , alternative sacrificial support, no alkali hydroxide	NRL-15	166	4.2-6.9	Calcined at 450°C, etched with acetic acid, calcined at 450°C
TiO ₂	NRL-16F	196	3.5-7.2	Calcined at 800°C, annealed at 1100°C
Sm-TiO ₂	NRL-19	269	2.9-3.9	450, air
Sm-TiO ₂	NRL-19A	50	1.8-3.8	1100, N ₂
NH ₃ -treated TiO ₂	NRL21D	42	3.3-5.7	600, NH ₃
TiO ₂ , 2 nd batch of NRL-3	NRL-46	220	3-5	450, air

5 nm TiO₂ supported on 400 nm SiO₂ Stöber spheres was synthesized as a reference. This material demonstrated modest activity towards 2-CEES oxidation under visible excitation, as was demonstrated in our earlier publication [1]. The newly synthesized TiO₂ materials revealed significantly higher BET surface area of 170-270 m²/g in comparison to 5 nm TiO₂/SiO₂ reference (30 m²/g), while maintaining the same crystallite size of *ca* 5 nm. The synthesis conditions were optimized in order to increase surface area and improve visible light absorption and photocatalytic activity. We attempted also to dope TiO₂ with Sm (NRL-19 and NRL-19A), and N (NRL-21D) in order to boost its photocatalytic activity. However, only Sm doping led to improvement in catalytic activity. XPS and UV-Vis spectra of Pajarito synthesized materials, along with their atomic surface compositions are provided in the SI (Figures S7-S12 and Tables S3-S4).

Jonathan Boltersdorf attempted to reproduce synthesis of TiO₂ (NRL-3 and NRL-46) and Sm-doped TiO₂ (NRL-19) that demonstrated high photocatalytic activity towards 2-CEES decomposition under visible light excitation. The results of his synthetic effort are provided below.

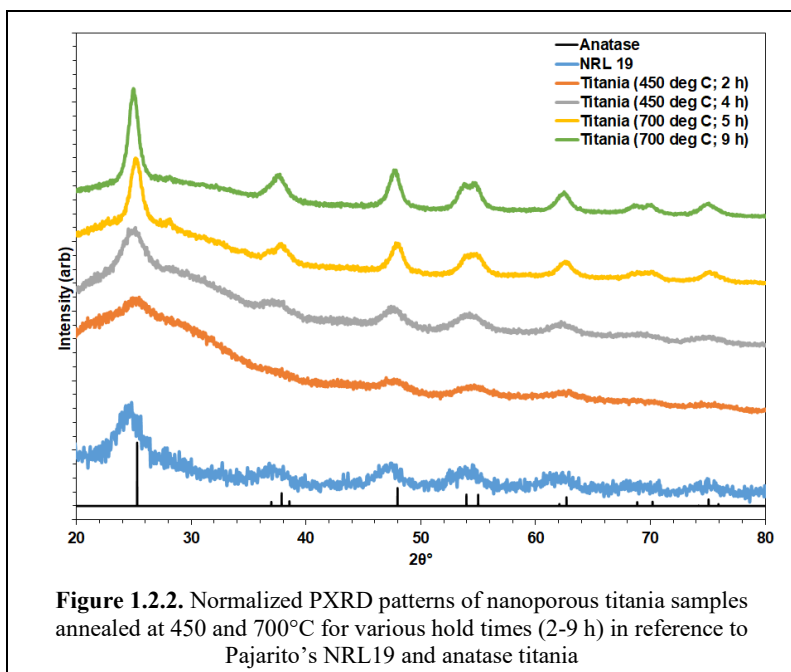
An aqueous slurry of fumed silica and titanium(IV) bis(ammonium lactato)dihydroxide was mixed for approximately one hour to form a sol-gel, then dried in air at $\sim 80^{\circ}\text{C}$ for ~ 24 hours. The target mass ratio was 80% silica and 20% titania. The dried solids were then pulverized by ball milling for 30 min.



Thermogravimetric analysis (TGA) was performed on the unreacted powder mixtures from room temperature to 700°C under nitrogen to determine the mass loss of off-gassed reactants and the thermal stability region for obtaining pure crystalline anatase phase titania, as shown Figure 1.2.1. Mass losses determined from TGA in Figure 1.2.1 correspond to 2.5 wt% surface water ($<100^{\circ}\text{C}$), 9.8 wt% water ($>100^{\circ}\text{C}$, $<200^{\circ}\text{C}$), 18.7 wt% and 4.7 wt% bis(ammonium lactato)dihydroxide ligand decomposition products ($>200^{\circ}\text{C}$). A combination of TGA and high-resolution powder X-ray diffraction (PXRD) determined that anatase phase titania can be obtained within 450°C to 700°C , but further annealing in air or oxygen is needed to remove the black carbon byproduct as

carbon dioxide. The reactant powder mixtures were calcined from 450°C to 700°C for 4-12 h with a ramp rate of 10°C per minute to obtain the anatase phase of titania.

The products were characterized by high-resolution powder X-ray diffraction (PXRD). In Figure



1.2.2, PXRD is shown for the nanoporous titania samples annealed at 450 and 700°C for various hold times (2-9 h) in comparison to Pajarito's NRL19 and the reference powder pattern for anatase titania. Broad amorphous background from 20 - 38° 2θ apparent in all samples is due to the glass substrate sample holder used for PXRD. All samples exhibited the anatase titania phase with improved crystallinity, increased peak intensity, and improved peak broadness with an increase in annealing temperature and time. Annealing at lower temperatures and for shorter reaction times resulted in amorphous black carbon solids. Increasing the surface area

exposure of the reactants and annealing at 450°C as low as 4 h increased the crystallinity and improved decarbonization of the product, while maintaining the nanoporous high surface area. The PXRD patterns of the nanoporous titania and 3% doped Sm-titania at the optimized reaction conditions of 450 °C for 4 h are shown in Figure 1.2.3 and are very similar to the reaction conditions used by Pajarito Powder for NRL19. The powders were transferred to ~7 M KOH solution that was heated to ~80°C to etch away the fumed silica for 48 h. The titania solids were collected via centrifugation after washing several times with 7 M KOH, 1.5 M KOH, and finally ultrapure water to remove silica byproducts. The final product was brought to a neutral pH and then dried in air at ~80°C for ~24 hours. The dried solids were ball milled for 30 min to yield a fine white powder. The samarium-doped titania was synthesized and purified following the same procedure, with a 97:3 Ti:Sm molar ratio, adjusted utilizing a $\text{Sm}(\text{NO}_3)_2$ reagent. TEM images in Figure 1.2.4 show similar nanoporous morphology and size (<10 nm) for both the titania and samarium-doped titania samples annealed at 450°C for 4 h under air.

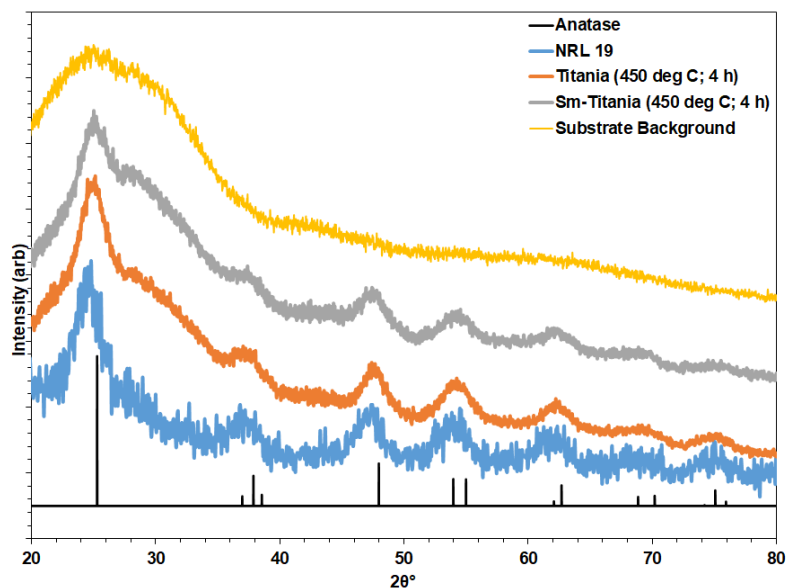


Figure 1.2.3. Normalized PXRD patterns for of nanoporous titania and 3% doped Sm-titania samples annealed at 450°C for 4 h in reference to Pajarito's NRL19, anatase titania, and the glass substrate sample holder

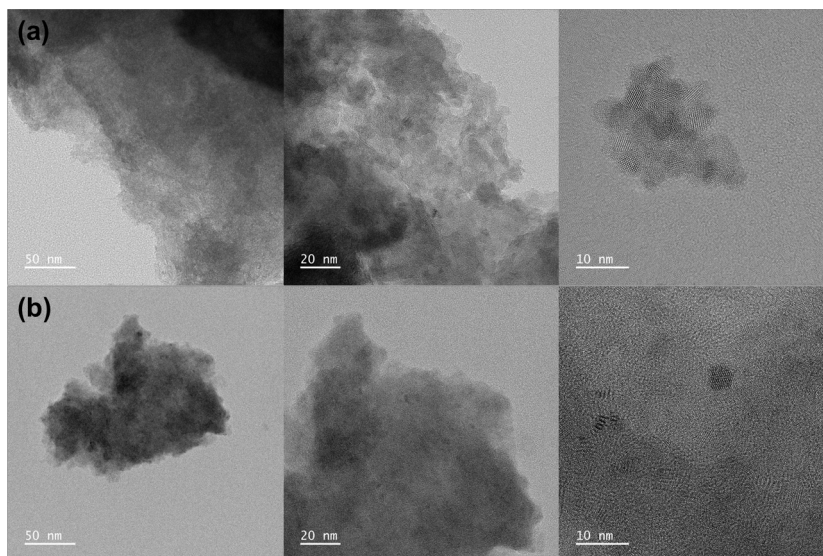


Figure 1.2.4. TEM images of nanoporous (a) titania and (b) 3% doped Sm-titania samples annealed at 450°C for 4 h under air

The synthesis procedure and purity of the nanoporous titania substrates was further refined using a flowing oxygen gas annealing furnace. Similarly, an aqueous slurry of fumed silica and titanium(IV) bis(ammonium lactato)dihydroxide with a target mass ratio was 80% silica and 20% titania was mixed for 1 h to form a sol-gel, then dried in air at $\sim 80^\circ\text{C}$ for ~ 24 hours. The dried solids were then pulverized by ball milling for 30 min and then calcined at 450°C for 4 h with a ramp rate of 2°C per minute in a flowing oxygen atmosphere to obtain the anatase phase of titania. Increasing the atmospheric oxygen content while annealing in flowing oxygen improved the crystallinity and decarbonization of the product, as shown in Figure 1.2.5, while maintaining the nanoporous high surface area ($\sim 200\text{ m}^2/\text{g}$). The powders were etched with $\sim 7\text{ M KOH}$ solution at $\sim 80^\circ\text{C}$ for 48 h to remove the fumed silica. Titania solids were collected via centrifugation after washing several times with 7 M KOH , 1.5 M KOH , and finally ultrapure water to remove silica byproducts. The final product was brought to a neutral pH and then dried in air at $\sim 80^\circ\text{C}$ for ~ 24 hours. The dried solids were ball milled for 30 min to yield a fine white powder. The samarium-doped titania was synthesized and purified following the same procedure, with a 97:3 Ti:Sm molar ratio, adjusted utilizing a $\text{Sm}(\text{NO}_3)_2$ reagent. The oxygen-annealed nanoporous titania and samarium-doped titania was utilized as the substrate for the hybrid plasmonic nanoparticles in Subtask 1.3.

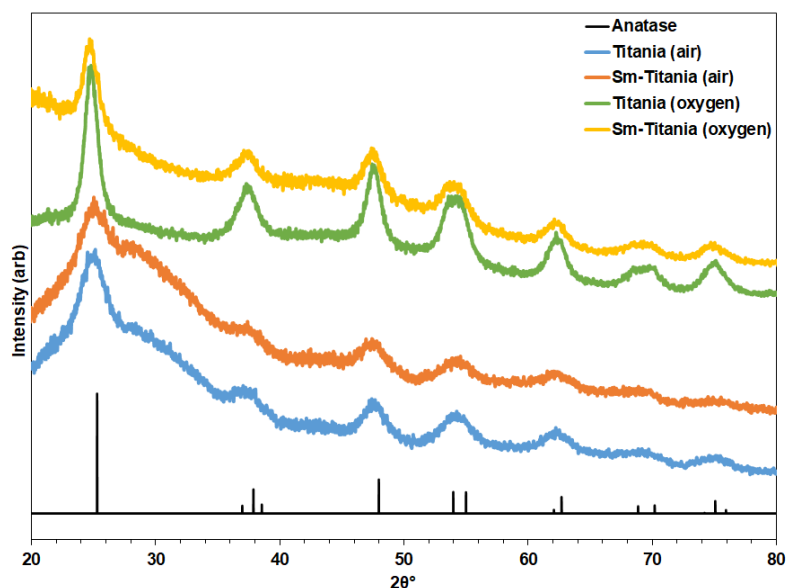


Figure 1.2.5. Normalized PXRD patterns for of nanoporous titania and 3% doped Sm-titania samples annealed at 450°C for 4 h under air and flowing oxygen

Subtask 1.3 Deposition of plasmonic nanoparticles on open-frame TiO_2 supports

Au pALD on open-frame TiO_2 supports with and without Al_2O_3 precoat (Benjamin Greenberg and Boris Feygelson)



Fig. 1.3.1. Schematic of pALD reactor configuration for preliminary trials of Au pALD on powder consisting of open-frame TiO_2 supports.

In performing subtask 1.1, we found that the nucleation and growth of Au on TiN nanoparticles is not conducive to pALD of thin continuous Au shells. Therefore, we transitioned to a fundamentally different approach: direct deposition of Au nanoparticles onto open-frame TiO_2 supports. TiO_2 directly coated with Au by pALD has the potential to exhibit the required plasmon-enhanced chemical sensing properties without the need for TiN coated with continuous Au shells with

~5 nm thickness. Fig. 1.3.1 shows the pALD reactor configuration used in our studies of direct deposition of Au NPs onto Pajarito high-surface-area TiO₂ nanopowder. To maximize Au precursor exposure, we placed the TiO₂ nanopowder in a weigh boat within 3 cm of the pALD reactor inlet, and we used the previously developed high dose of Au precursor (6 pulses, 30 s each). The Au pALD deposition temperature was 110 C.

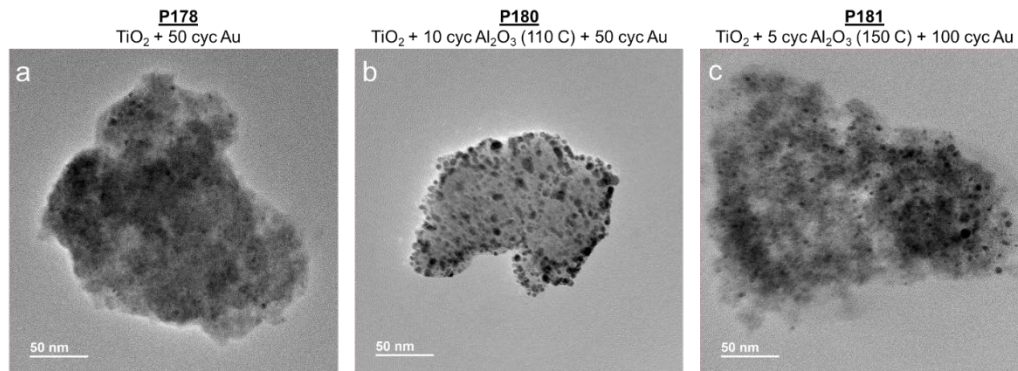


Fig. 1.3.2. TEM of Au-coated open-frame TiO₂ without and with Al₂O₃ pALD prior to Au pALD. (a) P178. (b) P180. (c) P181.

Fig. 1.3.2a shows TEM after 50 cycles of Au pALD (P178). Au NPs were observed throughout the specimen, although the quantity of Au deposited appeared to be lower than the highest quantities previously obtained from Au pALD on TiN nanopowder under the same pALD conditions. We hypothesized that Au deposition on the TiO₂ surface was less energetically favorable than Au deposition on the TiN surface, possibly due to carbon contamination on the TiO₂ surface.

In an effort to increase the surface energy of the TiO₂ and thereby enhance Au deposition, we developed a new approach: pALD of a high-surface-energy oxide onto the TiO₂ prior to Au pALD. For the high-surface-energy oxide, we chose Al₂O₃, for which we have well-established pALD recipes. Fig. 1.3.2b shows TEM of TiO₂ nanopowder coated with 10 pALD cycles of Al₂O₃ at a deposition temperature of 110 C, which is expected to produce a conformal Al₂O₃ coating with ~2 nm thickness, followed by 50 cycles of Au pALD (P180). Compared to P178 (Fig. 1.3.2a, no Al₂O₃), P180 contains significantly more Au; the deposition density of Au NPs is higher, and on average the NPs are larger.

Additionally, a comparison of the UV-vis spectra of P178 and P180 (Fig. 1.3.3) reveals that the absorption of P180 is

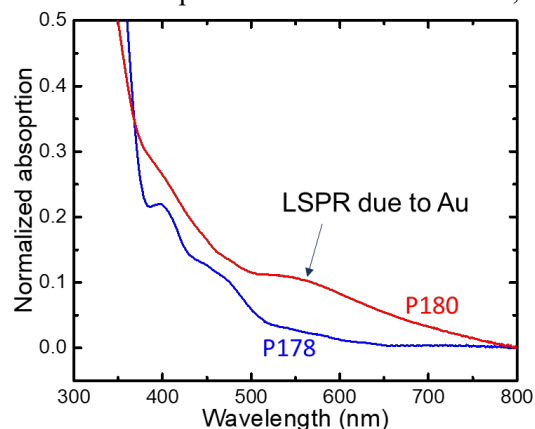


Fig. 1.3.3. UV-vis of Au-coated TiO₂ without (P178) and with (P180) Al₂O₃ pALD prior to Au pALD.

significantly enhanced around ~550 nm, which we attribute to stronger localized surface plasmon resonance absorption of the greater quantity of Au. Therefore, we continued to explore this Al₂O₃-pALD-based approach in the following run, P181. In this run, in an effort to minimize the impact of the Al₂O₃ coating on photocatalytic activity, we reduced the number of Al₂O₃ pALD cycles from 10 to 5 (reduced the expected coating thickness from ~2 to ~1 nm) and increased the deposition temperature from 110 to 150 C (expected to reduce carbon contamination of the Al₂O₃). Also, in an effort to increase the quantity of Au further, we increased the number of Au pALD cycles from 50 to 100. TEM of this sample (Fig. 1.3.2c), however, indicates that the quantity of Au decreased relative to that of P180, suggesting that the quantity of Au deposited is highly sensitive to Al₂O₃ pALD parameters. It is possible that Au pALD is affected not only by an increase in substrate surface energy due the Al₂O₃ coating but also by the reduction of the substrate surface area due to filling of the TiO₂ pores with Al₂O₃.

Table 4. XPS of Au-coated open-frame TiO₂ without and with Al₂O₃ pALD prior to Au pALD.

Sample	P178	P180	P181A	P181B	P184 (light)	P184 (dark)
ALD cycles	50 Au	10 Al ₂ O ₃ + 50 Au	5 Al ₂ O ₃ + 100 Au	5 Al ₂ O ₃ + 100 Au	5 Al ₂ O ₃	5 Al ₂ O ₃
	At. %					
O1s	36.74	44.82	52.65	34.91	50.14	53.99
Ti2p	42.69	10.63	6.22	5.06	13.71	6.36
C1s	12.46	18.42	15.1	44.01	11.5	14.86
Al2p	-	16.56	12.71	7.79	21.16	21.16
Au4f	-	2.88	1.34	.28	-	-
K2p	1.78	2.11	3.36	1.44	1.93	2.68
Si2p	2.56	-	2.73	2.4	-	-
P2p	1.26	4.29	5.87	2.27	-	-
N1s	-	-	-	1.46	-	-
In3d	2.38	0.29	-	0.37	0.52	0.11
Cl2p					1.04	0.84

As shown in Table 4, to obtain a detailed understanding of surface compositions, we performed XPS measurements of P178 (TiO₂ + 50 cyc Au), P180 (TiO₂ + 10 cyc Al₂O₃ + 50 cyc Au), and P181 (TiO₂ + 5 cyc Al₂O₃ + 100 cyc Au). The P181 powder contained two regions of slightly different color, one relatively gray and the other relatively beige, which we separated into two subsamples, P181A and P181B, respectively. For comparison, we produced an additional sample, P184, consisting of TiO₂ nanopowder coated only with 5 pALD cycles of Al₂O₃ and no Au, and of this sample we performed XPS measurements both before and after light exposure. We found that all Au-containing samples produced P2p peaks, indicating that phosphorous from the Au pALD precursor, Me₃AuPMe₃, is not completely removed during the oxidation steps in the pALD process. This finding is consistent with previous STEM/EDX data. Additionally, all samples produced C1s peaks, which we attribute to combinations of adventitious carbon and carbon originating from TiO₂ synthesis and Au and Al₂O₃ pALD. Notably, P181B produced a significantly stronger carbon signal than P181A, while P181A produced a significantly stronger phosphorous signal.

To obtain a better understanding of the mechanism of Au deposition enhancement and ultimately maximize the quantity deposited, we studied the effect of varying the Al₂O₃ deposition temperature. For this study, we used P25 TiO₂ nanopowder, which allows us to develop general understanding and methods for Au pALD on TiO₂ nanopowder while we await delivery of chemical precursors for replication of Pajarito high-surface-area TiO₂ nanopowder. As shown in Fig. 1.3.4a, in each experiment, we deposited 5 cycles of Al₂O₃ on P25 TiO₂ powder (as well as a Si wafer witness) at 70, 110, or 150 C and then deposited 50 cycles of Au at 110 C. Fig. 1.3.4b shows the UV-vis spectra of the resultant TiO₂/Al₂O₃/Au powders as well as the spectra of TiO₂/Au (50 cycles of Au with no Al₂O₃) and uncoated TiO₂ samples. The plasmonic absorption near 550 nm is enhanced by the Al₂O₃ nucleation layer deposited at 150 C and further enhanced by Al₂O₃ deposited at 110 C; it is not enhanced, however, by Al₂O₃ deposited at 70 C (the reason for the low baseline absorption of this sample is not clear at this time; regardless, the lack of enhanced plasmonic absorption is clear). The greater efficacy of 110 C Al₂O₃ relative to 150 C Al₂O₃ is consistent with our previous preliminary results, and the inefficacy of 70 C Al₂O₃ indicates that Au deposition is maximized at some intermediate Al₂O₃ deposition temperature (likely not far from 110 C). We hypothesize that, as Al₂O₃ deposition temperature is lowered, there is a tradeoff between increasing the Al₂O₃ surface energy (which promotes Au nucleation and growth) and decreasing the conformality and completeness of the Al₂O₃ coating (which leaves uncoated TiO₂ that is less conducive to Au nucleation and growth).

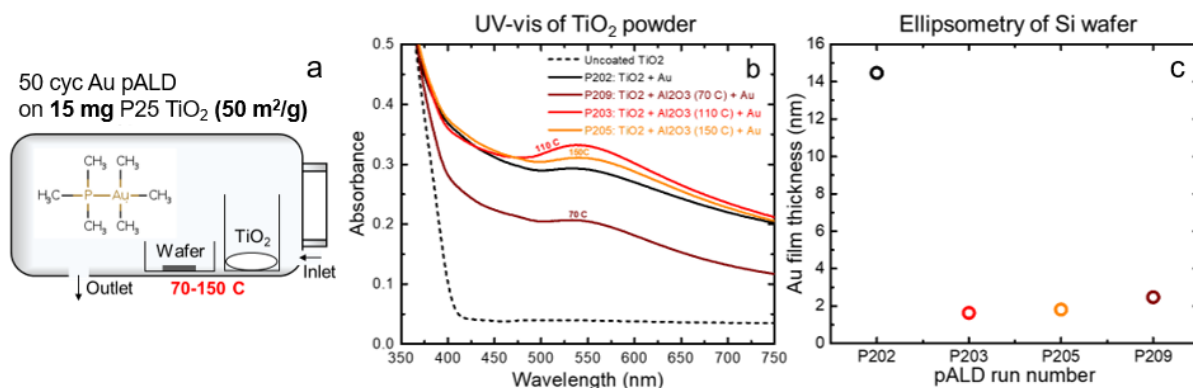


Fig. 1.3.4. Au pALD on P25 TiO₂ NP powder without and with Al₂O₃ pALD at varied temperature prior to Au pALD: P202, P203, P205, P209. (a) Schematic of reactor configuration. (b) UV-vis spectra. (c) Equivalent film thickness, from ellipsometry, of Au coatings on witness Si wafers.

As for the Au deposited on the Si witness wafers, the equivalent film thickness measured via ellipsometry (Fig. 1.3.4c) was between 1.5 and 2.5 nm for the three Al₂O₃/Au experiments (a typical range for 50 cycles Au pALD) but, strikingly, was nearly 15 nm in the case of Au pALD without Al₂O₃ pALD. We note that this Au-pALD-only run (P202) was the first in the series and was preceded by removal, cold storage, and reattachment of the Au precursor (Me₃AuPMe₃), and in the future we will monitor for any signs that this procedure temporarily increases the Au pALD growth per cycle. A possibility to consider is that the Me₃AuPMe₃ has partially decomposed over time and is no longer a homogeneous liquid. In the meantime, the apparent lack of proportionally enhanced Au deposition on the TiO₂ powder in run P202 suggests that we are operating in a pALD regime in which the general amenability of the powder surface to Au nucleation and growth is more important than the quantity of Me₃AuPMe₃ delivered to the chamber.

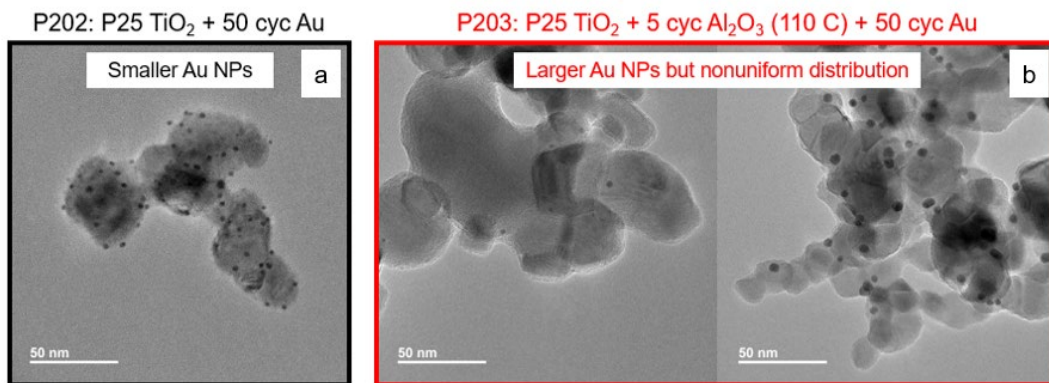


Fig. 1.3.5. TEM of Au-coated P25 TiO₂ NP powder. (a) P202: without Al₂O₃ pALD. (b) With Al₂O₃ pALD prior to Au pALD.

We used TEM to obtain a better understanding of the differences between the P202 and P203 Au-coated TiO₂ nanopowders. Fig. 1.3.5a shows that the P202 TiO₂/Au nanopowders contains relatively small Au nanoparticles (NPs), while Fig. 1.3.5b shows that the P203 TiO₂/Al₂O₃/Au nanopowder contains relatively large Au NPs; however, the Au NPs are not distributed uniformly throughout the sample, and some regions contain very few Au NPs.

Au pALD on open-frame TiO₂ supports: scaling up and increasing Au uniformity and quantity

We transitioned to a new Au pALD strategy in order to improve the uniformity of Au deposition while also scaling up the process in order to coat significantly larger surface areas of TiO₂ nanopowder. Specifically, we increased the TiO₂ surface area by a factor of 20, scaling up from ~15 mg of commercial TiO₂ with a specific surface area of 50 m²/g (~0.75 m² total surface area) to ~75 mg of ARL-synthesized

TiO₂ with a specific surface area of 200 m²/g (~15 m² total surface area). Our new strategy entails using a rotary drum to agitate the TiO₂ nanopowder so that the entire powder surface is exposed to the Au pALD precursors on a relatively short timescale.

Our preliminary pALD test runs with the high-surface-area powder revealed that the coated powder yield is low due to wall losses and escape from the drum when previously developed rotation rates for nanopowders are used. In order to increase yield of the nanopowder after pALD we developed new strategies for agitation of nanopowder which has very high surface area. The strategy involves slow rotation (5 rpm as opposed to ~100 rpm for our typical rotary pALD process) combined with vibration of the drum. As a result of adjusting parameters of rotation and vibration, we can demonstrate that slow rotation prevents powder aerosolization and thereby prevents escape from drum and that the combination of slow rotation and vibration minimizes adhesion of powder to drum wall. We tested this approach using Pt pALD based on trimethyl(methylcyclopentadienyl)platinum (MeCpPtMe₃), and O₃, which is potentially more conducive to metal deposition on nanopowders than any currently available ALD processes for Au. Therefore Pt pALD is both a good test process for our powder agitation procedure development as well as a good candidate for future precoating of TiO₂ to create high-surface-energy seeds that promote Au nucleation and growth.

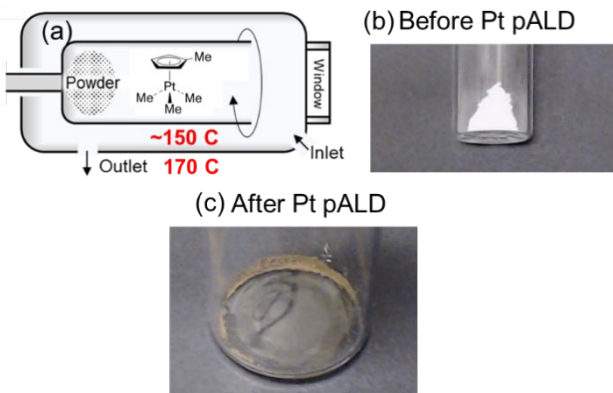


Fig. 1.3.6. (a) Schematic of Pt pALD on open-frame TiO₂ powder. (b) Powder before Pt pALD. (c) Powder after Pt pALD.

In our Pt pALD trials, the rotary drum was heated by heating the chamber walls; in transparent metal oxide pALD processes, the rotary drum is heated via IR lamp through an IR window, but we chose a different strategy because of uncertainty in the transmission of the IR window during pALD of an IR-absorbing metal. Heating the drum wall to 170 °C resulted in a rotary drum temperature of 150 °C (Fig. 1.3.6a). We heated the MeCpPtMe₃ to 75 °C to produce sufficient vapor pressure. 20 pALD cycles were carried out, and each cycle consisted of a Pt dose, first N₂ purge, O₃ dose, and second N₂ purge. A Pt dose consisted of a 10 s pulse, followed by a 30 s hold during which MeCpPtMe₃ infiltrated the sliding powder bed. An O₃ dose consisted four microdoses, each consisting of a 40 s O₃ pulse followed by a 30 s hold and 30 s pump step; this O₃ dose procedure was previously developed for Au pALD on TiO₂ powders. The results of this run were highly encouraging. As shown in Fig. 1.3.6b,c, Pt pALD resulted in a uniform change in powder color from white to brown, which indicates uniform Pt deposition throughout the powder; evidently the slow rotation and vibration and long MeCpPtMe₃ holds allowed infiltration of the powder. Moreover, the Pt-coated TiO₂ powder mass yield was 88%, indicating that powder loss through adhesion and aerosolization was minimal.

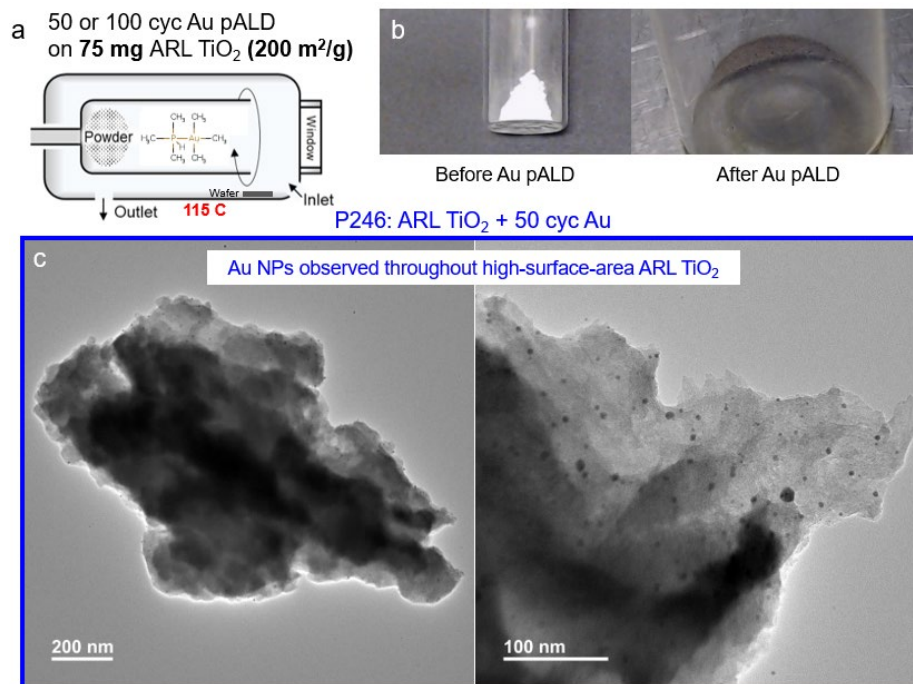


Fig. 1.3.7. (a) Schematic of Au pALD on larger batches of ARL-synthesized open-frame TiO₂ powder. (b) Photographs of powder before and after Au pALD. (c) TEM of the Au-coated powder.

Applying this combination of slow rotation and vibration to Au pALD on ~75 mg of ARL-synthesized TiO₂ with a specific surface area of 200 m²/g (~15 m² total surface area) resulted in Au-coated TiO₂ nanopowder mass yields of approximately 80% as well as uniform color changes of the TiO₂ nanopowder, suggesting spatially uniform Au deposition (Fig. 1.3.7a,b). Indeed, TEM revealed Au NPs throughout the regions of the TiO₂ nanopowder where there was sufficient contrast between TiO₂ and Au for the Au NPs to be visible (Fig. 1.3.7c). Although it is not possible to determine from these images the depth of Au penetration into the micron-sized particles of high-surface-area TiO₂ (far from the particle edges, where the particle is thicker and appears darker, there is insufficient contrast between Au and TiO₂), the spatial uniformity of the visible Au NPs, along with the uniform powder color change, suggests that the rotary pALD approach produces a significantly more uniform sample than the static-powder pALD approach.

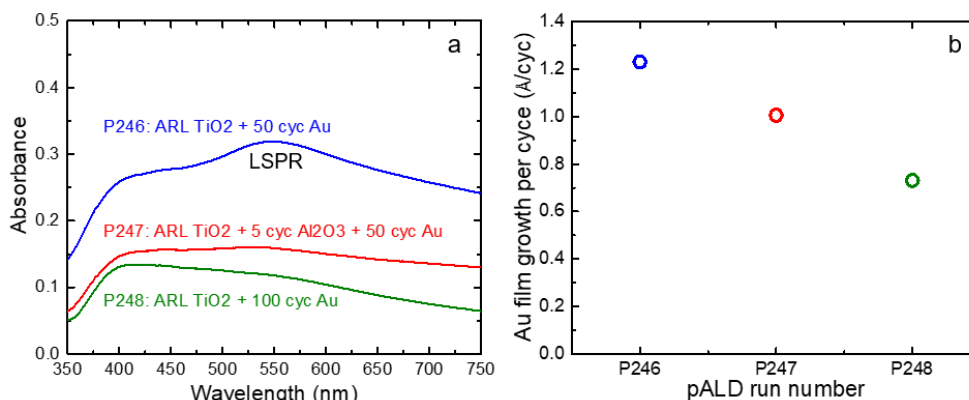


Fig. 1.3.8. (a) UV-vis spectra of ARL-synthesized open-frame TiO₂ coated with Au without (P246, P248) and with (P247) Al₂O₃ pALD before Au pALD. The samples are numbered chronologically. (b) Corresponding Au growth per cycle, from ellipsometry, on Si witness wafers.

Fig. 1.3.8a shows UV-vis spectra of Au-coated ARL TiO₂ nanopowders produced by our new rotary pALD approach. The blue spectrum, Au pALD run P246 (50 cycles of Au pALD on ~75 mg ARL TiO₂ nanopowder), corresponds to the TEM images shown in Fig. 1.3.7c. In this spectrum, there is clear LSPR absorption peaking near 550 nm, as in the spectra of the smaller batches of Au-coated commercial TiO₂, confirming a successful 20× scale-up of Au pALD on TiO₂ nanopowder. In subsequent pALD runs, we attempted to increase this LSPR absorption by precoating the TiO₂ with 5 cycles of Al₂O₃ (red spectrum, P247) or by increasing the number of Au pALD cycles from 50 to 100 (green spectrum, P248). Surprisingly, the P247 and P248 spectra show decreased LSPR absorption. Similarly, ellipsometry revealed that the quantity of Au deposited on Si witness wafers decreased from P246 to P247 to P248. This suggests that, in general, there is an uncontrolled variable that causes Au deposition to decrease over the course of a sequence of Au pALD runs. Currently, we suspect decomposition of the Au precursor, Me₃AuPMe₃. Future experiments may include studying the effect of placing the Me₃AuPMe₃ in cold storage between pALD runs. We are also expecting delivery of new Me₃AuPMe₃ which should perform in a more consistent way. This delivery has been delayed by supply chain issues upstream of the Me₃AuPMe₃ supplier.

We investigated another potential source of inconsistency and reduced Au deposition: temperature nonuniformity in our pALD reactor. As shown in Fig. 1.3.9a, a heater jacket is used to heat the exterior of the outer chamber to 115 °C, but this jacket cannot heat the back wall, which is the interface between the chamber and the inert atmosphere glovebox; we estimate that the back wall's exterior temperature is approximately 40 °C. Therefore, we expect a temperature gradient in the rotary drum with lower temperature at the back of the drum. Given that the powder substrate is located at the back of the drum during pALD, it is possible that this temperature gradient affects deposition. Specifically, if the back of the drum is sufficiently cold that the powder substrate temperature is below the Au ALD temperature window (the process window for well-behaved ALD), this could cause low Au ALD growth per cycle and/or particularly high sensitivity to precursor degradation or other variables.

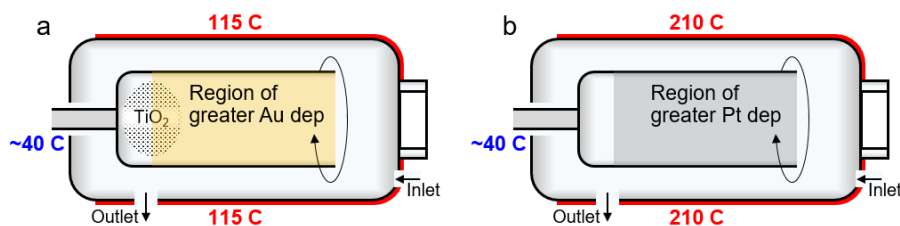


Fig. 1.3.9. (a) Schematic of rotary pALD reactor showing region greater Au deposition. (b) Schematic showing region of greater Pt deposition.

As shown in Fig. 1.3.9a, over time we have observed, by eye, less accumulated Au deposition near the back of the rotary drum. This observation alone, however, does not confirm a temperature effect, because during many Au pALD process development runs, there may have simply been insufficient Au precursor to coat the drum's entire surface area uniformly. To gain a better understanding of the effect of the drum temperature gradient on metal pALD, we performed a test using Pt pALD, which has the advantage of producing a pressure trace with an unambiguous saturation signal; i.e., the pALD chamber pressure clearly flattens when the deposition reaction is completed, confirming that there is sufficient precursor to coat all sufficiently hot surfaces in the chamber. Under saturating conditions, we deposited a visible quantity (>200 ALD cycles) of Pt on a rotary drum identical to that used for Au pALD, and we observed a deposition pattern very similar to that of the Au with decreased deposition near the back wall (Fig. 1.3.9b). Thus we concluded that the low temperature of the back wall hinders Pt deposition and that a similar effect on Au deposition is indeed plausible.

Fig. 1.3.10 illustrates our current work on solving the temperature gradient challenge. We have filled the back of the drum with thermally insulating borosilicate glass so that the powder is held farther from the drum's cold back wall and positioned in the region where there has been more Au deposition (but still far

from the drum opening to minimize the escape of powder from the drum). Preliminary tests with Pt ALD reveal that on and near the glass surface, where the TiO_2 powder will be located, the quantity of metal deposited is greater than that in the back of a typical rotary drum without glass. We plan to use the glass-filled drum as well as the new $\text{Me}_3\text{AuPMe}_3$ in upcoming efforts to increase the uniformity and quantity of Au deposited on open-frame TiO_2 structures by Au pALD.

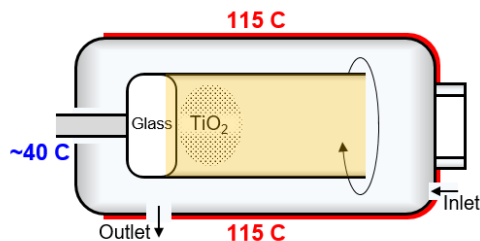


Fig. 1.3.10. Schematic of pALD reactor with rotary drum modified to shift powder to region of greater Au deposition.

Incorporation of TiN, Cu and Au NPs onto open-frame TiO_2 supports (Geoff McCool, Pajarito Powders)

TiN, Cu and Au NPs were deposited onto the most photocatalytically active TiO_2 (NRL-3) support. The list of synthesized materials is given in Table 5. 50 nm commercial (PlasmaChem) TiN nanoparticles were deposited by a simple mixing of TiN nanoparticles with suspension of TiO_2 under ultrasonic excitation (NRL-8). Cu nanoparticles were incorporated into TiO_2 matrix either during sacrificial support synthesis (NRL-20) or obtained by a Cu impregnation (NRL-21A, B, and C). The latter method was also used for deposition of Au nanoparticles (NRL-46 A). 1 wt% Cu/ TiO_2 (P25, commercial support) and 1 wt% TiN/ TiO_2 (P25) photocatalysts were synthesized as a reference. Surface composition by XPS and UV-Vis spectra of the synthesized materials are provided in Table S2 and Figure S12 in the SI. The target loading of plasmonic NPs on the TiO_2 support was 1 wt%. However, to investigate the effect of loading, the Cu/ TiO_2 photocatalysts with 5 wt% (NRL-21A), 10 wt% (NRL-21B) and 20 wt% (NRL-21C) loadings were also synthesized. Although we intended to synthesize *ca* 5 nm Au and Cu nanoparticles, they appeared to be either smaller or larger than 5 nm. For example, Cu crystallite size for the catalysts with 5 -20 wt% Cu loading varied between *ca* 14 to 28 nm depending on the loading. Larger nanoparticles were obtained at higher Cu loading. Cu 2p high resolution spectra indicated the presence of Cu or Cu_2O species on the surface of all cu samples (Figure S11), which are not distinguishable by XPS. UV-Vis spectra were collected to characterize visible light absorption of the hybrid photocatalysts. The most pronounced maximum (assigned to localized surface plasmonic resonance) was observed for Cu/ TiO_2 (NRL-20) (800 nm, violet line in Figure S12b), synthesized by introducing Cu pre-cursor during sacrificial support synthesis. Broader and weaker plasmonic resonance were established by 1 wt% TiN/ TiO_2 (650 nm, NRL-8, black line in Figure S12c), and 1 wt% Au/ TiO_2 (550 nm, NRL-46A, magenta curve in Figure S12d). The morphology of Au NPs within TiO_2 matrix was characterized by TEM (Figure S13). Au nanoparticles were present in two different morphologies: (1) 1 to 3 nm roughly spherical nanoparticles and (2) larger, irregularly shaped nanoparticles on the order of 30 nm. Energy Dispersive X-Ray analysis revealed that Au nanoparticles were not evenly distributed on the support. The densely Au populated areas were located sometimes next to the areas occupied by the TiO_2 nanoparticles only. TiO_2 particles in Fig.S13 were observed in large, disordered aggregates. Individual TiO_2 crystallites appeared spherical with diameters in the regime of 5 nm, in agreement with XRD. Introduction of Au nanoparticles into TiO_2 matrix did not change the morphology of the TiO_2 matrix.

The photocatalytic experiments with TiN/ TiO_2 and Cu/ TiO_2 nanoparticles carried out in FY20 revealed that both TiN and Cu nanoparticles promoted 2-CEES hydrolysis instead of oxidation. Therefore,

in FY21, attention was focused on synthesis of the Au/TiO₂ photocatalysts comprising open-frame TiO₂ support (NRL-3) and *ca* 5 nm Au nanoparticles. This goal was achieved utilizing both *p*-ALD and wet chemistry methods.

Table 5. Cu/TiO₂, Tin/TiO₂ and Au/TiO₂ photocatalysts synthesized by Pajarito Powders

Sample composition	Sample number	BET, m ² /g	Crystallite size, nm	Heat treatment t-re, °C
1%TiN/TiO ₂	NRL-8	252	3.4-5.1 (TiO ₂)	50, vacuum
1%TiN/TiO ₂ (P25)	NRL-11	45	7.0-37.3	50, vacuum
Cu/TiO ₂	NRL-20	252	2.2-4.4	450, air
Cu/TiO ₂ , H ₂	NRL-20C	102	2.9-4.9	440, H ₂ /N ₂
1%Cu/TiO ₂ (P25)	NRL-34	47	7.3-37.3	450, air
1%Cu/TiO ₂ (P25), H ₂	NRL-34A	43	7.3-34.3	400, H ₂ /N ₂
5 wt% Cu/TiO ₂	NRL-21A	81	2.5-4/14 (TiO ₂ /Cu)	500, air
10 wt% Cu/TiO ₂	NRL-21B	72	1.7-4.2/20-22	500, air
20 wt% Cu/TiO ₂	NRL-21C	64	4.5/16.8-37	500, air
1 wt% Au/TiO ₂	NRL-46A	252	3-4.5	450, air

Incorporation of Au NPs onto nanoporous TiO₂ supports by wet chemistry methods (Jonathan Boltersdorf, ARL)

The main focus of these investigations was to mitigate agglomeration of core-shell NPs on the TiO₂ support related to the absence of chemical driven interaction of zero-valent metal (Au) with oxygenated species on the surface of TiO₂. The deposition of Au NPs on the surface of TiO₂ were investigated using photochemical deposition methods, ultrasonication, shaker milling, and surface functionalization. The Au NPs were deposited with a 1 wt% loading on three different titania samples: (1) commercially available P25 that is an optimal mix of the anatase and rutile polymorphs, (2) NRL provided Pajarito TiO₂ matrix, and (3) NRL provided Sm-doped TiO₂. All of the samples were photosensitized with Au NPs, washed, dried, and then characterized using UV-vis DRS, as shown in Figure 1.3.11.

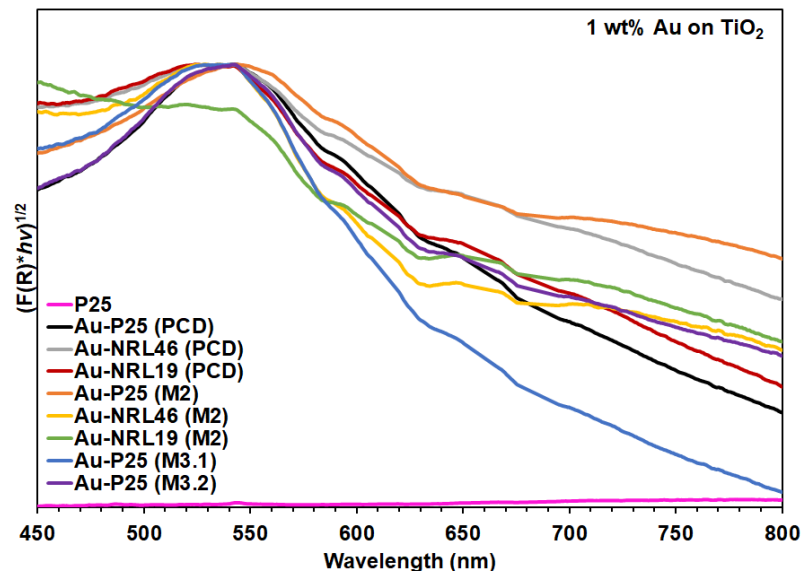


Figure 1.3.11. Normalized UV-vis DRS of 1 wt% Au on three different titania samples prepared using three different synthesis methods

Three methods used to grow and attach Au NPs to TiO_2 :

1. Photochemical deposition (PCD) method utilizes a sacrificial reagent that is preferentially oxidized by photogenerated holes in TiO_2 in the presence of a metal salt that is reduced by photogenerated electrons.[11, 12] The TiO_2 samples are mixed in solution with gold precursor and formic acid sacrificial agent that is irradiated with a UV-visible light source. The stirred solution turns from white to magenta as the Au(III) is reduced to Au(0) on the surface of TiO_2 , as shown in Figure 1.3.12 and Figure 1.3.13.
2. Au NPs were synthesized using the previously reported method that utilizes a dilute polyvinylpyrrolidone surfactant (PVP; MW $\sim 40,000$ g/mol) with an ethanol sacrificial reagent (M2).[13, 14] The Au NPs were confirmed using UV-vis spectroscopy and then combined with MPA-functionalized TiO_2 .
3. The TiO_2 samples were functionalized with MPA and mixed with Au nanoseeds made using the CTAB surfactant (M3.1). The TiO_2 samples were functionalized with trimethylamine (TEA) and mixed with Au nanoseeds made using concentrations diluted from 100 mM to 10 mM of the CTAB surfactant (M3.2).

In Figure 1.3.11, the UV-vis DRS of the Au- TiO_2 samples show the normalized spectra of the AuNPs exhibit a sharp absorbance peak in the visible spectrum ($\lambda_{\text{max}} = \sim 542$ nm) corresponding to its localized surface plasmon resonance. TEM images of 1 wt% Au deposited on P25 titania prepared by the PCD method show a nonuniform distribution of Au NPs (~ 25 nm) on the titania nanoparticles in Figure 1.3.12. While the Au NPs exhibited a better uniform distribution on the nanoporous titania, as shown in the STEM and elemental mapped images in Figure 1.3.13.

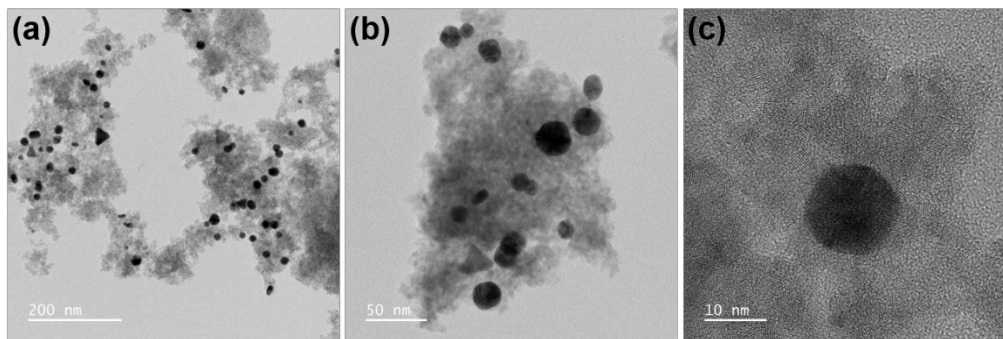


Figure 1.3.12. (a-c) TEM images of 1 wt% Au deposited on P25 titania prepared by the PCD method

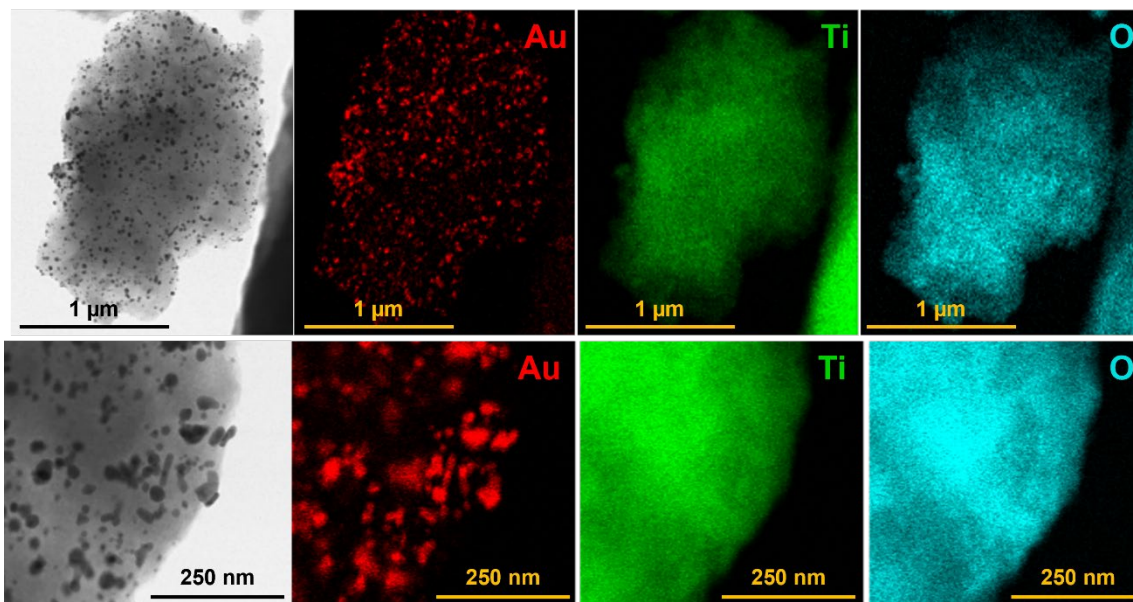


Figure 1.3.13. Bright field STEM images of 1 wt% Au deposited on ARL-synthesized nanoporous titania using the PCD method, with HAADF-STEM images of elemental mapping using EDXS for Au, Ti, and O species in the sample

Au/TiO₂ photocatalysts with 1 wt%, 5 wt% and 10 wt% Au loading were synthesized by (1) photochemical deposition and (2) the deposition of Au onto the TiO₂ support via combination of PVP-modified Au and MPA-functionalized TiO₂ (M2) for further comparison of the various loadings using the two deposition methods. The ARL-prepared titania and Sm-doped titania were used as photocatalytic substrates for plasmonically photosensitizing with Au nanoparticles (NPs), which were deposited with a 1 wt% Au NP loading. The Au NPs were synthesized using the previously reported method, Method 2 (M2), that utilizes a dilute polyvinylpyrrolidone surfactant (PVP; MW ~40,000 g/mol) with an ethanol sacrificial reagent. The Au NPs exhibit a sharp absorbance peak in the visible spectrum ($\lambda_{\text{max}} = \sim 542$ nm) corresponding to its localized surface plasmon resonance, consistent with previous samples that were prepared with NRL46 and NRL19. Mercaptopropionic acid (MPA) was used as the functional linker for AuNPs by stirring the titania in concentrated MPA for 24 h for attachment to the substrate surface. The Au NPs were confirmed using UV-vis spectroscopy and then combined with MPA-functionalized titania samples. All the samples were washed with ultrapure water, dried at 80°C for 24h, and then characterized using UV-vis DRS. The ARL-prepared samples were compared to Pajarito synthesized sample NRL46 with 1-10 wt% Au NPs, and found to exhibit similar plasmonic absorption, as shown in Figure 1.3.14. The ARL-prepared titania and Sm-doped titania samples were also prepared with 1 wt% Au NPS using the previously reported M1 and PCD methods for comparison to the Pajarito sample and for further time studies for photocatalytic oxidation of 2-CEES. Briefly, photochemical deposition (PCD) method utilizes a sacrificial

reagent that is preferentially oxidized by photogenerated holes in TiO_2 in the presence of a metal salt that is reduced by photogenerated electrons. The TiO_2 samples are mixed in solution with gold precursor and formic acid sacrificial agent that is irradiated with a UV-visible light source. The stirred solution turns from white to magenta as the Au(III) is reduced to Au(0) on the surface of TiO_2 . The M1 method utilizes titania samples functionalized with MPA and mixed with Au nanoseeds made using the CTAB surfactant.

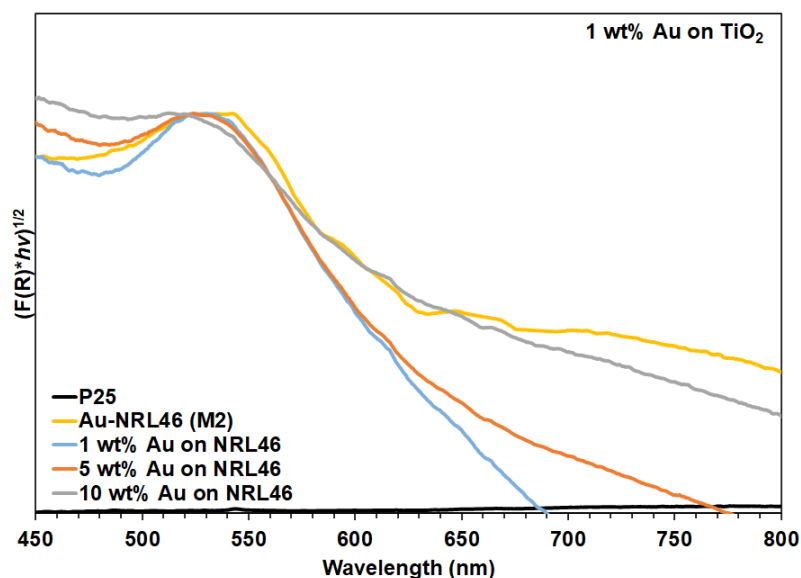


Figure 1.3.14. Normalized UV-Vis DRS of 1 to 10 wt% Au nanoparticles on nanoporous titania, shown for NRL46 samples and ARL-prepared titania, all prepared using the M2 synthesis method

The ARL-prepared titania and Sm-doped titania were used as photocatalytic substrates for plasmonically photosensitizing with Au nanoparticles (NPs), which were deposited with a 1 wt% Au NP loading using the PCD and M2 methods. The samples were supplied to NRL for studies of photocatalytic oxidation of 2-CEES.

Deposition of hybrid plasmonic NPs onto TiO_2 matrix (Jonathan Boltersdorf, ARL)

The ARL-prepared nanoporous titania and Sm-doped titania were used as photocatalytic substrates for plasmonically photosensitizing with 1 wt.% TiN-core – $\text{TiO}_2/\text{SiO}_2$ -shell – Pd/Pt hybrid plasmonic nanoparticles. The metal cocatalysts (Pd and Pt) were deposited on TiN with a 20 mol% Pd/Pt loading using the PCD method for all samples. All hybrid plasmonic nanoparticles were deposited on titania in ethanol while sonicating and stirring for 5 hours. The samples were washed with ethanol and centrifuged three times to remove any impurities. The excess solvent was removed, and the powders were dried at 80 °C overnight. The samples listed in Table 1 were supplied to NRL for studies of photocatalytic oxidation of 2-CEES.

Subtask 1.4 Modeling of optical properties of plasmonic core-shell nanoparticles

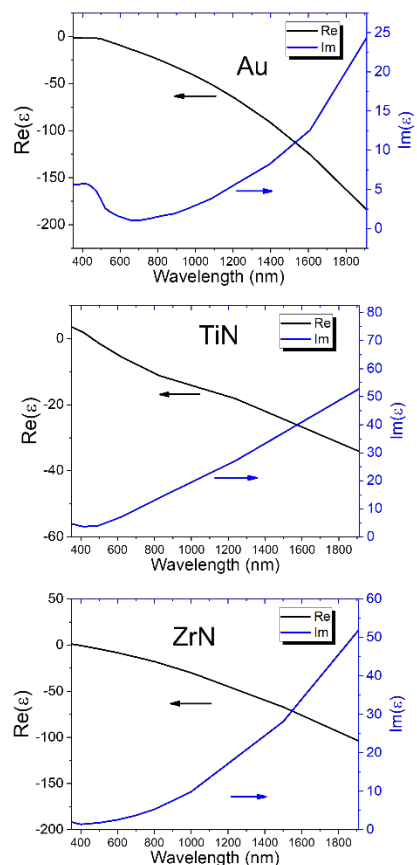


Figure 1.4.1: Dielectric functions of the materials used in the simulations. Literature sources: Johnson and Christy (Au), U. Guler, et al., Faraday Discussions, 178, 71, 2015 (TiN), and M. Veszeli, K. Andersson, C.-G. Ribbing, K. Jarrendahl and H. Arwin, Appl. Opt., 33, 1993–2001, 1994 (ZrN).

The OU team has accomplished a large set of computational tasks on hybrid nanostructures composed of plasmonic and photocatalytic components. Inexpensive plasmonic crystals, like TiN and ZrN, were the focus. For the photocatalytic materials, we used Au, Pt, and Pd, which are expensive, but can be used as thin coatings in small quantities in our plasmon-enhanced hybrids designed for the photochemistry of CWAs.

Single TiN, ZrN, and Au NPs. Testing the new materials and COMSOL software for those materials

For Subtask 1.4, the Ohio U. team started simulations with the simple single-material NPs. The spectral interval of interest is UV - vis - near-IR. The materials of interest include TiN, ZrN, Au@TiN (Au-shell, TiN core), Au@ZrN, and TiO₂ substrates. The calculations are performed using the COMSOL Multiphysics software package that solves Maxwell's equations within the local dielectric function approach. The first crucial step is to identify the local dielectric function of the materials. Figure 1.4.1 below shows the data used in our computations.

We present computational data for simple NPs in water. From these spectra, we will be able to identify plasmonic properties of the materials to be used for our purpose (chemical sensors) in the project. Those spectra are also important for the characterization of the TiN NPs by Dr. Baturina's group. From comparison between theory and experiment, we can interpret and understand the experimental extinction spectra shown in Figure 1.4.2. Figure 1.4.2 shows the spectra taken from the commercial TiN nanocubes. One can see a well expressed peak at 700nm. A similar peak ~ 700 nm is reproduced by us by simulating TiN nanocube in Figure 1.4.2b (blue curve). By looking at the physical properties of this peak, we concluded that it is a plasmon resonance; indeed, we observed a strong field-enhancement effect at this peak in our simulations, which is an indication of the plasmon resonance effect.

Figure 1.4.2b also shows simulations for Au and ZrN nanocubes. The Au case has been well studied in the literature and is given here for comparison. It is known that Au NPs are strongly plasmonic with a strong plasmonic resonance. In comparison to the Au NP, the TiN system is less plasmonic and has a weaker and broader resonance. Interestingly, the ZrN nanocubes exhibit in theory a strong resonance comparable to the gold case. This case is of interest for potential applications, since ZrN is cheap and widely used in technology.

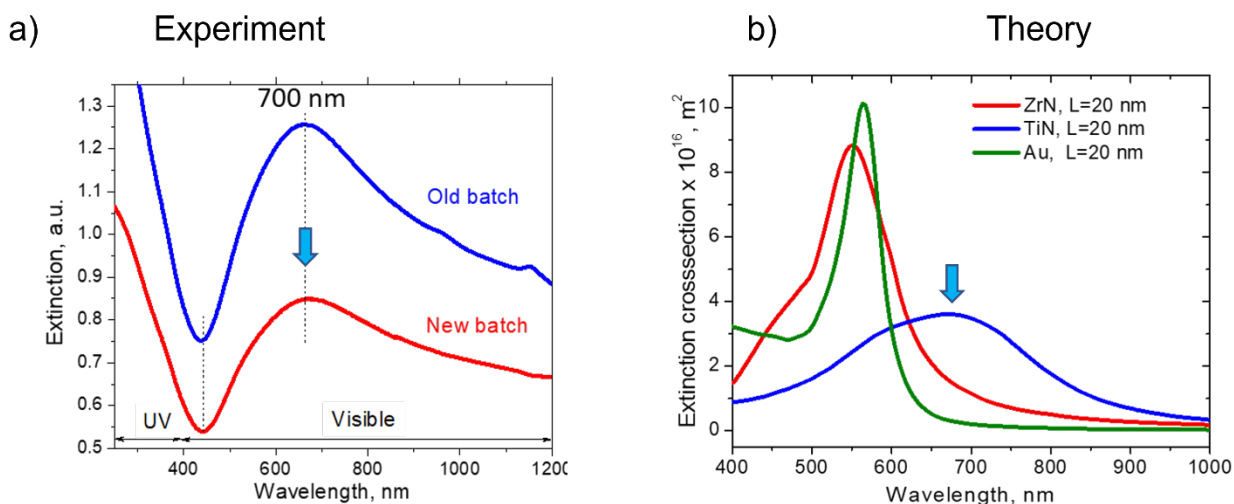


Figure 1.4.2: (a) Experimental UV-Vis spectrum of TiN (PlasmaChem) nanoparticles suspended in H₂O (b). Simulated extinctions for 20 nm ZrN, TiN and Au nanocubes.

We also should look at the structure of the extinction coefficients. Since our NPs are relatively small, the absorption effect should dominate. Indeed, we see such a behavior in our calculations shown in Figure 1.4.2 for TiN and ZrN. For a 30 nm TiN NP, the scattering cross section is barely seen on Figure 1.4.2. For a 50 nm ZrN, the scattering effect starts to play a role. Considering the use of these NPs for surface photocatalysis, we should avoid strong scattering since this effect does not lead to generation of excited carriers. To summarize, the above results on the optical properties of the NPs should be helpful for the project aiming at the realization of a chemical gas-phase sensing.

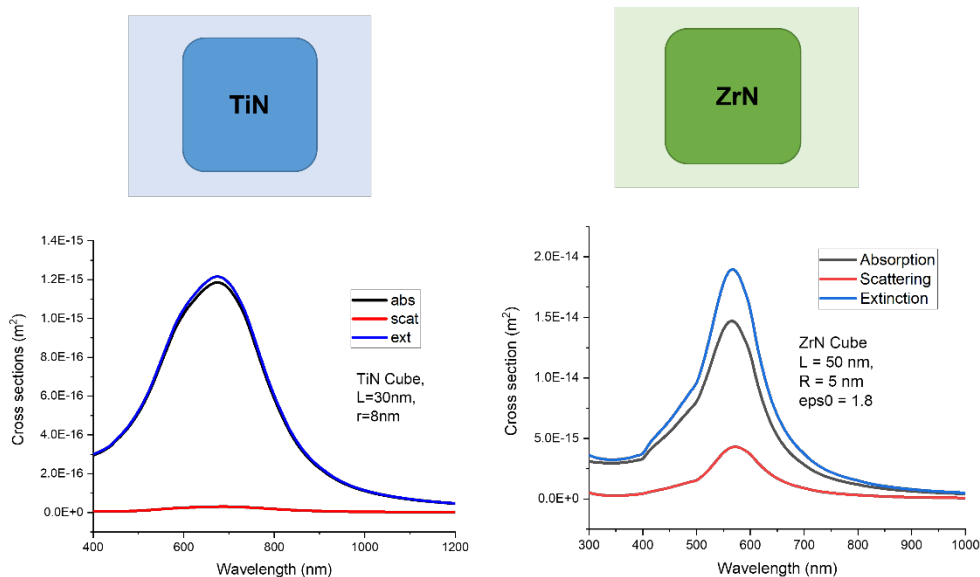


Figure 1.4.2: Structure of the extinction coefficient, including absorption and scattering. Two cases are shown: a 30 nm TiN cube and a 50 nm ZrN cubic NP

We start with the TiN system and increase the thickness of the Au shell, keeping the TiN size constant (20 nm). Figure 1.4.3 shows computational results for 0, 5, 10, and 20 nm shells. We observe that more plasmonic gold dominates the optical response as the thickness increases. Simultaneously, we see the appearance of strong scattering; for the 20 nm shell, the scattering signals become compatible with the absorption. Overall, the Au shells strongly enhance all the optical responses due to the plasmonic antenna effect.

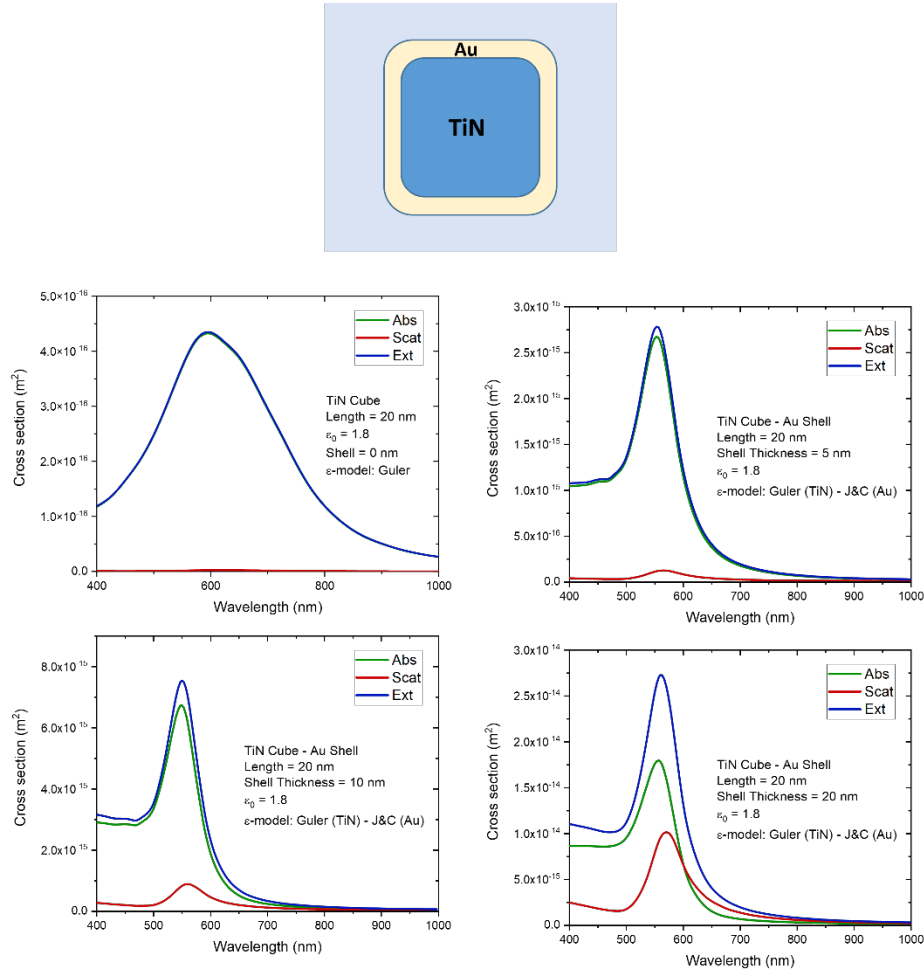


Figure 1.4.3: Structure of the optical extinction coefficient of the TiN-Au hybrid, including absorption and scattering. The TiN NP size is 20 nm, and the Au shells are 0, 5, 10, and 20 nm. The dielectric functions are by Guler at al. (TiN) and by J&C (Au).

In the next step, we look at the structure of absorption inside the hybrids. Figure 1.4.4 shows the computations. Since gold is a more absorbing and plasmonic material, the Au shell's energy dissipation rapidly grows with its thickness. Already for the 5 nm shell, the dissipations in the core TiN NP and the Au shell become almost equal. For the 20 nm shell, the Au component dominates the absorption, and the optical energy dissipates mainly in the gold. Since the Au-plasmon resonance becomes more and more dominating with increasing Au shell, the collective plasmon peak on the hybrid narrows significantly, as one can see in Figures 1.4.3 and 1.4.4.

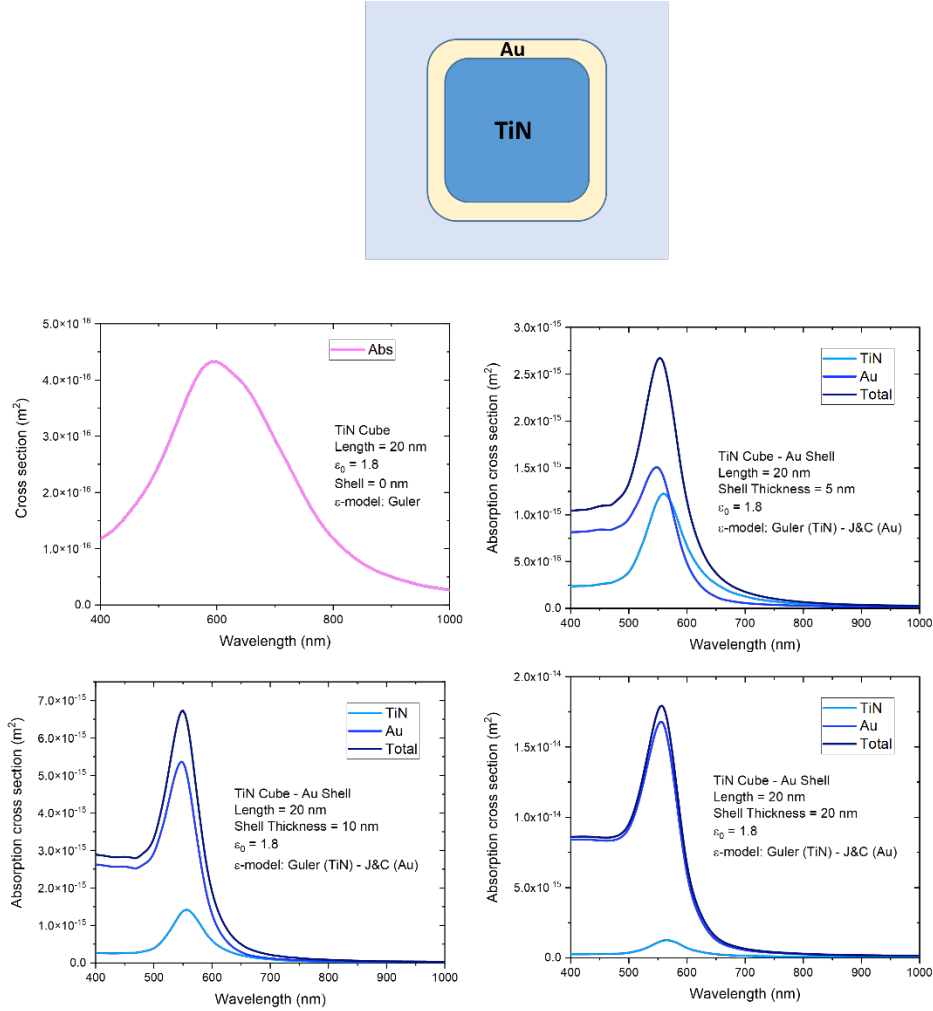


Figure 1.4.4: Contributions of the TiN and Au components to the total dissipation cross-section inside the TiN-Au hybrid. The matrix is water. The TiN core size is 20 nm, and the Au shells are 0, 5, 10, and 20 nm.

Before making general conclusions on the optical and absorbing properties of the core-shell hybrids, we look at the data for the ZrN-Au pair (Figure 1.4.5). First, ZrN, in theory, is more plasmonic than TiN, and the plasmon peak is narrower than the TiN case. Overall, we observe similar effects here compared to the TiN-Au system. The Au shell strongly amplifies all optical processes and leads to the narrowing of the plasmon peak.

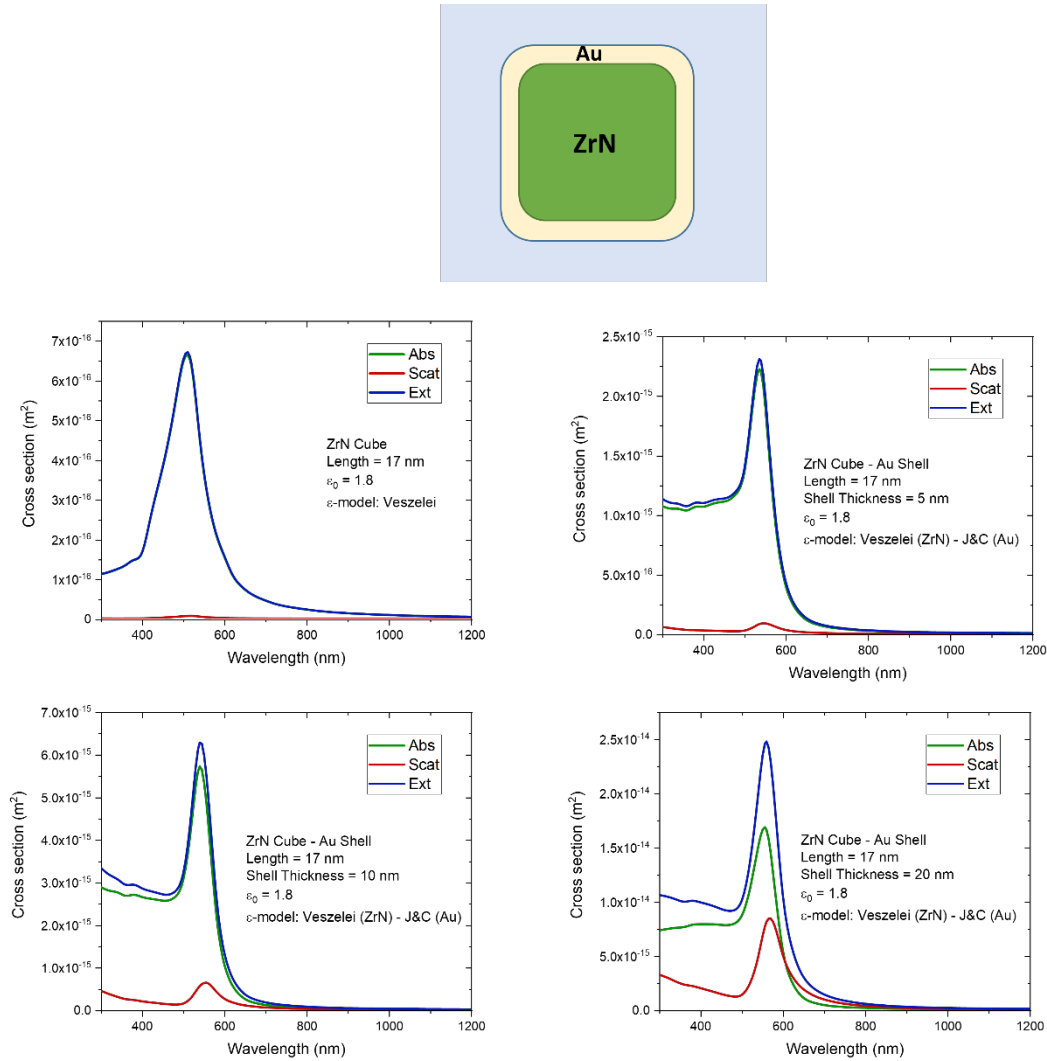


Figure 1.4.2: Structure of the optical extinction coefficient of the ZrN-Au hybrid, including absorption and scattering. The TiN NP size is 20 nm, and the Au shells are 0, 5, 10, and 20 nm. The dielectric functions are by Veszelei et al. (ZrN) and by J&C (Au).

We now conclude on the synergetic interactions in the TiN/ZrN-Au hybrids - we observe the following behaviors in the core-shell TiN-Au and ZrN-Au nanocubes.

- 1) Since our hybrid is composed of two plasmonic materials and gold is much more optically active, the gold properties start to dominate rapidly with increasing the shell.
- 2) The Au shell strongly amplifies optical responses, including the absorption signal, due to the optical antenna effect.
- 3) Larger Au shells lead to strong scattering that is not preferable for photochemistry. The scattering leads to loss of optical energy, whereas the absorption converts optical energy into heat and energetic electrons. Therefore, smaller shells are preferable for photochemical efficiency.
- 4) The core-shell TiN-Au and ZrN-Au nanocubes behave in similar ways.

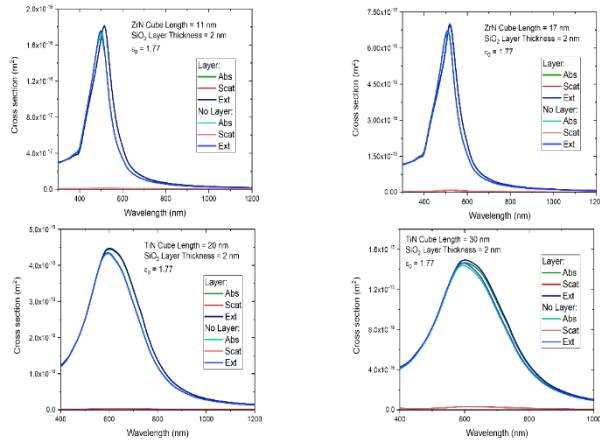
5) Certainly, thin Au shells can work as optical and photochemical amplifiers due to their plasmonic antenna effect. Simultaneously, the TiN and ZrN cores can work as supports and additional absorbers made of inexpensive materials.

Simple two-component hybrids with an oxide layer (TiN/ZrN/SiO₂) and their MEC parameters

Figure 1.4.6 shows the data for the simple hybrid TiN/ZrN/SiO₂. Here we observe the typical trends appearing due to the interaction between the plasmonic and dielectric components. We observe typical red shifts for the plasmon resonance. Below we will comment more on this. Such optical shifts are important in the fabrication process showing the chemical formation of eth oxide layers.

The mass extinction coefficients (MECs) are defined as the extinction cross section normalized to the mass of NP. Such figures of merit are used a lot in the photocatalysis technologies and also in the field of obscuration (smoke generators and grenades, US Army, AF, and Navy). Figure 1.4.6 shows the MECs data for the simple hybrids. These hybrids demonstrate overall excellent figures of merit as compared to many other materials, due to their high optical-absorption rates.

The effect of the SiO₂ shell



MECs for TiN vs ZrN

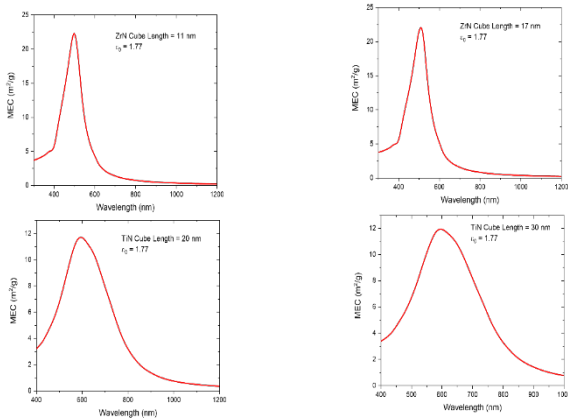


Figure 1.4.6: We show here the effect of the thin SiO₂ shell on the TiN and ZrN plasmons (upper). The lower panel presents the compares for the mass extinction coefficients (MECs) for TiN and ZrN. ZrN is more plasmonic and deficient at the plasmon resonance.

Hybrids for plasmonic photocatalysis TiN/ZrN- SiO₂-Pt/Pd – optical effects and MECs

In this step, by closely interacting with the groups at the NRL and the DEVCOM Army Research Laboratory, we continue with the computational study of hybrid nanocrystals, which should incorporate plasmonic, catalytic, and dielectric layers. The idea is to achieve synergetic optical catalytic properties using both inexpensive and experience elements and materials, including Au, Ag, TiN, ZrN, Pt, Pd, and O (Figure 1.4.7). Since the experimental realization of TiN-Au and ZrN-Au appeared to be challenging, we focus now on the hybrids TiN- SiO₂-Pt/Pd. These hybrids (TiN/ZrN- SiO₂-Pt/Pd) look feasible for the colloidal synthesis fabrication in the group of Dr. Jonathan Boltersdorf (DEVCOM Army Research Laboratory). Therefore, using COMSOL, we carry out modeling the relevant hybrid nanostructures (plasmonic nanocubes) composed of two or three components (Figure 1.4.8). In our studies, the bulk dielectric functions are taken from empirical tables, and the dimensions correspond to the fabrication capabilities based on colloidal wet chemistry. The corners and apexes are rounded as in typical experimental NPs.

PERIODIC TABLE OF ELEMENTS

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

Figure 1.4.7: The elements of Periodic Table used in our hybrids.

The following Figures 1.4.9 and 1.4.10 provide us with a set of data for the triple-component hybrids. Here, we are plotting both optical cross-sections and MECs.

COMSOL models

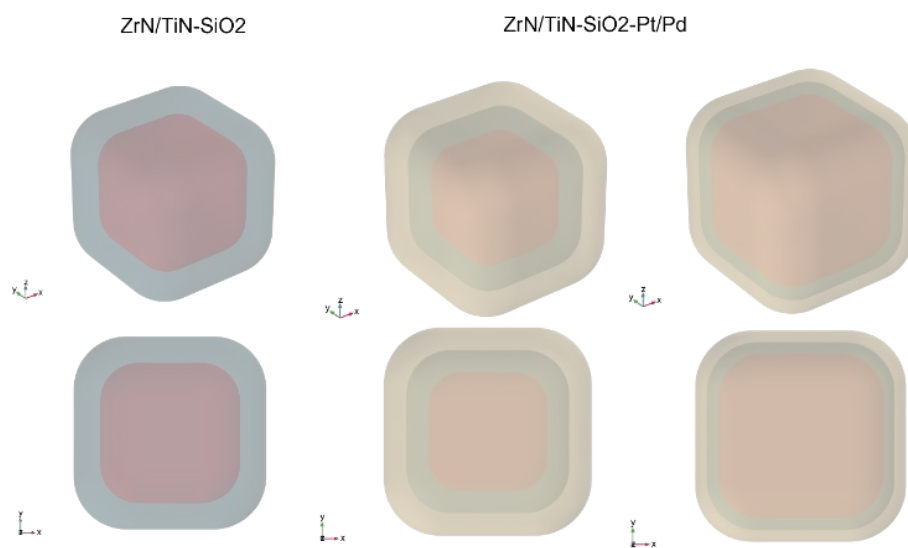


Figure 1.4.8: COMSOL models for the TiN/ZnN nanocubes with one and two shells.

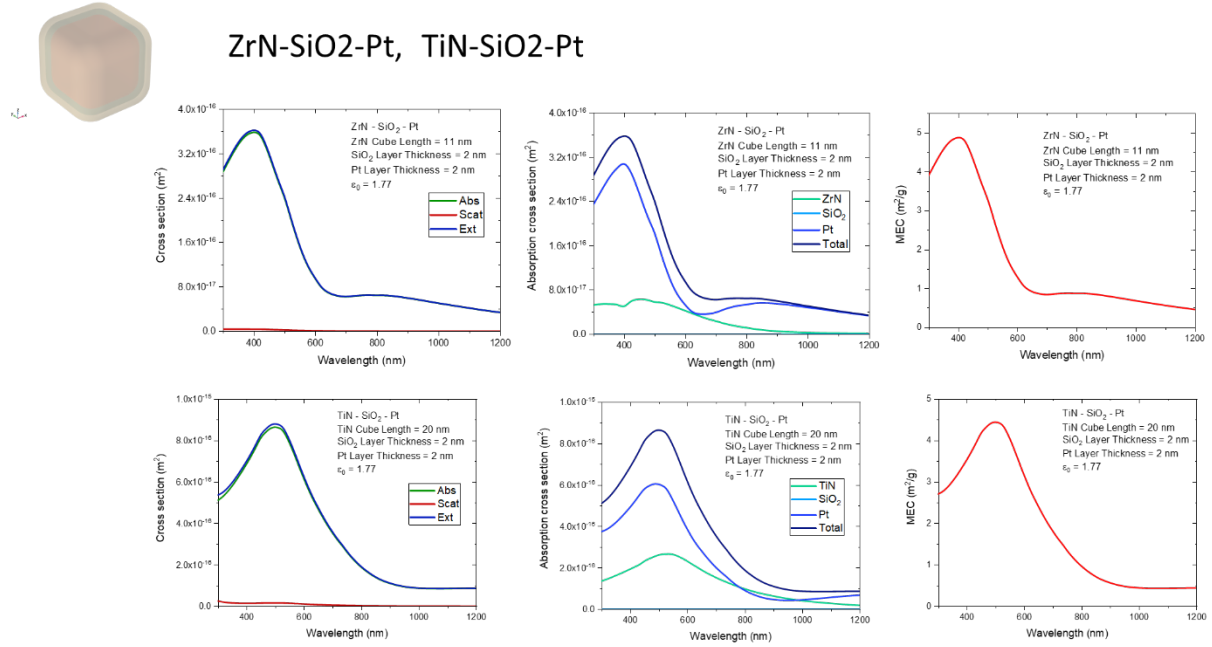


Figure 1.4.9: The set of optical spectra for the three-component hybrids, TiN/ZrN-SiO₂-Pt.

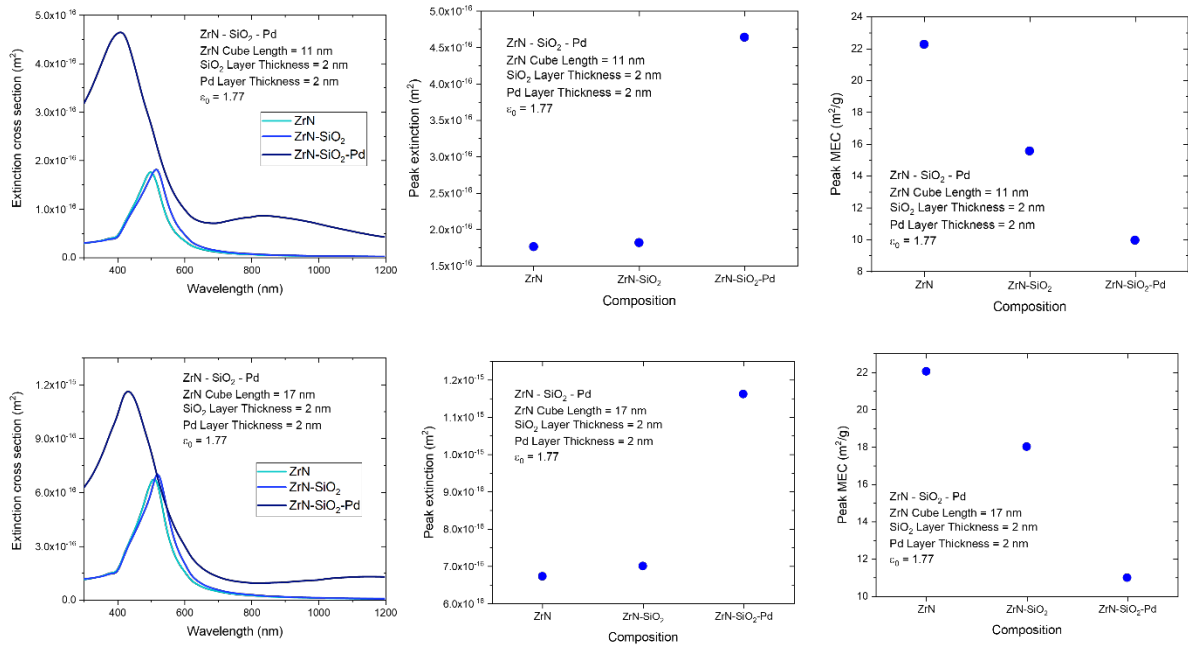


Figure 1.4.10: Analysis of the optical and opto-material properties of for the three-component hybrids, TiN/ZrN-SiO₂-Pt/Pd.

From all the above data, we can make the following conclusions applied to these topics (Hybrids of TiN/ZrN/SiO₂ and TiN/ZrN- SiO₂-Pt/Pd) that can guide and help the experiments.

Conclusions for the TiN/ZrN-SiO₂ and TiN/ZrN-SiO₂-Pt/Pd:

- 1) Characteristic red shifts for the plasmon resonance in TiN/ZrN-SiO₂. Can be useful as optical detection of the oxide-growth process in the fabrication process.
- 2) Our hybrid is composed of two metallic materials (TiN/ZrN and Pt/Pd), which interact optically. However, the plasmonic metal (TiN/ZrN) dominates the optical response, while the photocatalytic metal (Pt/Pd) is less optically active.
- 3) We observe the effect of damping of the TiN/ZrN plasmons due to the Pt/Pd shells. This is because Pt and Pd are very resistive.
- 4) Overall, the TiN/ZrN-based cubes strongly amplify optical responses, including the absorption and electromagnetic signals, due to the optical antenna effect.
- 5) TiN demonstrates lower plasmonic amplification coefficients than ZrN.
- 6) Certainly, the TiN/ZrN cubic cores can be used in photochemistry as optical amplifiers due to their strong plasmonic antenna effect.
- 7) Simultaneously, these TiN and ZrN core cubes work as a support material, which hold expensive photochemical components (Pt- and Pd-shells). Importantly, the above materials (TiN and ZrN) are inexpensive.

TiN/ZrN- SiO₂-Pt/Pd for photocatalysis and hot-electron generation

Here we used the already-developed models of TiN and ZrN hybrids and looked at the rates of generation of hot electrons (HEs). The optical properties for these structures were already reported by us. In this study we will be calculating the HE generation induced by surfaces, i.e., the HE generation via the so-called Kreibig mechanism. This mechanism governs the generation of high-energy carries in small NCs. The equation to use is the following:

$$Rate_{HE} = \frac{1}{4} \frac{2}{\pi^2} \frac{e^2 E_F^2}{\hbar} \frac{1}{(\hbar\omega)^3} \int_S \frac{|E_{\omega,normal}|^2}{E_0^2} ds \cdot \frac{2I_0}{c_0 \epsilon_0 \epsilon_{med}^{1/2}},$$

where the integral is taken over all surfaces, $E_{\omega,normal}$ is the electric field normal to the surface, E_F is the Fermi energy of the metal, I_0 – light intensity.

We start from the simplest hybrids: TiN-SiO₂ and ZrN-SiO₂. In Figures 4,5, we plot the rates and the HE efficiencies, $Eff_{HE} = Rate_{HE}/Rate_{photons}$, where $Rate_{photons}$ is the photon-absorption rate by a NC. For the high-energy over-barrier electrons ($Eff_{high-energy}$), we need to multiply the rate by the coefficient $\frac{(\hbar\omega - \Delta E_b)}{(\hbar\omega)}$. Then, Figures 1.4.11 and 1.4.12 show the results for the simple hybrids TiN/ZrN-SiO₂. Whereas the following figures (Figures 1.4.13 and 1.4.14) give the data for more complex, triple-material hybrids, TiN/ZrN-SiO₂-Pt/Pd.

Conclusions and messages from the hot-e calculations of the hybrids:

- 1) Both TiN and ZrN-based NPs demonstrate the resonant plasmonic generation of HEs.
- 2) ZrN-based NCs are “plasmonic” than the TiN ones.
- 3) The HE production efficiencies grow in the visible and red intervals due to the amplification of the plasmonic effects in these spectral intervals.
- 4) Pt/Pb shells create the damping of the plasmon resonances of the TiN/ZrN components.

- 5) The hybrids TiN/ZrN-Pt/Pb have two sources of generation of HEs: the Pt/Pb-water interface and TiN/ZrN-SiO₂ interface. The first one (i.e., Pt/Pb-water interface) is more important for our application since it provides HEs for the surface catalysis.
- 6) Overall, the triple-material hybrids – a plasmonic core (TiN/ZrN) --- a catalytic metal - (Pt/Pd) deserve further investigations and show interesting photophysical behaviors as HE generators.
- 7) The roles of the SiO₂ shell – (a) a red shift of plasmon, (b) an electronic barrier between TiN/ZrN and the photocatalytic metal (Pt/Pb), and (c) the protecting layer for TiN/ZrN.

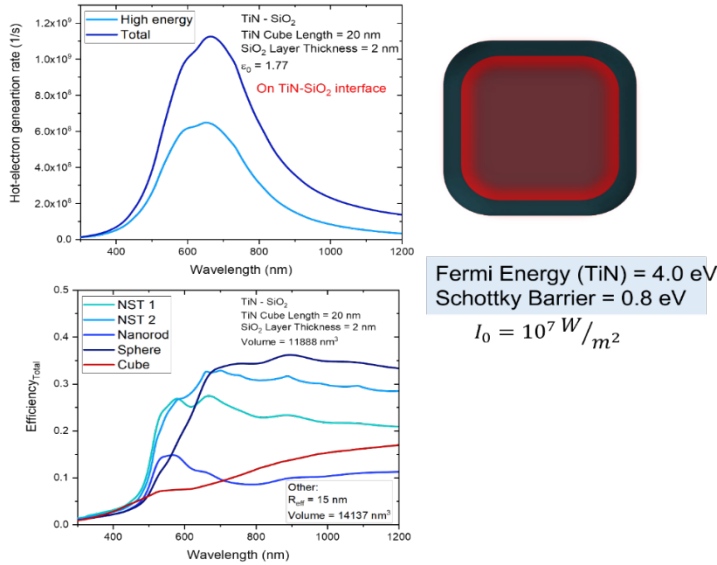


Figure 1.4.11: HE generation by the simple TiN-SiO₂ hybrid.

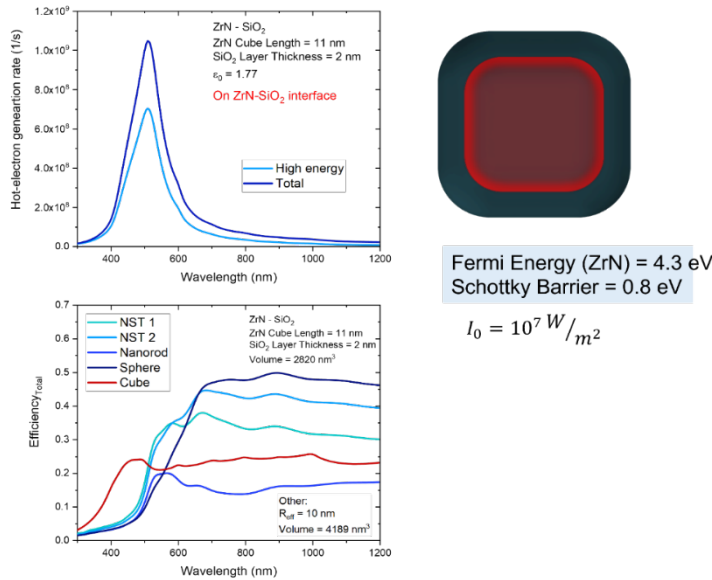


Figure 1.4.12: HE generation by the simple ZrN-SiO₂ hybrid.

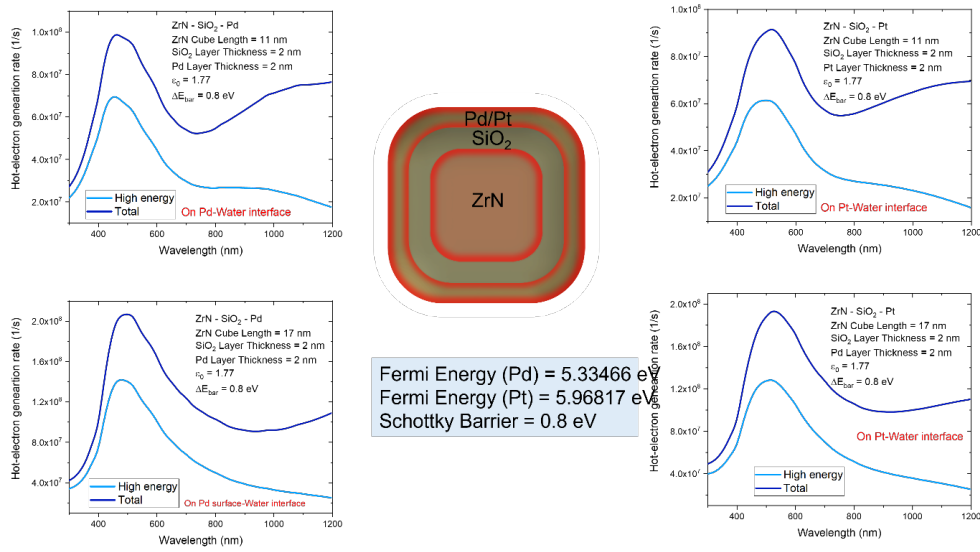


Figure 1.4.13: HE generation by the triple-material hybrids, TiN-SiO₂-Pt/Pb.

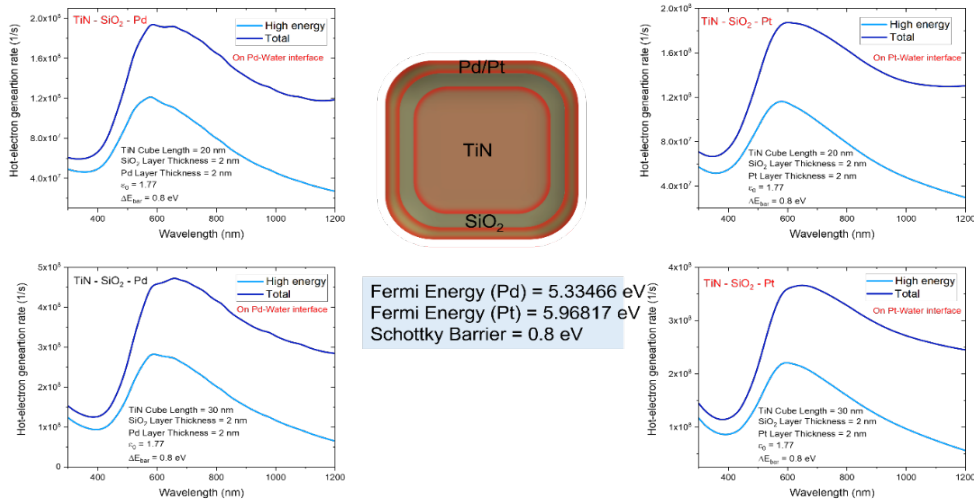


Figure 1.4.14: HE generation by the triple-material hybrids, ZrN-SiO₂-Pt/Pb.

TiN/ZrN- SiO₂-Pt/Pd – Analysis of the efficiency of hot-electron (HE) generation. The role of photothermal heat generation

In this section, we summarize and compare the photophysical properties of our hybrids without and with Pt/Pb shells. Figure 1.4.15 shows the case of TiN-SiO₂-Pt hybrid, and, for TiN-SiO₂-Pd, we observed similar spectra and properties. Overall, according to our calculations, the hybrids of interest demonstrate promising optical and material properties.

Conclusions and observations for the HE-efficiency parameters:

1. Plasmonic metal (TiN/ZrN) is an efficient resonator, while the photocatalytic metal (Pt/Pd) is more like a damper.
2. We observe the effect of damping of the TiN/ZrN plasmons due to the Pt/Pd shells. This is because Pt and Pd are very resistive.
3. Overall, the TiN/ZrN cubes strongly amplify optical responses, including the absorption and electromagnetic signals, due to the optical antenna effect.
4. Material efficiency (MEC) gets reduced in the presence of the Pt/Pb shells.
5. TiN and ZrN behave in similar ways. ZrN is more plasmonic in general.

Optical and Material Efficiencies of TiN/ZrN-SiO₂-Pt

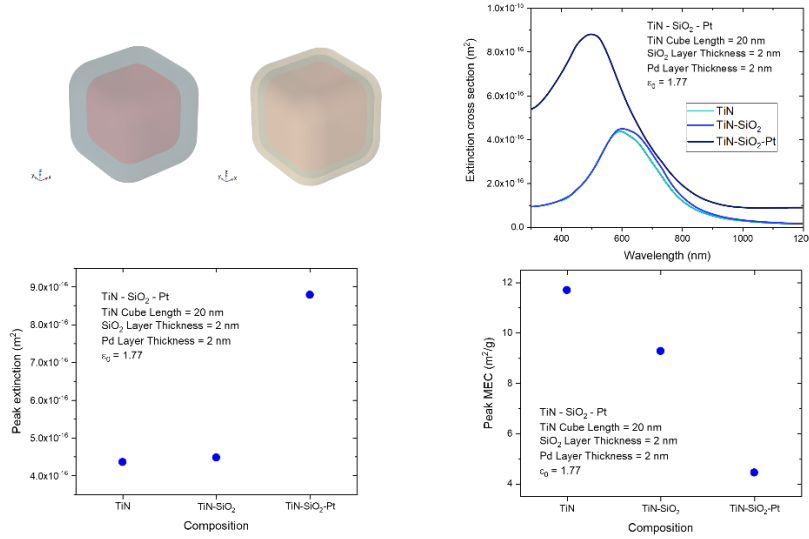


Figure 1.4.15: Summary of optical efficiencies for the TiN, TiN-SiO₂, and TiN-SiO₂-Pt hybrids.

Considering the photochemical properties, we need to look at how and where the production of hot electrons in our hybrids takes place (Figure 1.4.16). Hot-electron generation is very efficient at the surfaces where the linear-momentum conservation law is broken. Therefore, having more surfaces (or irregularities) in a plasmon NP is more preferable. For example, the ZrN-SiO₂-Pt hybrid in Figure 1.4.16 has three surfaces and we should sum up all three contributions. Simultaneously, we observed the other plasmonic near-field effect. We see that the Pt-shell suppresses the total hot-electron generation rate at the plasmon peak since the plasmon decay is stronger, and the electric field inside the hybrid structure is reduced. However, the Pt/Pd shells should be able to enhance the photochemistry because the nature of interaction between an adsorbate (CWA molecules) and the d-band of Pt/Pd. So, there are also other important photoreactive properties of the outer NP surface interacting with a CWA molecule, which should be tested/destroyed. Again, a well-known advantage of plasmonic NPs is that they (Au/Ag or TiN/ZrN) can strongly amplify electromagnetic fields via the plasmonic nano-antenna effect.

Hot-electron generation by ZrN-hybrids

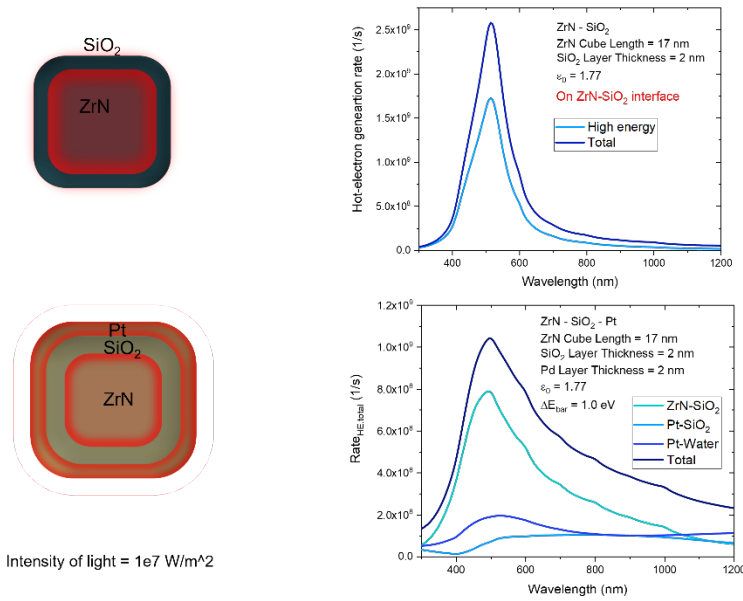


Figure 1.4.16: Computational data for the hot-electron generation at various surfaces in the ZrN-SiO₂ and ZrN-SiO₂-Pt hybrids.

Next, we computed the phototemperature mechanism (i.e., the photo-T generation) in the core-shell hybrids. Figure 1.4.17 shows some exemplary results for the ZrN-based nanocrystals. We are in the process of summarizing the data since the problem is a multiparametric one. Our findings are summarized below - please see Figure 1.4.17.

Along with the above-mentioned tasks, my group designed models of nanocrystals covered by Pt- and Pd-clusters on the surface of the TiO₂-TiN hybrids. The Army Lab (Dr. Jonathan Boltersdorf, Ph.D. Research Chemist, Energy Conversion Branch DEVCOM Army Research Laboratory) is working on the fabrication of such hybrid structures. Figure 1.4.18 shows the geometry we are thinking of and the first T-calculation for Pt-TiN hybrid. Overall, we observed in our COMSOL simulations that the effect of Pt-clusters is not very strong for the T-generation since the Pt clusters have a small total volume; however, these Pt-clusters can influence experimental spectra in the lab in terms of the plasmon-peak shift, plasmon-peak broadening, and photochemical efficiencies.

Conclusions and observations for the T-generation in the hybrids:

1. ZrN-hybrids are more efficient at the T-generation at the plasmon peak.
2. Pt-shells will increase the T-generation since it is a dissipative material; note that hot-e generation can be reduced due to the Pt-shell.
3. Overall, ZrN and TiN hybrids are dissipative and therefore are certainly efficient at T-generation.
4. The dependence on the material system and on the design for the phototemperature effect is complex and involves a multiparametric space. Once experimental samples are fabricated, we are ready to do special calculations for given designs. Our COMSOL models are ready for any needed computation.

Phototemperature in the TiN/ZrN hybrids

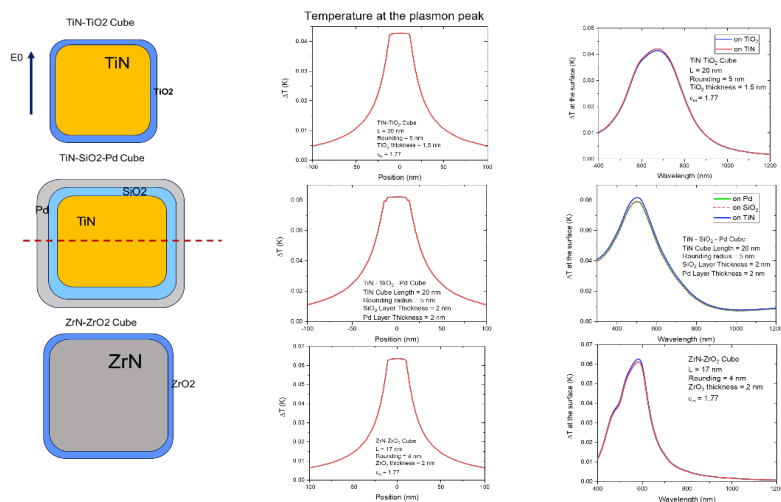


Figure 1.4.17: Computational data for the phototemperature in the TiN/ZrN hybrids. Here we show both spatial profiles and the spectra of the phototemperature at the surface.

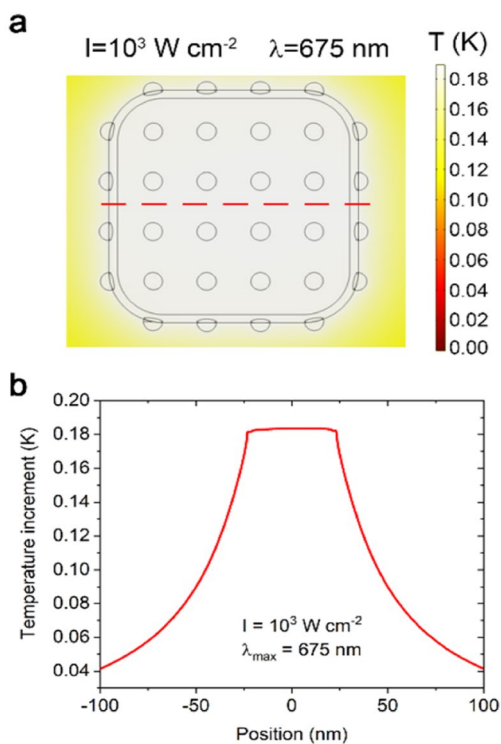


Figure 1.4.18: (a) COMSOL model of an TiO₂-TiN nanocube covered with Pt clusters in water. (b) The phototemperature generation inside and near the TiN-Pt hybrid.

Task 2. Testing and evaluation of photocatalytic activity of the synthesized supported nanoparticles towards CWAs stimulants decomposition

(NRL: Spencer Giles, Jeffrey Lundin; ASEE Post doc at NRL: Ashley Fulton)

Synthesized supported nanoparticles were subjected to photocatalytic activity assays to determine the decontamination activity and viability of the synthesized catalysts.

Subtask 2.1. Evaluation of photocatalytic activities of open-frame TiO_2 and doped open-frame TiO_2

The photocatalytic activity of the neat TiO_2 materials in Table 6 for the decomposition of 2-CEES were evaluated using dose extraction protocol described in the Experimental section. Materials denoted as “JAB...” and “ TiO_2 -1, ..., TiO_2 -5”, were synthesized by Jonathan Boltersdorf (ARL) and Alexey Serov (Oakridge National Lab), respectively, after Pajarito’s departure from the program, in an attempt to reproduce synthesis of TiO_2 and Sm-doped TiO_2 by a sacrificial support method. Although the results of XRD and BET characterizations were in agreement with the Pajarito’s analysis, photocatalytic properties of the newly synthesized materials appeared to be less impressive.

Table 6. List of TiO_2 -based materials evaluated for photocatalytic activity towards 2-CEES decomposition under visible light excitation

Sample Name	Sample Info
NRL 1-A	5 nm $\text{TiO}_2/\text{SiO}_2$
NRL-5	5 nm $\text{TiO}_2/\text{SiO}_2$
NRL-3	TiO_2 , open-frame
NRL-4	TiO_2 , open-frame, amorphous
NRL-6A	TiO_2 , open-frame
NRL-6B	TiO_2 , open-frame
NRL-15	TiO_2 , open-frame (synthesis with alternative sacrificial support)
NRL-16F	TiO_2 , open-frame (Calcined at 800 °C, annealed at 1100 °C)
NRL-19	Sm-doped TiO_2 , open-frame
NRL-19A	Sm- TiO_2 (Annealed at 1100 °C), open-frame
NRL-21D	NH_3 -treated TiO_2 , open-frame
NRL-46	TiO_2 (2 nd batch of NRL-3), open-frame
Degussa P-25	Commercial TiO_2
P184	p-ALD of Al_2O_3 on TiO_2 (NRL-46)
JAB – TiO_2	Reproduction of Pajarito’s method, ARL
JAB - Sm- TiO_2	Reproduction of Pajarito’s method, ARL
JAB1257A, TiO_2	450°C, 4h, O_2
JAB1257B, Sm- TiO_2	450°C, 4h, O_2
TiO_2 -1	TiO_2 , open-frame, 400°C, air, 143.m ² /g, Oakridge National Lab (ONL)
TiO_2 -2	TiO_2 , open-frame, 425°C, air, 250 m ² /g, ONL
TiO_2 -3	TiO_2 , open-frame, 450°C, air, 175 m ² /g, ONL
TiO_2 -4	TiO_2 , open-frame, 400°C, air, 212 m ² /g, carbon as sacrificial support, ONL
TiO_2 -5	TiO_2 , open-frame, 425°C, air, 162 m ² /g, carbon as sacrificial support, ONL

5 nm $\text{TiO}_2/\text{SiO}_2$ (NRL 1-A and NRL-5, different batches of the same material) served as a reference material. Previously [1], we demonstrated that this material is active towards 2-CEES photocatalytic oxidation mostly to sulfoxide under visible light excitation. In the beginning of the program, Pajarito

attempted to reproduce the synthesis described in the paper. Proposed in the paper reaction route consisted of photooxidation and hydrolysis pathways, as shown in Figure 2.1.1.

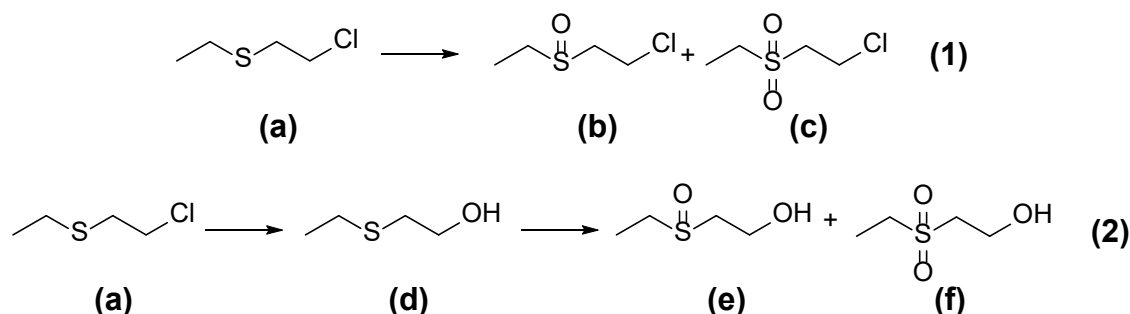


Figure 2.1.1. Potential reaction routes for the decontamination of 2-CEES (**a**). Oxidation of 2-CEES (**a**) via route 1 results in the formation of the 2-CEES sulfoxide (**b**) and 2-CEES sulfone (**c**). The hydrolysis of 2-CEES (**a**) by route 2 results in the formation of 2-(ethylthio)-ethanol (**d**) followed by oxidation to 2-(ethylsulfinyl)-1-ethanol (**e**) and 2-(ethylsulfonyl)ethanol (**f**).

Comparative analysis for NRL 1A and NRL 5 after 24-hour challenges are shown in Figure 2. Both materials are 5 nm TiO₂ nanoparticle supported on *ca* 400 nm SiO₂ Stöber spheres (two batches of the same material). The chromatographic analysis of both materials reveal that under visible light excitation the TiO₂/SiO₂ materials promote the oxidation of 2-CEES (product **a** in Figure 2.1.1) to form sulfoxide (product **b**) as the major product. NRL 1A additionally forms small amounts of the double oxidation product, sulfone (product **c**). When these samples are kept in the dark oxidation is not observed however, minimal amounts of the hydrolysis product, 2-(ethylthio)-ethanol (product **d**) is observed. The results indicate that 2-CEES still remain on the surface after 24-h exposure to visible light.

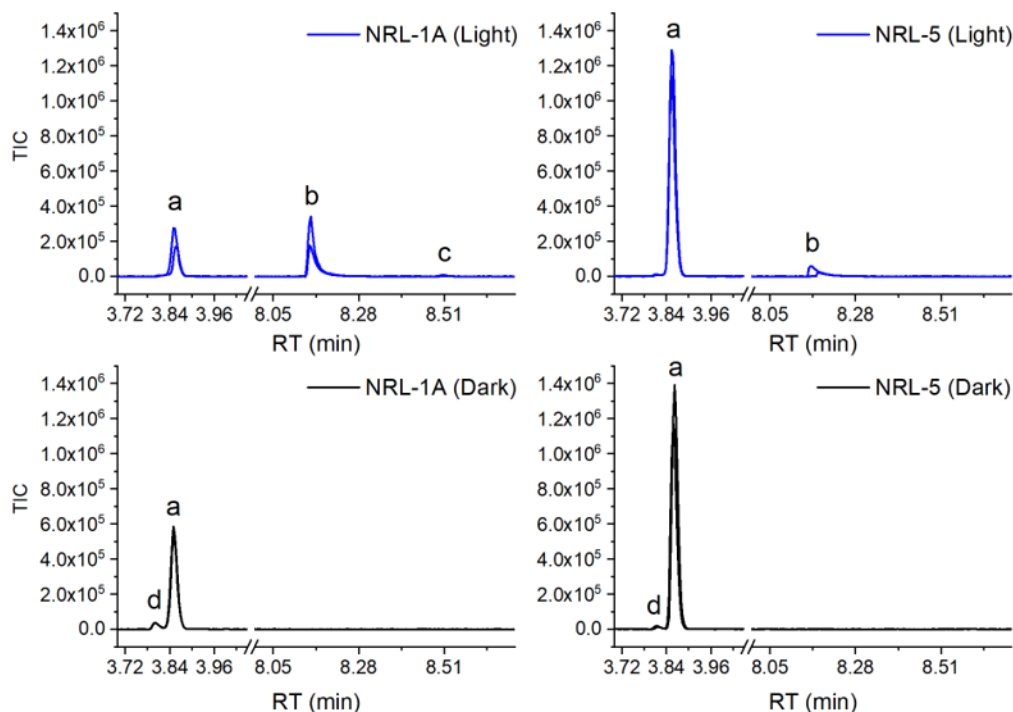


Figure 2.1.2. Gas chromatograph comparison of NRL 1A (left column) and NRL 5 (right column). Comparative performance for the samples under visible light exposure (top row) and when kept in the dark (bottom row). NRL 1A sample

masses range was 7.1 to 7.6 mg and NRL 5 masses range was 4.9 to 6.1 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μL of 2-CEES stock solution containing 19.25 μL of 2-CEES in 2 mL of methylene chloride

Analysis of the open-frame TiO_2 samples, which have much higher surface area in comparison to 5 nm $\text{TiO}_2/\text{SiO}_2$ (220-250 vs 30 m^2/g), but the same (*ca* 5 nm) TiO_2 crystallite size, was performed in the same manner as that of the $\text{TiO}_2/\text{SiO}_2$ samples. Gas chromatographic analysis of NRL 3 is shown in Figure 2.1.3. The result show that 2-CEES signal is not observed for both the samples exposed to visible light and those that were kept in the dark after 24 h challenge, implying that this material is much more active in comparison to 5 nm $\text{TiO}_2/\text{SiO}_2$. The samples of NRL 3 that were kept in the dark displayed a prominent amount of the hydrolysis product 2-(ethylthio)-ethanol (product **d**) with no additional products observed. In comparison, the samples that were exposed to visible light did not show formation hydrolysis product (2-(ethylthio)-ethanol), but instead multiple peaks at longer retention times were observed. Mass spectrum analysis of these peaks indicate the presence of photooxidation products such as sulfone as well as oxidation product of 2-(ethylthio)-ethanol to give the sulfone product ($\ddagger$) and oxidation of the hydrolysis product 1,2 bis(ethylthio)ethane resulting in the peak at retention time 13.095 minutes (+). Surprisingly, no sulfoxide (the desired product) was detected. We hypothesized that the residual KOH on the surface of the catalyst promoted hydrolysis of 2-CEES.

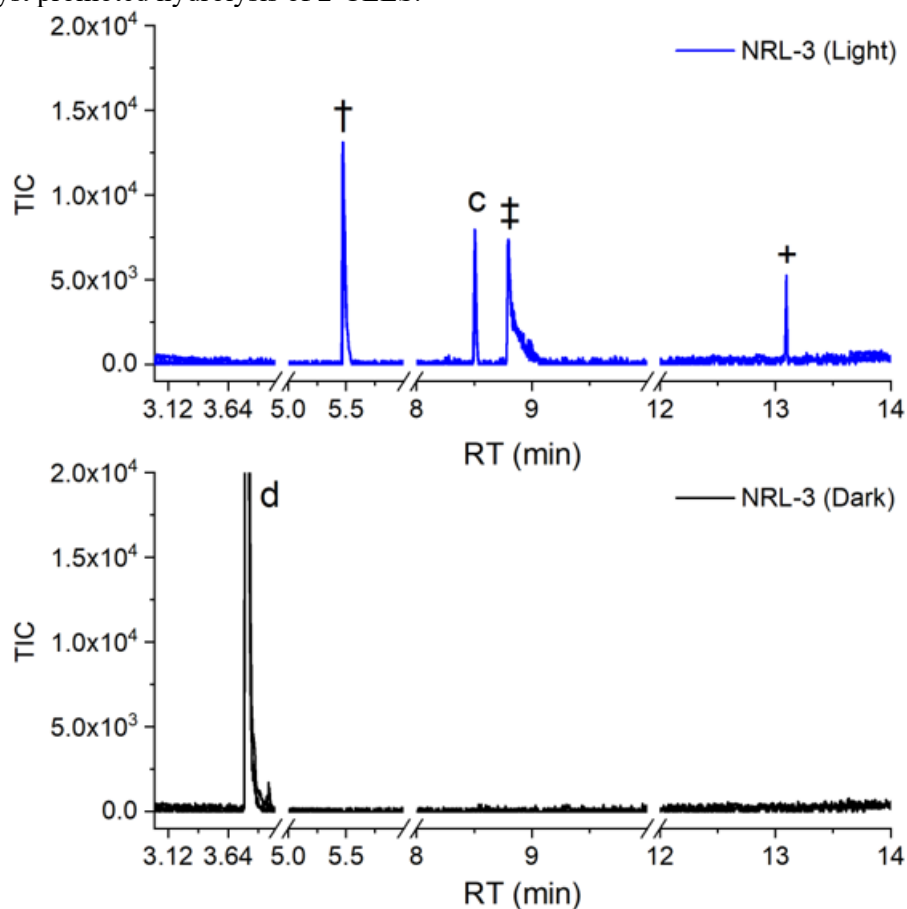


Figure 2.1.3. Gas chromatograph analysis of NRL 3. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). NRL 3 sample masses range was 7.1 to 7.6 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μL of 2-CEES stock solution containing 19.25 μL of 2-CEES in 2 mL of methylene chloride.

To compare photocatalytic activity of Pajarito's open-frame TiO_2 (NRL-3) with commercial P25 TiO_2 (Degussa, 80% anatase+20% rutile, *ca* 50 m^2/g surface area), we performed 24h challenge, following

the same protocol as for Pajarito's materials. The results from the 24 hour challenge of the neat commercial TiO₂ support are shown in Figure 4. Minimal reactivity of the commercial TiO₂ is observed with the main route for reaction with 2-CEES being hydrolysis to form minor amounts of 2-(ethylthio)-ethanol (d) and 1,2 bis(ethylthio)ethane (*). The commercial TiO₂ reactivity results in minimal reduction to the overall 2-CEES signal and very limited photooxidation observed (Figure 2.1.4, top).

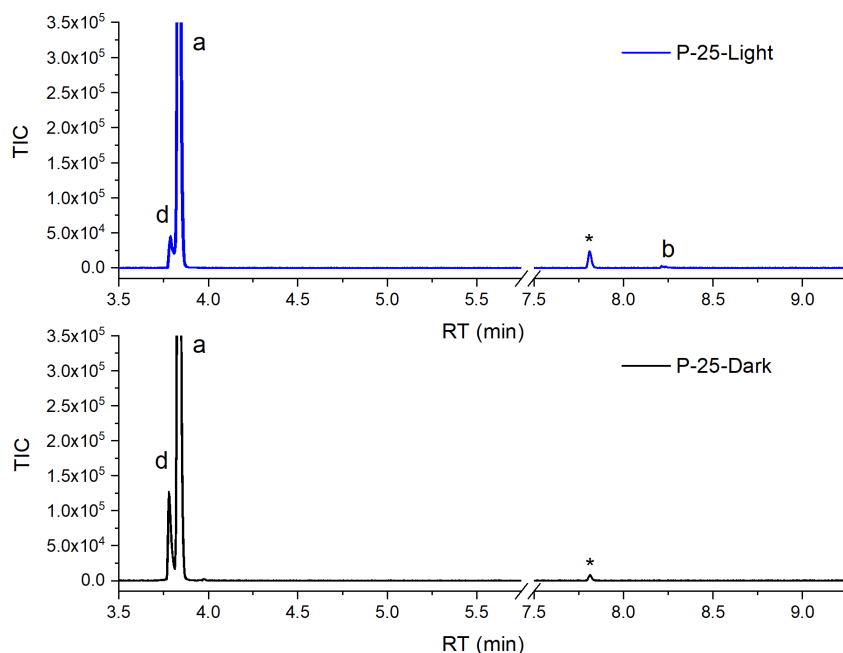


Figure 2.1.4. Gas chromatograph analysis of commercial TiO₂ (Degussa P-25). Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). Commercial TiO₂ (Degussa P-25) sample masses range was 7.0 to 7.6 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of methylene chloride.

Decontamination analysis of NRL-3 (Figure 2.1.3) showed the complete removal of 2-CEES via a photooxidation pathway. This prompted the assessment of NRL-3 via time trials to determine how rapidly 2-CEES is photo oxidized on the surface of the NRL-3 catalyst. Time trial experiments were conducted with duplicate samples following the same deposition and extraction procedure as the 24 hour preliminary assessment but extractions were performed after 1, 2, 3 and 4 hour visible light exposure intervals. Figure 2.1.5 shows the chromatographic results from each duplicate challenge for NRL-3 samples at the exposure intervals. The results show that both hydrolysis and oxidation of 2-CEES begins to occur within the first hour of the challenge via the formation of both 2-(ethylthio)-ethanol (d) and 2-CEES sulfoxide (b). As the time intervals increase the amount of observed 2-CEES and the hydrolysis product 2-(ethylthio)-ethanol (d) begin to decrease as the oxidation to sulfoxide (b) and 2-(ethylsulfinyl)-1-ethanol (e) increase. At the longest time interval of 4 hours the majority of 2-CEES has been transformed to oxidation products via both direct 2-CEES photooxidation and photooxidation of 2-(ethylthio)-ethanol (Figure 2.1.5, bottom row). To conclude, 4 hours is sufficient to almost completely convert 2-CEES to photooxidation products. Although the desired reaction product, sulfoxide, is produced in the largest quantities, the process lacks selectivity.

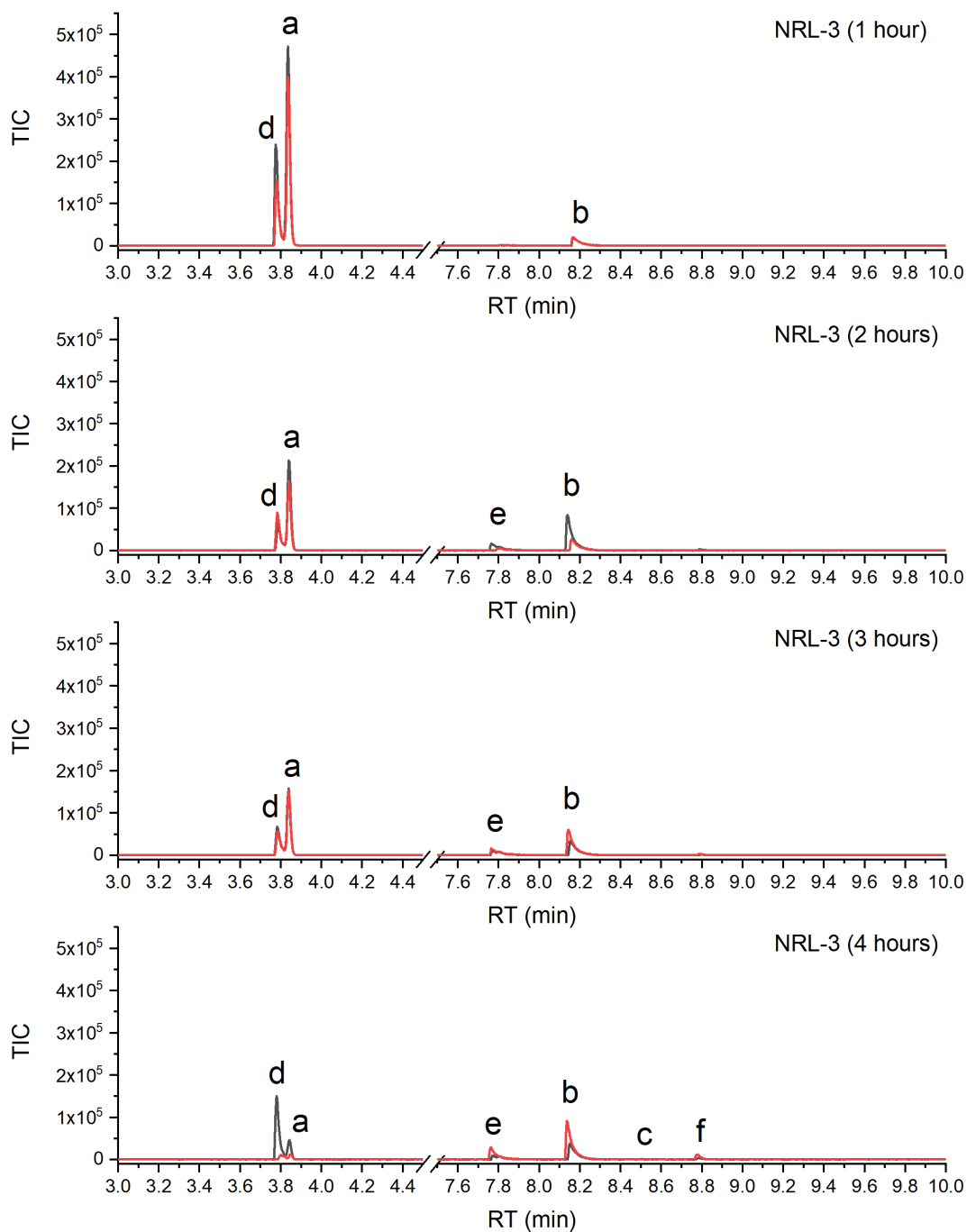


Figure 2.1.5. Gas chromatograph analysis of NRL 3 time trials. Performance for the sample under visible light exposure at time intervals of 1, 2, 3 and 4 hours of visible light exposure. NRL 3 sample masses range was 7.0 to 7.4 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μL of 2-CEES stock solution containing 19.25 μL of 2-CEES in 2 mL of methylene chloride.

A number of other catalysts were synthesized with the aim to promote selectivity and activity of open-frame TiO_2 .

NRL-4 (amorphous TiO₂, 6 m²/g BET surface area) did not demonstrate activity towards 2-CEES decomposition most likely due to low surface area. Chromatographs for 2-CEES challenges are illustrated in Figure S14.

NRL-6A&NRL-6B demonstrated activity towards hydrolysis, which is illustrated by chromatographs, shown in Figure S14.

NRL-15 was synthesized using an alternative support to exclude KOH from etching process. Unexpectedly, no light effect was detected for this material. The corresponding chromatographs are presented in Figure S15.

NRL-16F was calcined at higher temperature than other catalysts (800 vs 450°C), and then annealed at 1100°C to increase the number of defects on the surface. However, almost no effect of visible light was observed for this material, as shown in Figure S16.

Doping was explored as a strategy to promote TiO₂ photocatalytic activity and selectivity towards sulfoxide production. Further testing on TiO₂ support materials was undertaken via analysis of a Sm-doped TiO₂ material. The challenge results in Figure 2.1.6 show that the Sm-doped TiO₂ promotes the oxidation of 2-CEES under visible light excitation. The route for reaction of 2-CEES is a mix of both direct oxidation of 2-CEES with the formation of 2-chloroethyl ethyl sulfoxide (b), sulfone (c), and hydrolysis followed by oxidation resulting in production of 2-(ethylsulfonyl)ethanol (f) (Figure 2.1.6, top). In comparison, the samples held in the dark only promote the hydrolysis of 2-CEES during the 24 hour challenge (Figure 2.1.6, bottom).

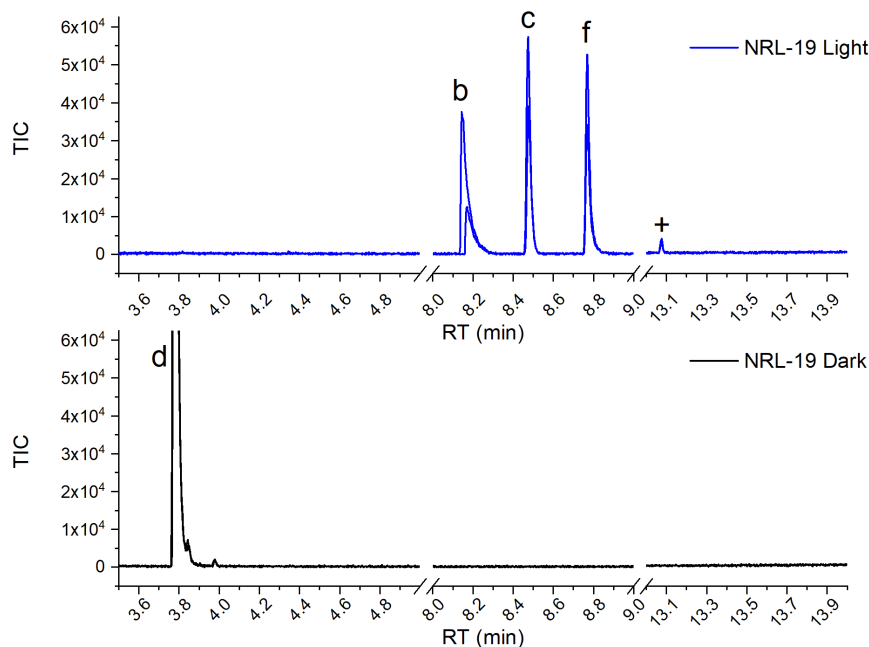


Figure 2.1.6. Gas chromatograph analysis of NRL 19. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). NRL 19 sample masses range was 7.1 to 7.5 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of methylene chloride.

Next, Sm-doped TiO₂ was annealed at 1100°C to increase the number of defects on the surface. However, such a treatment did not lead to an increase in a photocatalytic activity. Figure 2.1.7 shows the reactivity of NRL-19A, which appeared to be much less active than NRL-19. 2-CEES appears to be the prominent product indicating minimal reactivity over a 24-hour period.

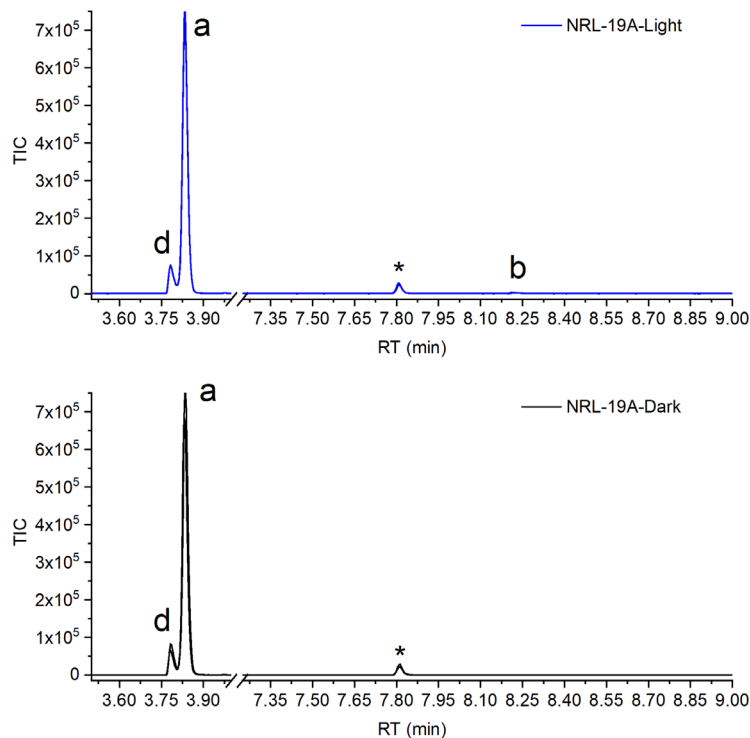


Figure 2.1.7. Gas chromatograph analysis of NRL-19A. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). NRL-19A sample masses range was 7.2 to 7.6 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of methylene chloride.

In addition to the Sm-doped TiO_2 support, an ammonia (NH_3) treated TiO_2 support (NRL-21D) was synthesized with the aim to dope TiO_2 with nitrogen and promote its photocatalytic activity. The challenge results for NRL-21D shown in Figure S17 illustrate that the NH_3 treatment of the TiO_2 does not appear to promote the oxidation of 2-CEES. Hydrolysis of 2-CEES was observed under both visible light excitation and in the dark with the formation of 2-(ethylthio)-ethanol (**d**) and minor formation of 1,2 bis(ethylthio)ethane (*).

NRL-46 is a second batch of open-frame TiO_2 (NRL-3). The result show that remaining 2-CEES (**a**) was not observed for NRL-46 as well as for NRL-3 under both visible light excitation and when kept in the dark (Figure 2.1.8). Both samples that were exposed to visible light did not show formation of hydrolysis product, 2-(ethylthio)-ethanol (**d**), but instead multiple peaks related to oxidation products were observed. Mass spectrum analysis of these peaks indicate the presence of 2-CEES sulfone (**c**) as well as oxidation of 2-(ethylthio)-ethanol (**d**) to give the sulfone product (**f**) for NRL-3, while NRL-46 showed sulfoxide formation with products 2-CEES sulfoxide (**b**) and a minor amount of 2-(ethylsulfinyl)-1-ethanol (**e**) as well. Finally, NRL-3 and NRL-46 both displayed a prominent amount of the hydrolysis product 2-(ethylthio)-ethanol (**d**) with no additional products observed when kept in the dark. Comparison of chromatographs presented in Figure 2.1.6 and 2.1.8 clearly shows that NRL-46 provides selective oxidation to sulfone (product **f**), which is not a desired reaction product, while Sm-doped TiO_2 promotes generation of sulfoxide as well.

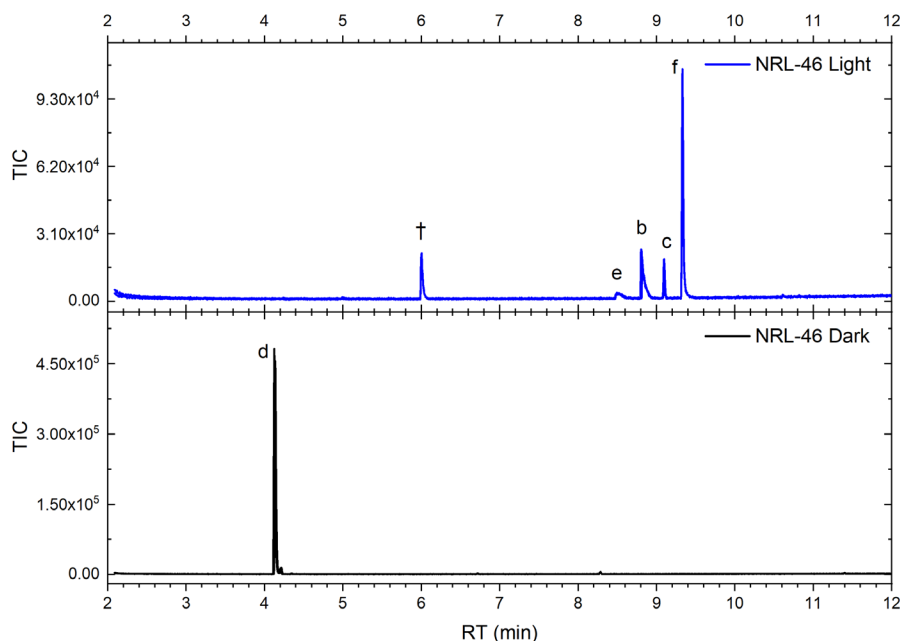


Figure 2.1.8. Gas chromatograph analysis of NRL 46. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). NRL 46 sample masses range was 7.0 to 7.4 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μL of 2-CEES stock solution containing 19.25 μL of 2-CEES in 2 mL of methylene chloride

Photocatalytic assessments of TiO_2 prepared with Al_2O_3 via *p-ALD* was performed in order to provide a baseline assessment for future TiO_2 ALD modifications. Al_2O_3 layer was deposited to promote uniform Au deposition on the surface of the photocatalyst.

The gas chromatographic results from the 24-hour 2-CEES challenges for $\text{TiO}_2/\text{Al}_2\text{O}_3$ are shown in Figure 2.1.9. The modification of TiO_2 using ALD did appear to promote selective visible light driven oxidation of 2-CEES to sulfoxide. However, the rate of oxidation was low, as 2-CEES still remained on the surface after 24 h visible light exposure. The low reactivity may indicate the potential for surface bound species (i.e. sulfoxide, sulfone or hydrolysis product) that were not readily extracted. Additionally differences in the extracted 2-CEES from the surface of the samples kept in the dark also potentially indicate surface interactions altering the extraction. To verify the hypothesis on the presence of the surface bound 2-CEES photooxidation product on the surface of $\text{TiO}_2/\text{Al}_2\text{O}_3$ sample, XPS analyses of the powders exposed to visible light and maintained in the dark were carried out. The results indicate the presence of Cl2p peak that can be attributed either to adsorbed 2-CEES or CH_2Cl_2 which was used as a solvent for 2-CEES. In addition, a very weak S2p peak was detected, confirming the presence of surface bound species. Interestingly, even very thin (less than 1 nm) Al_2O_3 layer can significantly alter photocatalytic activity of TiO_2 .

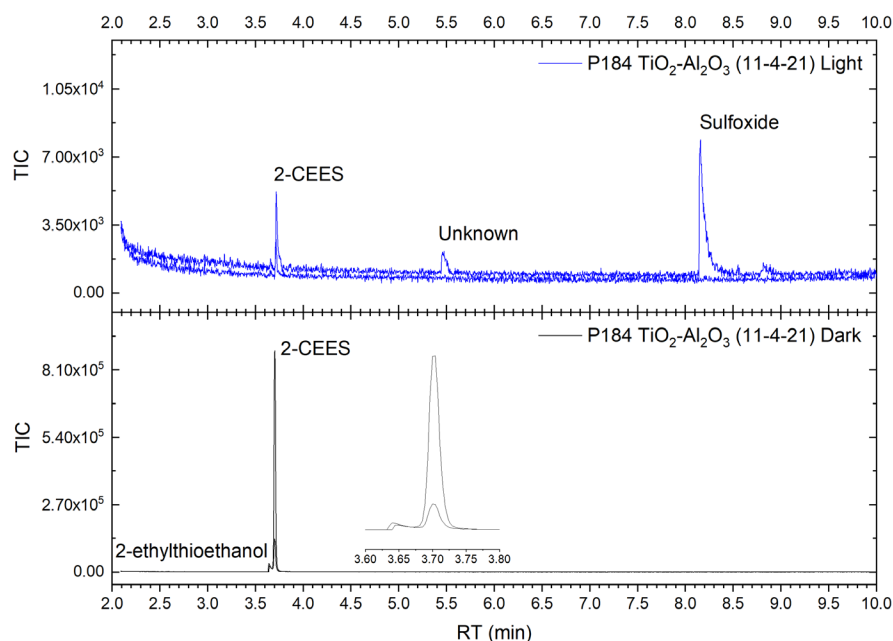


Figure 2.1.9. Gas chromatograph analysis of P184 TiO₂/Al₂O₃. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). P184 TiO₂/Al₂O₃ sample masses range was 6.6 to 7.7 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of methylene chloride

Materials denoted “JAB-TiO₂, ...”, and “TiO₂-1,...TiO₂-5” in Table 6 did not exhibit as high photocatalytic activity as Pajarito’s material, with 2-CEES still remaining on the surface after 24 h challenge. The results of assessment of their photocatalytic activity are provided in the quarterly reports. Further optimization of the materials is required.

Task 2.2 Evaluation of photoctalytic activities of plasmonic nanoparticles-modified TiO₂ and doped TiO₂

Plasmonic TiN, ZrN, Cu, and Au nanoparticles were deposited on TiO₂ in order to boost its visible light absorption. To optimize plasmonic effect, the effect of the deposition method and Au nanoparticles loading (1 wt%, 5 wt% and 10 wt%) on the photocatalytic activity of the TiO₂ was explored. The list of all the tested materials is provided in Table 7.

NRL-8 is a composite material of 1% titanium nitride (TiN) on a TiO₂ support (NRL-3) which was previously analyzed for decontamination of 2-CEES. The gas chromatographic results from the 2-CEES challenges are shown in Figure 2.1.10. Similar to NRL-3, 2-CEES was completely converted in 24 hours. Contrary to NRL-3, the chromatographs show the presence of the hydrolysis product 2-(ethylthio)-ethanol (d). Unlike NRL-3, oxidation products are dominated by 2-(ethylsulfinyl)-1-ethanol (e), produced by photooxidation of hydrolysis product **d**. Overall, TiN/TiO₂ (NRL-8) is more selective towards sulfoxide production (as product **e** is also sulfoxide) than NRL-3, but, on the other side, it promotes 2-CEES hydrolysis to 2-(ethylthio)-ethanol slightly higher than NRL-3. The latter can be assigned to the presence of OH groups on the surface of TiN nanoparticles surrounded by a very thin native TiO₂ layer.

Table 7. TiO₂ and doped TiO₂ modified by plasmonic nanoparticles

Sample Name	Sample Info	Method
NRL-8	1% TiN on NRL-3 TiO ₂	
NRL-11	1% TiN on Degussa P25	
NRL-20	Cu/TiO ₂	
NRL-34	1%Cu/P25 TiO ₂	
JAB 1183B	ZrN/TiO ₂ (P25)	
NRL-46A	Au/TiO ₂ (1% Au supported on NRL-46)	
JAB 1222A	Au/TiO ₂ (1 wt% Au supported on P25)	Photochemical deposition (PCD)
JAB 1222B	Au/TiO ₂ (1 wt% Au supported on NRL-46)	PCD
JAB 1222F	Au/TiO ₂ (1 wt% Au supported on NRL-19)	PCD
JAB 1227A	Au/TiO ₂ (1 wt% Au supported on NRL-46)	M3.1 The TiO ₂ samples were functionalized with MPA and mixed with Au nanoseeds made using the CTAB surfactant (M3.1)
JAB 1227B	Au/TiO ₂ (1 wt% Au supported on NRL-19)	M3.1
JAB 1227C	Au/TiO ₂ (1 wt% Au supported on P25)	M2: The Au NPs are synthesized using PVP and combined with MPA-functionalized TiO ₂ .
JAB 1227D	Au/TiO ₂ (1 wt% Au supported on NRL-46)	M2
JAB 1227E	Au/TiO ₂ (1 wt% Au supported on NRL-19)	M2
JAB 1228B	Au/TiO ₂ (1 wt% Au supported on P25), 50 mM CTAB surfactant	M3.2: The TiO ₂ samples were functionalized with trimethylamine (TEA) and mixed with Au nanoseeds made using concentrations diluted from 100 mM to 10 mM of the CTAB surfactant.
JAB 1228C	Au/TiO ₂ (1 wt% Au supported on P25), 10 mM CTAB surfactant	M3.2
JAB 1233A	Au/TiO ₂ (1wt%Au – NRL-46)	PCD
JAB 1233B	Au/TiO ₂ (5wt%Au – NRL-46)	PCD
JAB 1233C	Au/TiO ₂ (10wt%Au – NRL-46)	PCD
JAB 1234D	Au/TiO ₂ (1wt%Au – NRL-46)	M2: The Au NPs are synthesized using PVP and combined with MPA-functionalized TiO ₂
JAB 1234E	Au/TiO ₂ (5wt%Au – NRL-46)	M2
JAB 1234F	Au/TiO ₂ (10wt%Au – NRL-46)	M2

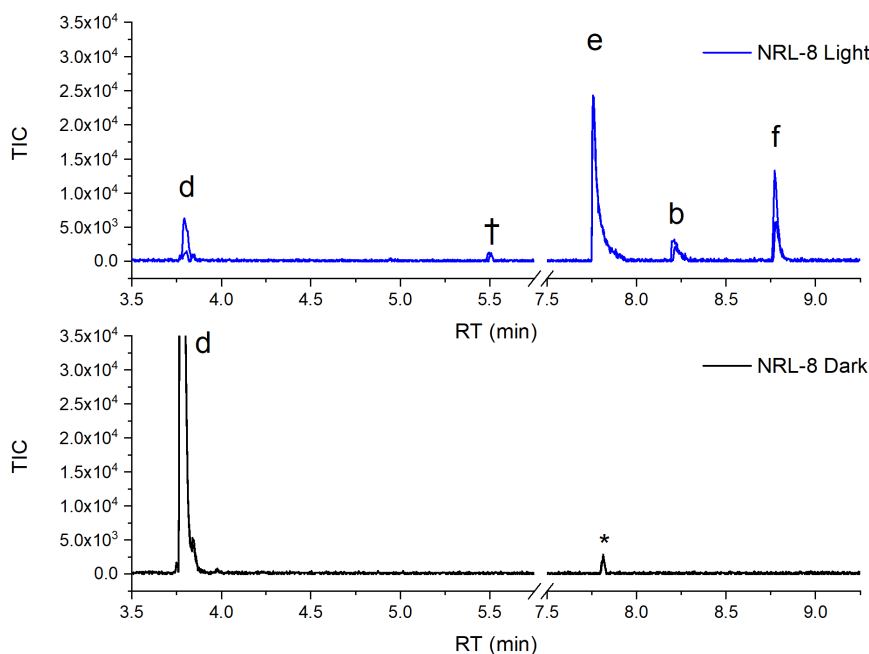


Figure 2.1.10. Gas chromatograph analysis of NRL 8. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). NRL 8 sample masses range was 7.3 to 7.6 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μL of 2-CEES stock solution containing 19.25 μL of 2-CEES in 2 mL of methylene chloride.

NRL-11 has a similar composition to that of NRL-8 with 1% TiN on a commercial TiO_2 support (Degussa P-25) for comparative analysis on the influence of TiO_2 morphology. Figure 2.1.11 shows the results for the 2-CEES challenges with NRL-11, which is vastly different from that of NRL-8. NRL-11 displays limited reactivity toward 2-CEES with minimal photooxidation being observed over the same 24 hour exposure time. Figure 2.1.11 shows that NRL-11 does promote hydrolysis of 2-CEES under both light and dark conditions but to a significantly lesser degree than NRL-8. The results in Figure 2.1.10 and Figure 2.1.11 illustrate that the morphology of the TiO_2 support significantly influences the reactivity of these materials with 2-CEES.

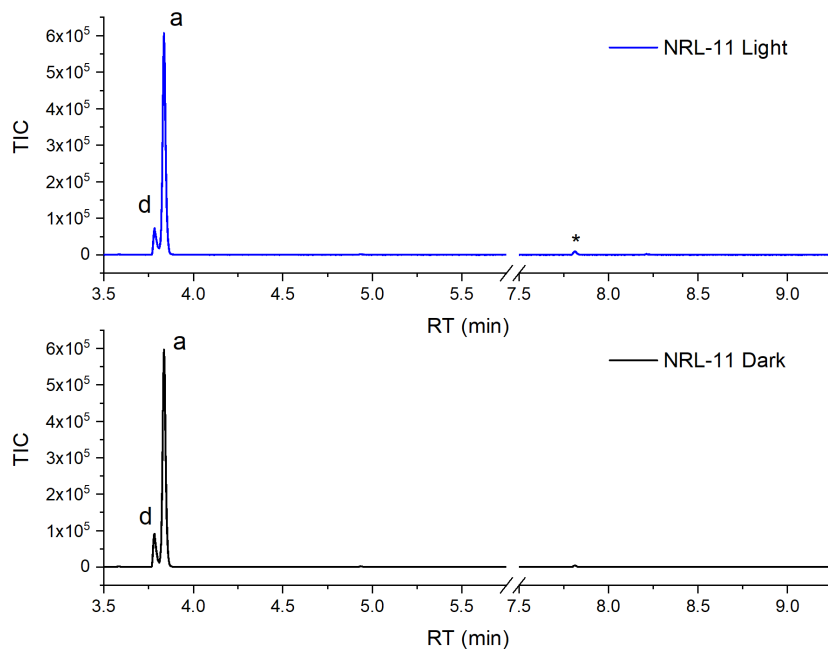


Figure 2.1.11. Gas chromatograph analysis of NRL 11. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). NRL 11 sample masses range was 7.0 to 7.4 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μL of 2-CEES stock solution containing 19.25 μL of 2-CEES in 2 mL of methylene chloride.

Doping of TiO_2 with copper (Cu) was also utilized to promote TiO_2 photocatalytic activity towards 2-CEES oxidation. We compared activities of an open-frame TiO_2 support modified with Cu (NRL-20) and commercial P25 TiO_2 doped with 1% Cu (NRL-34). Photo oxidation was observed for neither sample tested. NRL-20 promotes the complete hydrolysis of 2-CEES to form 2-(ethylthio)-ethanol (d) and 1,2 bis(ethylthio)ethane (*). NRL-34 only shows minor reactivity over the same period of time with 2-CEES being the predominant peak in the GC-MS with minor formation of both 2-(ethylthio)-ethanol (d) and 1,2 bis(ethylthio)ethane (*). This confirms that oxide layer on the surface of Cu nanoparticles promotes hydrolysis of organic molecules.

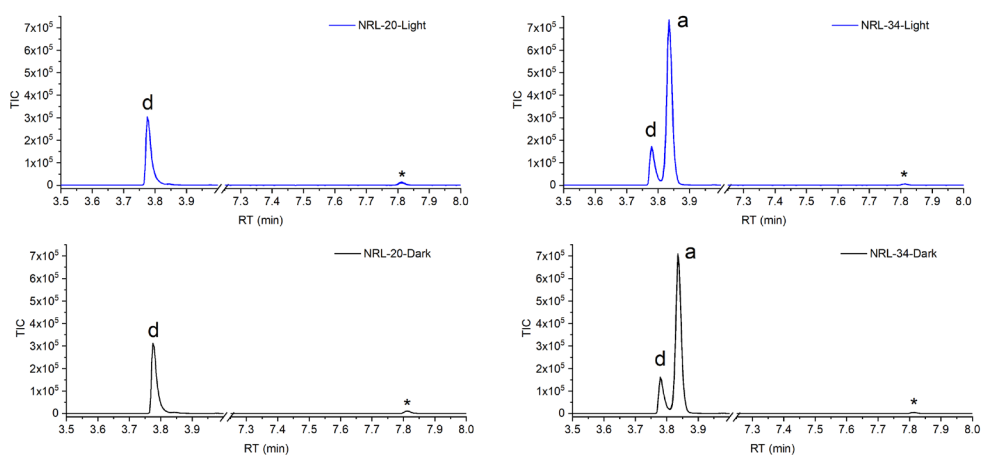


Figure 2.1.12. Gas chromatograph analysis of NRL 20 (left) and NRL 34 (right). Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). NRL 20 sample masses range was 7.1 to 7.4 mg and NRL 34 sample masses ranged from 7.0 to 7.3 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μL of 2-CEES stock solution containing 19.25 μL of 2-CEES in 2 mL of methylene chloride.

ZrN supported on P25 TiO₂ (JAB1183B) promoted minimal hydrolysis and photochemical driven oxidation (Figure S28). With direct oxidation of the thioether sulfur to 2-CEES-sulfoxide (**b**) being preferential to C-H activation and the proposed formation of diethyl disulfide (CH₃CH₂S₂CH₂CH₃). Unfortunately, we did not have a chance to evaluate photocatalytic activity of ZrN nanoparticles supported on open-frame TiO₂ or Sm-doped TiO₂.

We found that photocatalytic activity of Au/TiO₂ materials was significantly affected by Au deposition technique. For example, for Pajarito's sample NRL-46A (1 wt% Au/TiO₂), we observed that Au nanoparticles promoted more selective photooxidation to a desired 2-chloroethyl ethyl sulfoxide (product **b**, Figure 2.1.13). But on the other hand, the rate of photocatalytic reaction was lower than that on the neat TiO₂ support, as 2-CEES was not completely consumed within 24 h challenge.

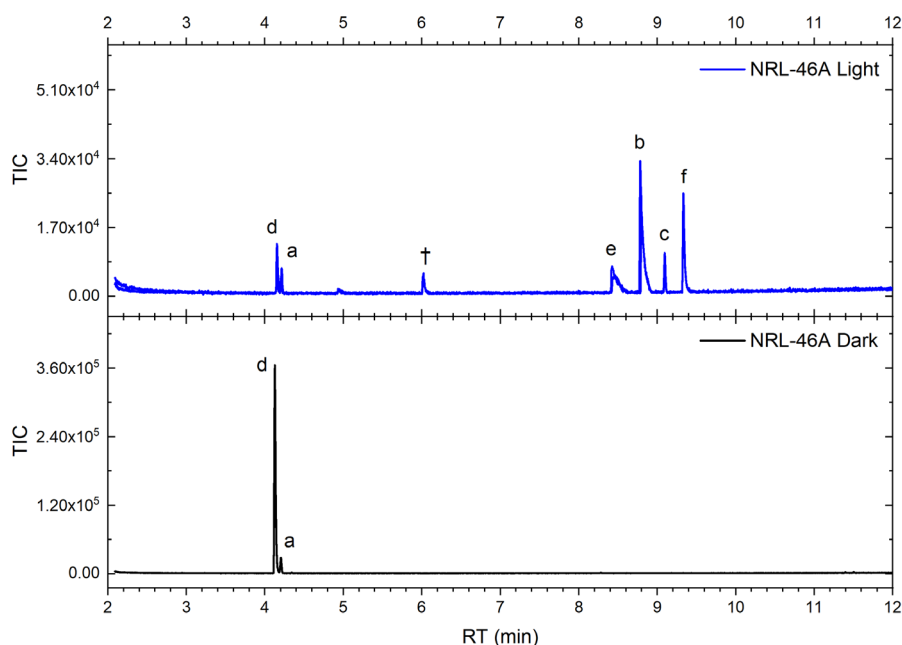


Figure 2.1.13. Gas chromatograph analysis of NRL 46A. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). NRL 46A sample masses range was 7.0 to 7.5 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of methylene chloride.

Effect of Au deposition method on photocatalytic activity of Au/TiO₂ and Au/Sm-doped TiO₂ materials

After Pajarito's departure from the program, Jonathan Boltersdorf (ARL) used four different methods (PCD, M2, M3.1, and M3.2) briefly described in Table 7 to deposit Au nanoparticles on the three TiO₂ support materials (TiO₂, Sm-doped TiO₂, and P25 TiO₂) to optimize both Au nanoparticle deposition method and support material. Note that method M3.2 was utilized only for P25 support due to a shortage of Pajarito's TiO₂ (NRL-46) and Sm-doped TiO₂ (NRL-46) powders.

Below we will present the results for the PCD method only. The results for the Au/TiO₂ photocatalysts synthesized by the three other methods (M2, M3.1, and M3.2) are provided in the SI (Figures S18-S19, and S21-S25)

The gas chromatographic results from the 24-hour 2-CEES challenges for 1 wt% Au on P25 TiO₂ via PCD (JAB 1222A, Table 1) are shown in Figure 2.1.14. The modification of P25 with 1 wt% Au did not appear to promote significant visible light driven oxidation however, hydrolysis of the C-Cl bond to generate 2-(ethylthio)-ethanol (**d**) was observed regardless of visible light excitation.

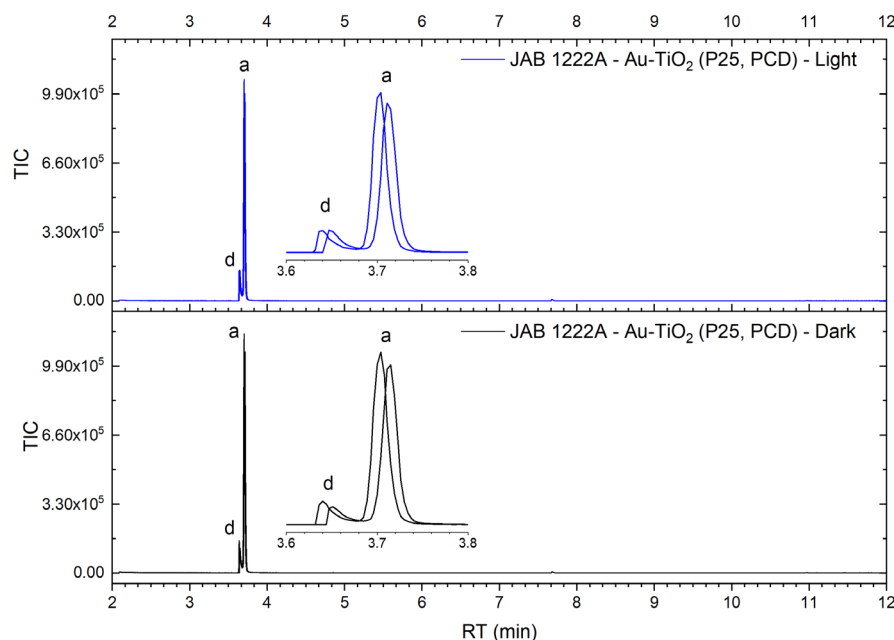


Figure 2.1.14. Gas chromatograph analysis of JAB 1222A. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). JAB 1222A sample masses range was 6.9 to 7.2 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μL of 2-CEES stock solution containing 19.25 μL of 2-CEES in 2 mL of methylene chloride.

Potential oxidation from visible light on a minimal scale is hypothesized from the mass fragmentation pattern comparison shown in Figure 2.1.15 between the light and dark peaks around 3.64 minutes (Figure 2.1.14). The additional mass fragments at m/z : 66, 94, and 122 indicate potential co-elution of 2-(ethylthio)-ethanol (**d**) with another reaction byproduct in the visible light exposed sample. The fragments indicate the potential formation of diethyl disulfide ($\text{CH}_3\text{CH}_2\text{S}_2\text{CH}_2\text{CH}_3$), which is a result of potential oxidation of the C-H bond alpha to the thioether sulfur [<https://pubs.acs.org/doi/abs/10.1021/es0209767>].

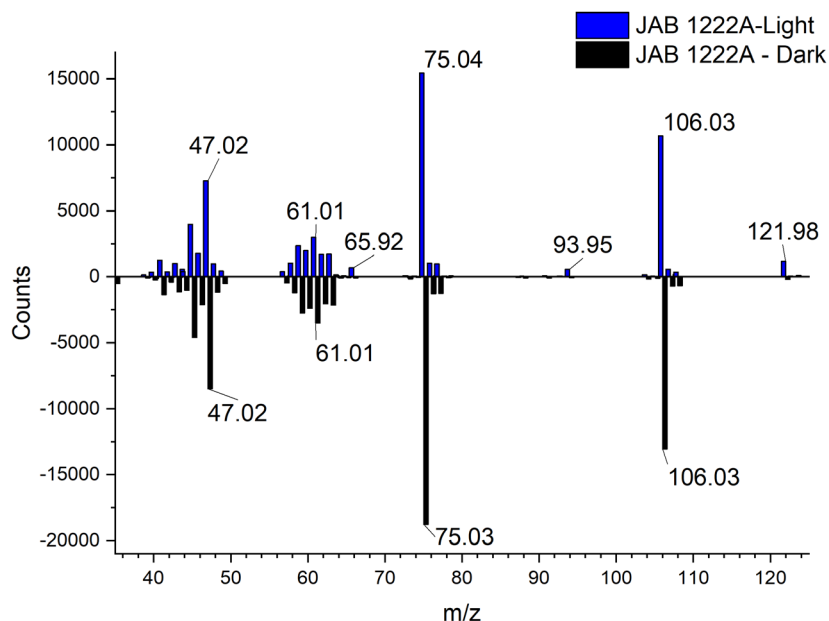


Figure 2.1.15. Head to tail mass fragmentation comparison for the chromatograph peaks at RT of approximately 3.64 minutes from JAB 1222A challenges in Figure 14.

Challenges with JAB 1222B and 1222F were also performed to determine the effect of 1 wt% Au on the photochemical reactivity of synthesized TiO₂ supports NRL-46 and NRL-19, respectively. Previous analysis of NRL-46 showed that the reactivity of the material is competitive between the hydrolysis of the C-Cl bond with consecutive photooxidation of hydrolysis product and the direct oxidation of the thioether sulfur under visible light excitation. Analysis of JAB 1222B (Figure 2.1.16) shows that the major reaction byproduct observed in the chromatographs is sulfoxide **(b)** with minor formation of 2-CEES sulfone **(c)**. In one duplicate run, minor hydrolysis was observed however, the preference for oxidation to the sulfoxide appears to be the dominant reaction pathway. In contrast, when JAB 1222B was not exposed to visible light, the hydrolysis of 2-CEES to 2-(ethylthio)-ethanol **(d)** was observed, but 2-CEES was still the dominant species further supporting the observations from the results from visible light exposure. In addition, when kept in the dark JAB 1222B promoted minor oxidation to 2-CEES sulfoxide **(b)**.

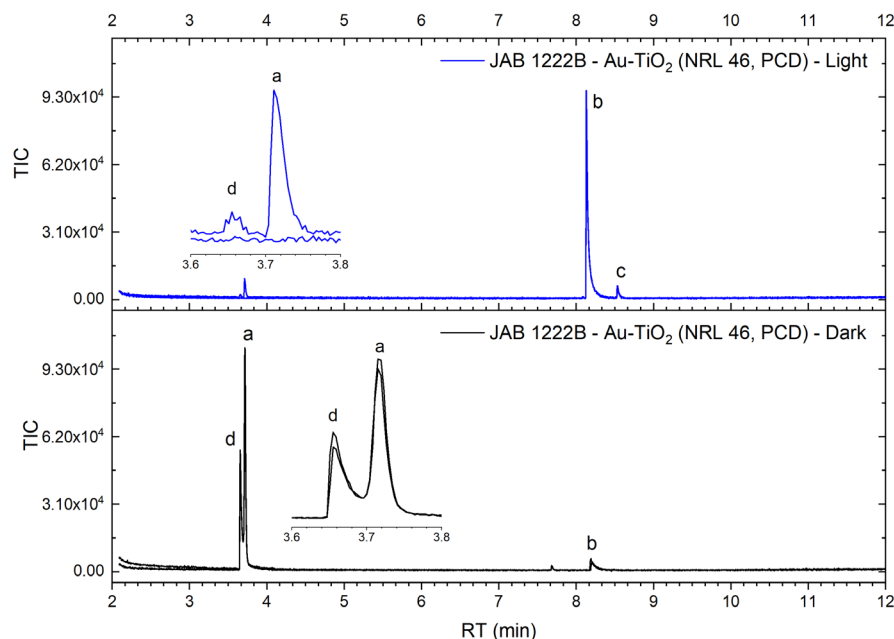


Figure 2.1.16. Gas chromatograph analysis of JAB 1222B. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). JAB 1222B sample masses range was 7.1 to 7.2 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μL of 2-CEES stock solution containing 19.25 μL of 2-CEES in 2 mL of methylene chloride.

Previous analysis of NRL-46A (Figure 2.1.13), which was a 1% Au loaded sample, showed minimal alteration of the reactivity from that of NRL-46 with reaction route competition between hydrolysis and oxidation. Note that retention time differences between figures is due to instrument maintenance and column length changes. Overall, JAB 1222B in contrast to NRL-46A shows the ability to tune the reactivity of the TiO_2 support in the desirable direction in which hydrolysis is limited and oxidation to sulfoxide is the dominant reaction pathway.

NRL-19 is a Sm-doped TiO_2 support. The route for reaction of 2-CEES is a mix of both direct oxidation of 2-CEES with the formation of 2-CEES sulfoxide (**b**), 2-CEES sulfone (**c**), and hydrolysis followed by oxidation resulting in the presence of 2-(ethylsulfonyl)ethanol (**f**) as shown in Figure 2.1.6.

Modification of NRL-19 with 1 wt% Au resulted in a shift in the reactivity in that direct oxidation appears to be preferential based upon byproduct peaks in Figure 2.1.17 in comparison to those in Figure 2.1.6. The photochemical deposition of Au on the surface appears to alter the reactivity to favor the selective oxidation pathways similar to JAB 1222B. Sulfoxide still remains the dominant reaction product. Additionally oxidation of the thioether sulfur is also observed in the dark similar to JAB 1222B shown in Figure 16. The hydrolysis reactivity of JAB 1222F is still competitive enough to result in the formation of 2-(ethylsulfonyl)ethanol (**f**) which is not the case for JAB 1222B in Figure 2.1.16.

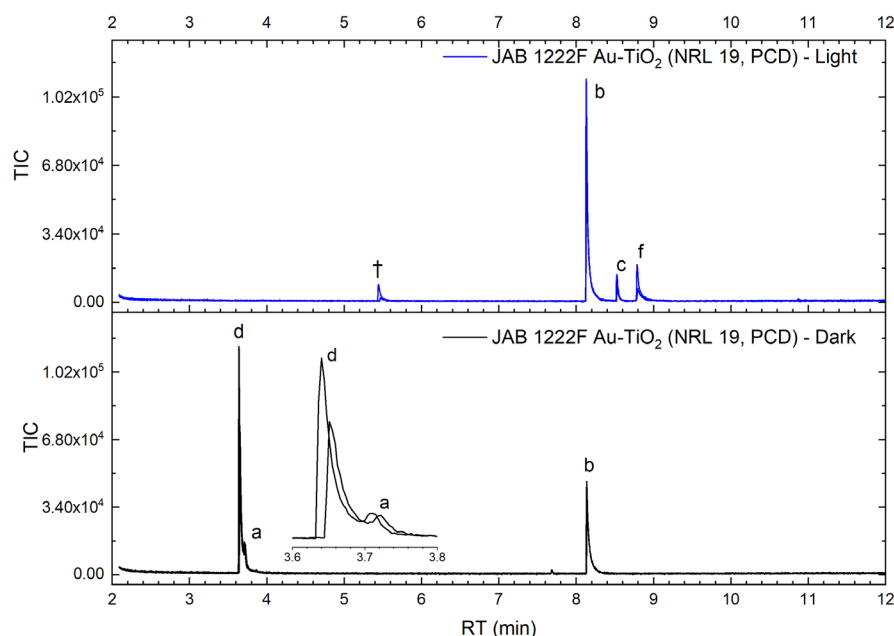


Figure 2.1.17. Gas chromatograph analysis of JAB 1222F. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). JAB 1222F sample masses range was 7.0 to 7.4 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μL of 2-CEES stock solution containing 19.25 μL of 2-CEES in 2 mL of methylene chloride.

Overall, the deposition of 1 wt% Au onto the synthetic TiO_2 supports, NRL-46 and NRL-19, appear to drive selectivity of the visible light driven reactivity toward the desired oxidation product 2-chloroethyl ethyl sulfoxide and limits competition with the hydrolysis pathways. Modification of P25 does not appear to improve the visible light driven oxidation pathway, which is consistent with previous results.

Effect of Au loading on the TiO_2 (NRL-46) photocatalytic activity

Challenges with Au/ TiO_2 photocatalysts synthesized by PCD (JAB 1233A, B and C) and M2 method (JAB 1234D, E, and F) were also performed to determine the effect of Au loading. Photocatalysts with 1, 5 and 10 wt% Au/ TiO_2 (NRL-46) have been assessed. Previous analysis of NRL-46 showed that the reactivity of the material is competitive between the hydrolysis of the C-Cl bond of 2-CEES and the oxidation of the thioether sulfur under visible light excitation. Analysis of JAB 1233A (1 wt% Au/ TiO_2 , Figure 2.1.18) showed directed reactivity toward oxidation to sulfoxide (b) and sulfone (c) and limited hydrolysis reactivity toward 2-CEES in the dark (see tiny 2-ethylthioethanol peak) in comparison to unmodified NRL-46.

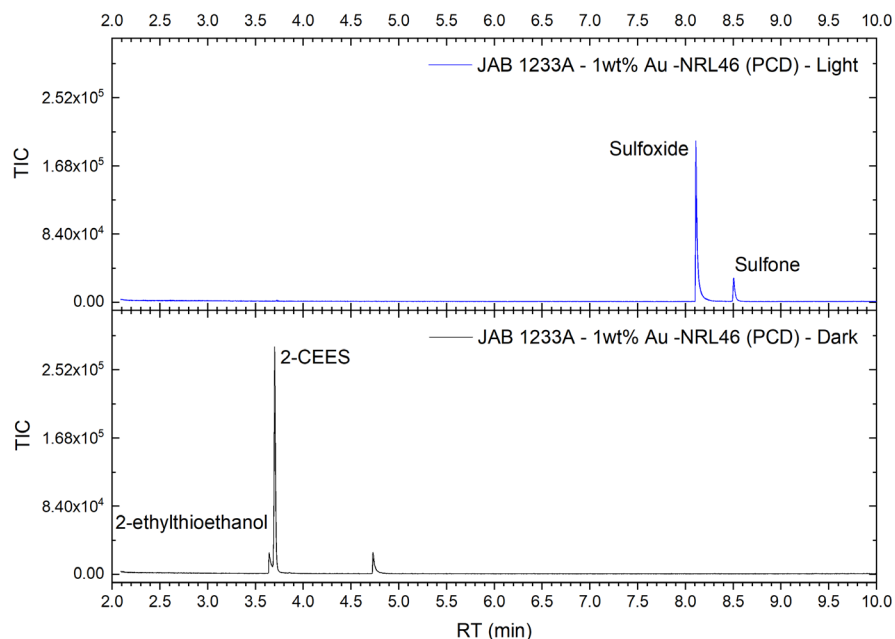


Figure 2.1.18. Gas chromatograph analysis of JAB 1233A. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). JAB 1233A sample masses range was 7.0 to 7.4 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μL of 2-CEES stock solution containing 19.25 μL of 2-CEES in 2 mL of methylene chloride.

Analysis of JAB 1233B (Figure 2.1.19) with 5wt% Au loading shows similar reactivity to that of JAB 1233A with 1wt% Au with the major reaction byproduct observed in the chromatographs is 2-CEES sulfoxide (**b**) with minor formation of 2-CEES sulfone (**c**). Small amounts of 2-CEES are observed in the chromatographs for the samples exposed to visible light. This indicates a reduced rate of the photocatalytic activity as a function of Au loading. When the samples are kept in the dark limited hydrolysis activity appears to be maintained which limits the competitive reactivity during photo excitation.

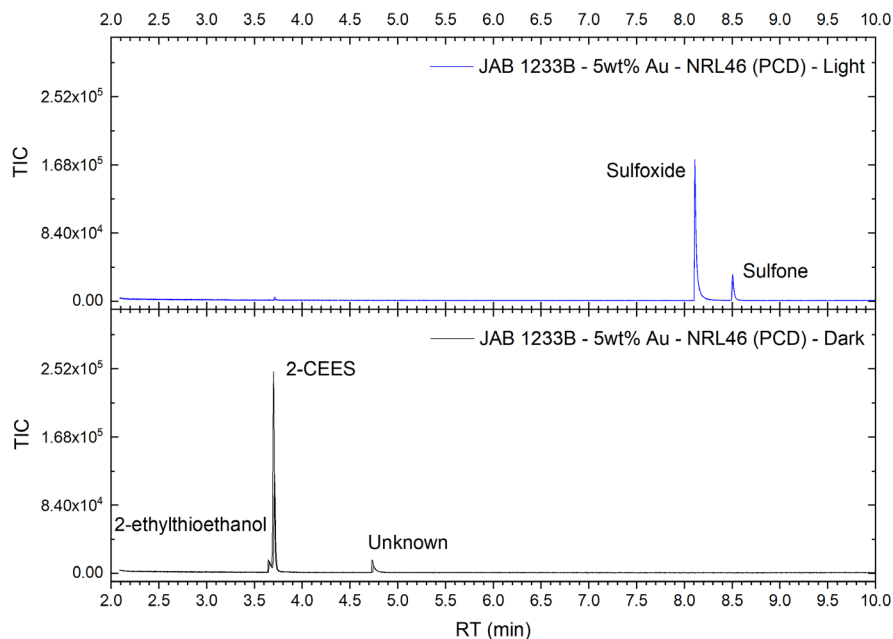


Figure 2.1.19. Gas chromatograph analysis of JAB 1233B. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). JAB 1233B sample masses range was 7.2 to 7.4 mg. Depositions of 2.07×10^{-6}

6×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of methylene chloride.

Increasing the Au loading up to 10 wt% in JAB 1233C (Figure 2.1.20) shows further reduction in the photocatalytic behavior of the samples. The presence of 2-CEES after 24 hours indicates that the reactive surface is altered potentially limiting the active sites available for photochemical reactions. Additionally when the JAB 1233C is kept in the dark the hydrolysis rate appears to be further limited as a small shoulder where 2-(ethylthio)-ethanol (**d**) elutes in the chromatograph is observed in comparison to JAB 1233A and B which show peaks.

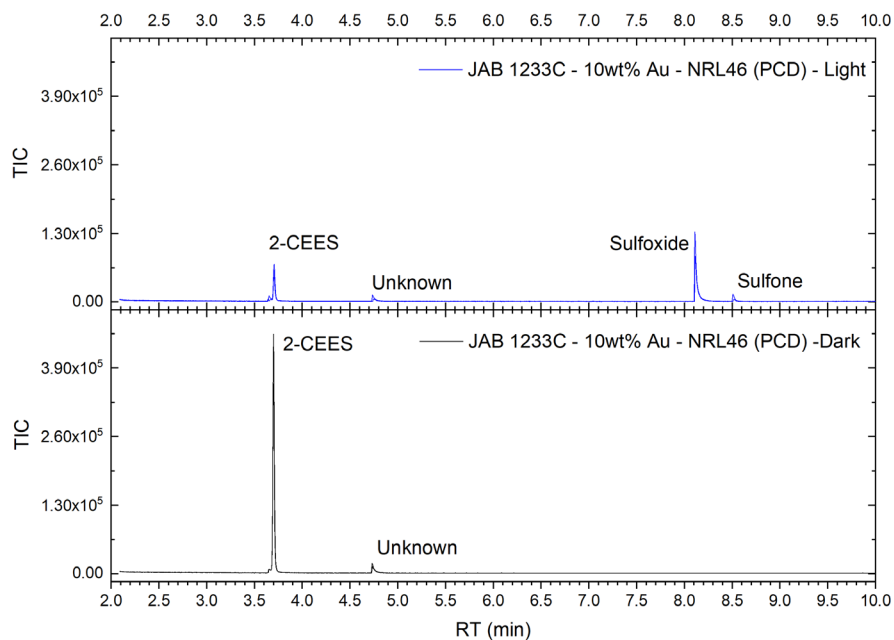


Figure 2.1.20. Gas chromatograph analysis of JAB 1233C. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). JAB 1233C sample masses range was 7.1 to 7.5 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of methylene chloride.

Comparative analysis of samples with 1, 5, and 10 wt% Au on NRL-46 (JAB 1234 D, E and F, respectively) using a method M2 were also analyzed. The chromatographic results for the solution based modified TiO_2 , JAB 1234 D, E and F, are shown in Figure 2.1.21, Figure 2.1.22, and Figure 2.1.23, respectively. Consistent with the PCD samples the reactivity of the photo excited samples was also toward the direct oxidation of the thioether sulfur to generate both 2-CEES sulfoxide (**b**) with minor formation of 2-CEES sulfone (**c**). There are two distinct differences observed between the reactivity results for JAB 1233 A, B, and C in comparison to JAB 1234 D, E and F. First, all three samples appear to remove the majority of 2-CEES with only a minor peak observed for the 10 wt% Au sample JAB 1234 F. This is in contrast to JAB 1233 C, which showed a significant peak for residual 2-CEES in comparison to JAB 1234 F. Second, the hydrolysis for all three samples (JAB 1234 D, E and F) appears to be mitigated, as the chromatographs for all three samples when kept in the dark show little to no hydrolysis of 2-CEES. In comparison, JAB 1233 A, B, and C showed minor formation of 2-ethylthio ethanol in the dark for all three samples.

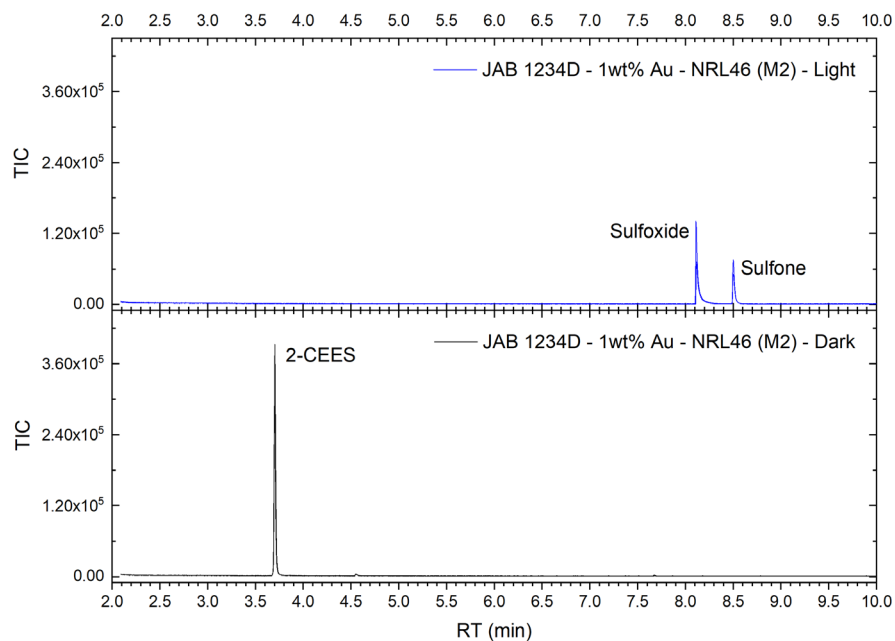


Figure 2.1.21. Gas chromatograph analysis of JAB 1234D. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). JAB 1234D sample masses range was 7.1 to 7.3 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μL of 2-CEES stock solution containing 19.25 μL of 2-CEES in 2 mL of methylene chloride.

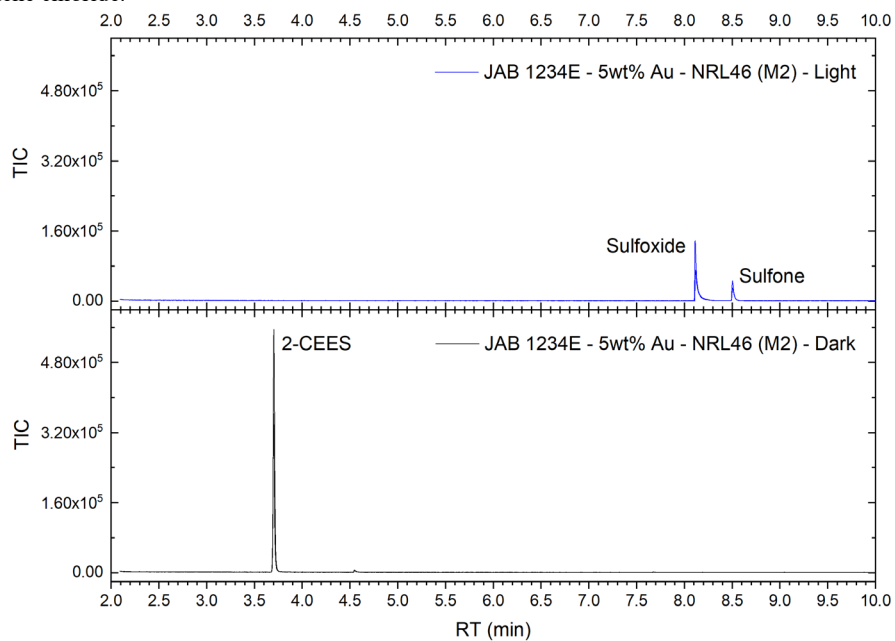


Figure 2.1.22. Gas chromatograph analysis of JAB 1234E. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). JAB 1234E sample masses range was 7.2 to 7.5 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μL of 2-CEES stock solution containing 19.25 μL of 2-CEES in 2 mL of methylene chloride.

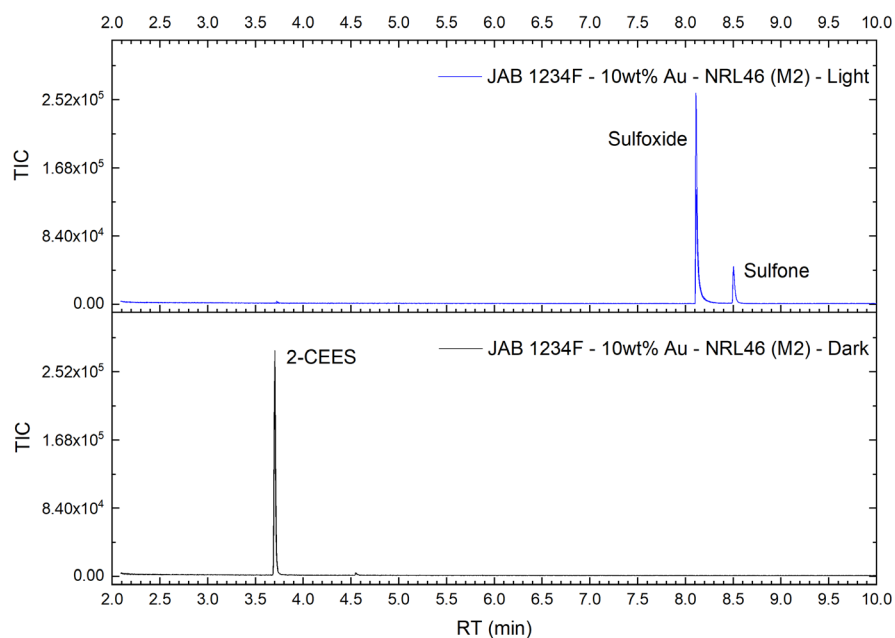


Figure 2.1.23. Gas chromatograph analysis of JAB 1234F. Comparative performance for the sample under visible light exposure (top row) and when kept in the dark (bottom row). JAB 1234F sample masses range was 7.0 to 7.7 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μL of 2-CEES stock solution containing 19.25 μL of 2-CEES in 2 mL of methylene chloride.

In addition to the differences stated above, one additional observation is under consideration with respect to the observed amount of 2-CEES sulfoxide (**b**), which needs support from additional data from selective ion monitoring (SIM) for 2-CEES sulfoxide (**b**) and surface analysis of the materials post extraction. The chromatographically observed 2-CEES sulfoxide (**b**) appears to decrease with increased Au loading from 1 and 5 wt% samples JAB 1233 A and B to the 10 wt% sample JAB 1233 C consistent with the appearance of residual 2-CEES in JAB 1233 C (Figure 2.1.20). Similar peak area analysis (Figure 2.1.21-2.1.23) of JAB 1234 D, E and F shows an opposite trend with the 1 and 5wt% samples JAB 1234 D and E showing lower average peak areas than the 10wt% sample JAB 1234 E (Figure 2.1.24). The peak areas from the duplicate samples fall within the standard deviation of each other therefore further assessment is necessary to determine the validity and magnitude of these trends.

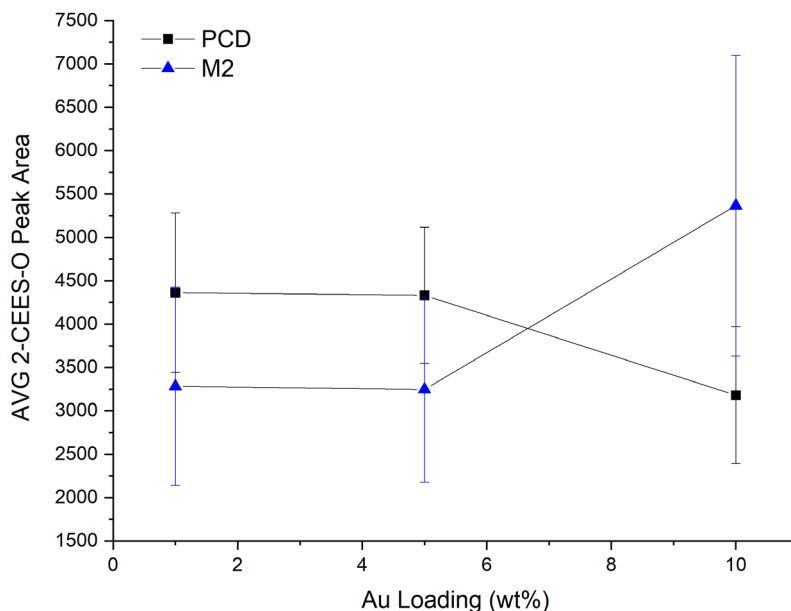


Figure 2.1.24. Average peak area integration of 2-CEES sulfoxide (b) for JAB 1233 A, B, and C and JAB 1234 D, E, and F to evaluate trends in byproduct formation with Au wt% loadings.

In conclusion, the deposition of Au onto the synthetic TiO_2 support NRL-46 via PCD and M2, drives selectivity of the visible light driven reactivity toward the desired oxidation pathway (selective generation of sulfoxide (b)) and limits competition with the hydrolysis pathways at all Au loadings. The PCD procedure for NRL-46 modification did result in photooxidation of 2-CEES, however the surface modification by Au appears to limit the oxidation in comparison to M2 at higher Au loadings (10 wt%). An opposite trend is observed for Au/ TiO_2 photocatalyst, synthesized by method M2, as increased sulfoxide generation is observed at 10 wt% Au loading. Therefore, the optimal Au loading for boosting selective 2-CEES oxidation to sulfoxide is 10 wt%, and the optimal deposition method of Au nanoparticles on the TiO_2 (NRL-46) support is M2. However, at lower Au loadings of 1 and 5 wt% Au/ TiO_2 photocatalyst made by PCD method outperforms the one made by M2. To save an expensive Au, it is acceptable to utilize 1 wt% Au/ TiO_2 photocatalyst made by PCD.

Time Dependent Photocatalytic Evaluation of Au nanoparticles deposited on Sm-doped TiO_2 (NRL-19) and TiO_2 (NRL-46)

The time dependent photocatalytic activity of JAB1222B (1 wt% Au/ TiO_2 , PCD) and JAB1222F (1 wt% Au/Sm- TiO_2 , PCD), with details shown in Table 7, were assessed for the decomposition of 2-CEES via a dose extraction protocol. The reasoning behind selection of the 1 wt% Au/ TiO_2 photocatalyst made by PCD method is provided above. The materials were challenged for one, four and eight-hour intervals in sealed vials under visible light exposure.

The initial 24-hour photocatalytic assessments of TiO_2 samples NRL-46 and NRL-19 are shown in Figures (2.1.8 and 2.1.6, respectively). The competitive hydrolysis and oxidation reaction pathways for the unmodified support materials promote the complete transformation of the deposited 2-CEES providing a promising platform for modification that was performed via the deposition of 1 wt% Au nanoparticles for modifying the reactivity.

The 24-hour reactivity of the 1 wt% Au modified supports previously reported for materials JAB 1222B and 1222F are shown in Figures 2.1.16 and 2.1.17, respectively. These materials displayed promising modified reactivity in that the deposition of Au onto the support directed the reactivity toward visible light driven oxidation via limiting the hydrolysis reactivity.

Analysis of JAB 1222B time dependent reactivity is shown in Figure 2.1.25. Limited oxidation is observed from the exposure of JAB 1222B at eight hours. Additionally limited hydrolysis is also observed from JAB 1222B was observed which is consistent with the results shown in Figure 16. A key observation from Figure 2.1.25 is that the 2-CEES peak is not consistent between the two trials performed at the same time intervals, which potentially indicates surface interactions that may not extract easily upon addition of the solvent acetonitrile.

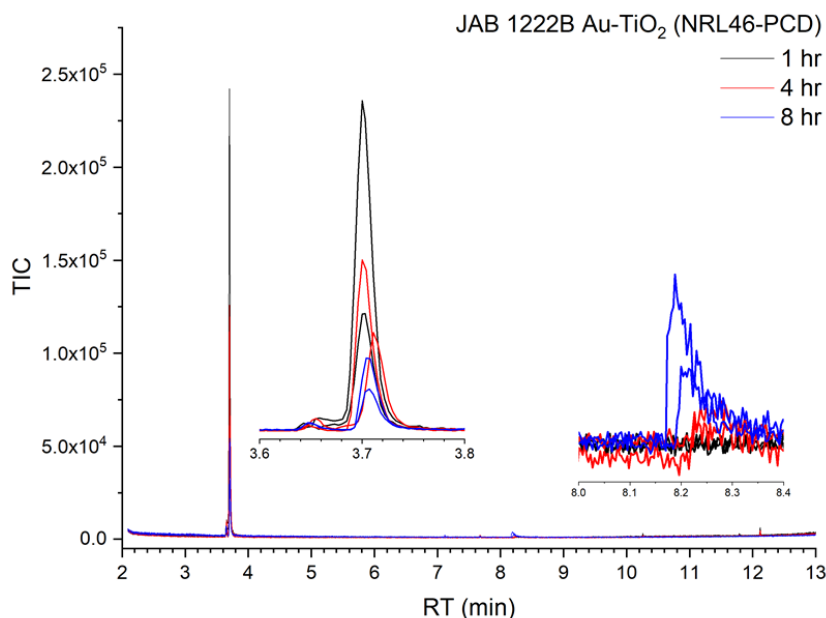


Figure 2.1.25. Gas chromatograph analysis of time dependent reactivity of JAB 1222B. The materials were under visible light exposure for one, four and eight hour time intervals prior to extraction. JAB 1222B sample masses range was 6.8 to 7.3 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of methylene chloride.

Figure 2.1.26 shows similar time trial reactivity assessment for JAB 1222F. From the GC-MS analysis of JAB 1222F the time dependent reactivity is better than that of JAB 1222B with greater amounts of oxidation products observed and the complete removal of 2-CEES in under eight hours. The variability observed in the 2-CEES peak is consistent with that observed in Figure 26B for JAB 1222B. Both materials were modified using the PCD method, which may have implications on the surface sites and potential binding of 2-CEES and byproducts altering the extraction.

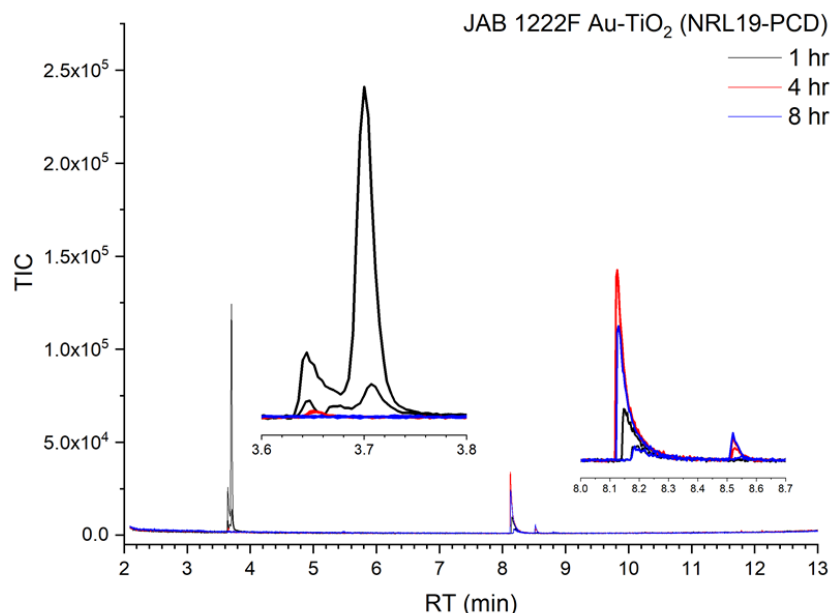


Figure 2.1.26. Gas chromatograph analysis of time dependent reactivity of JAB 1222F. The materials were under visible light exposure for one, four and eight hour time intervals prior to extraction. JAB 1222F sample masses range was 6.9 to 7.1 mg. Depositions of 2.07×10^{-6} mol of 2-CEES onto the catalyst surface from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of methylene chloride.

We hypothesize that the surface activity of Au nanoparticles deposited by PCD method towards binding reaction products is due to the cleanliness of their surface. As a matter of fact, PCD method provides the cleanest conditions during deposition of metallic nanoparticles. To verify this hypothesis, time trials of JAB1227B (1 wt% Au/Sm-TiO₂, M3.1) were carried out to determine if the results are more consistent in the presence of surfactant on the surface. The results of this experiment are provided in the SI (Figure S20). The complete transformation of 2-CEES from JAB 1227B appears to be between four and eight hours with minor residual 2-CEES remaining after four hours of visible light exposure. Oxidation of 2-CEES to the sulfoxide and sulfone appear to be the main reaction pathway with no hydrolysis observed at the one-hour time point. The consistency of the extraction results shown in Figure S20 illustrate a potential difference in surface chemistry in moving from the PCD method for deposition to the M3.1 method.

Overall, the reactivity with respect to time for JAB 1222B, 1222F and 1227B are promising in directing reactivity from hydrolysis to photochemical driven oxidation. Material JAB 1222B and 1222F appear to display complex surface chemistry that is observed in the variability in the 2-CEES and by-product extraction. The PCD method may lend toward surface chemistry that promotes binding of 2-CEES and byproducts which could explain differences observed in the results shown in Figures 26 and 27. The results for JAB 1227B show a more consistent extraction with results showing less variability. Regarding the rate of 2-CEES transformation, nearly complete 2-CEES selective photooxidation to sulfoxide (with minor sulfone observed) was observed for 1 wt% Au/Sm-TiO₂ (JAB 1222F, PCD) and 1 wt% Au/Sm-TiO₂ (JAB 1227B, M3.1).

Photocatalytic activity of hybrid TiN-SiO₂(TiO₂)-Pt(Pd) plasmonic nanoparticles supported on TiO₂ and Sm-doped TiO₂

Plasmonic hybrid nanoparticles utilizing refractory transition metal TiN core and Pt or Pd nanoclusters were synthesized to take advantage of plasmonic properties of TiN and catalytic properties of Pt and Pd nanoparticles. SiO₂ or TiO₂ interlayer were used to protect TiN core from oxidation. Note, that 1-2 nm TiO₂ layer forms naturally on TiN nanoparticles.

Table 8. Hybrid TiO₂-and Sm-TiO₂ supported plasmonic nanoparticles

Sample ID	Sample Group	Materials
JAB1257A	TiO ₂ , 450 °C, 4 h O ₂	TiO ₂
JAB1257B	3% Sm-doped TiO ₂ , 450 °C, 4 h O ₂	Sm-TiO ₂
JAB1261E	Hybrid Plasmonic NPS on nanoporous Titania TiN-SiO ₂ -Pt/Pd (1wt%) on TiO ₂ or 3% Sm-doped TiO ₂	TiN-SiO ₂ -Pd on TiO ₂
JAB1261F		TiN-SiO ₂ -Pt on TiO ₂
JAB1261G	Hybrid Plasmonic NPS on nanoporous Titania TiN-SiO ₂ -Pt/Pd (1wt%) on TiO ₂ or 3% Sm-doped TiO ₂ Hybrid Plasmonic NPS on nanoporous Titania TiN-TiO ₂ -Pt/Pd (1wt%) on TiO ₂ or 3% Sm-doped TiO ₂	TiN-SiO ₂ -Pd on Sm-TiO ₂
JAB1261H		TiN-SiO ₂ -Pt on Sm-TiO ₂
JAB1261A		TiN-TiO ₂ -Pd on TiO ₂
JAB1261B		TiN-TiO ₂ -Pt on TiO ₂
JAB1261C	Hybrid Plasmonic NPS on nanoporous Titania TiN-TiO ₂ -Pt/Pd (1wt%) on TiO ₂ or 3% Sm-doped TiO ₂	TiN-TiO ₂ -Pd on Sm-TiO ₂
JAB1261D		TiN-TiO ₂ -Pt on Sm-TiO ₂

The photocatalytic activity of all the materials listed in Table 8 was tested against 2-CEES. Full details of sample ID, experimental replicate, and experimental nomenclature is shown in Table 9.

Table 9. List of photocatalysts used and the names of the replicates used throughout the experiment.

Sample#	Replicates		Sample ID
	Light	Dark	
1	1L, 1L2	1D, 1D2	JAB1257A
2	2L, 2L2	2D, 2D2	JAB1257B
3	3L, 3L2	3D, 3D2	JAB1261E
4	4L, 4L2	4D, 4D2	JAB1261F
5	5L, 5L2	5D, 5D2	JAB1261G
6	6L, 6L2	6D, 6D2	JAB1261H
7	7L, 7L2	7D, 7D2	JAB1261A
8	8L, 8L2	8D, 8D2	JAB1261B
9	9L, 9L2	9D, 9D2	JAB1261C
10	10L, 10L2	10D, 10D2	JAB1261D

Reaction products from both light and dark environments were identified using GC-MS analysis to identify the reaction pathway for each catalyst. Results for JAB1257A and JAB1257B are presented in the SI (Figures S26 and S27, respectively).

For JAB1261E (TiN-SiO₂-Pd on TiO₂), hydrolysis of 2-CEES to 2-ethylthioethanol and oxidation to 3-methylthiopropyl occurred in light and dark (Figure 2.1.27) meaning that the effect is purely catalytic (not photocatalytic). This is the first demonstration of acetate (benign product of 2-CEES oxidation) formation in our program. Obviously, it is related to presence of Pd nanoparticles on the surface of 2-CEES.

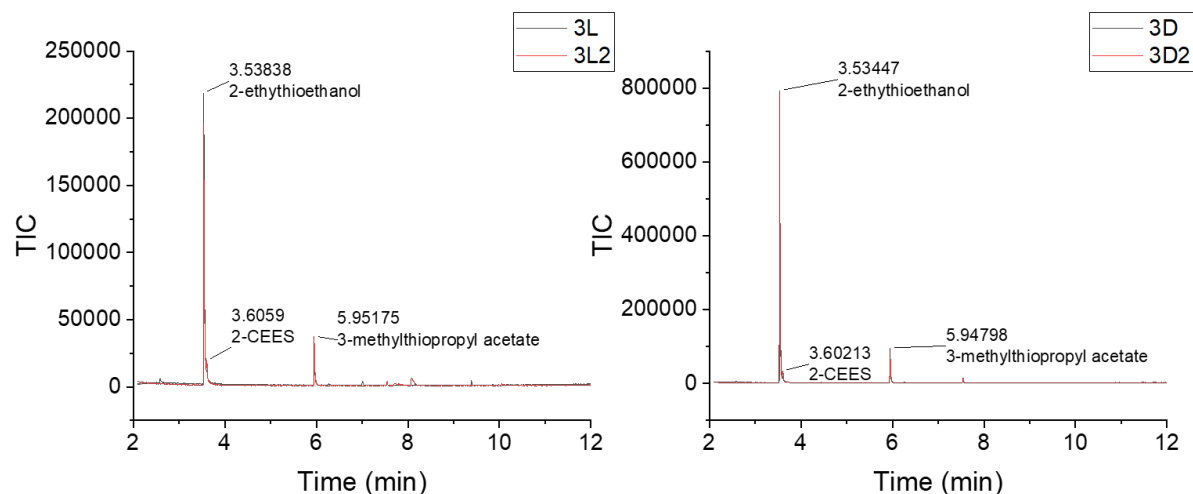


Figure 2.1.27. GC-MS chromatographs of 2-CEES 24 h assessment for JAB1261E (7 mg). The sample was assessed under light (A) and dark (B) conditions. Deposition of 2.07×10^{-6} mol of 2-CEES into the vial from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of dichloromethane.

In Figure 2.1.28, JAB1261F (TiN-SiO₂-Pt on TiO₂) is shown to result in hydrolysis of 2-CEES in light and dark. No oxidation occurred in either condition.

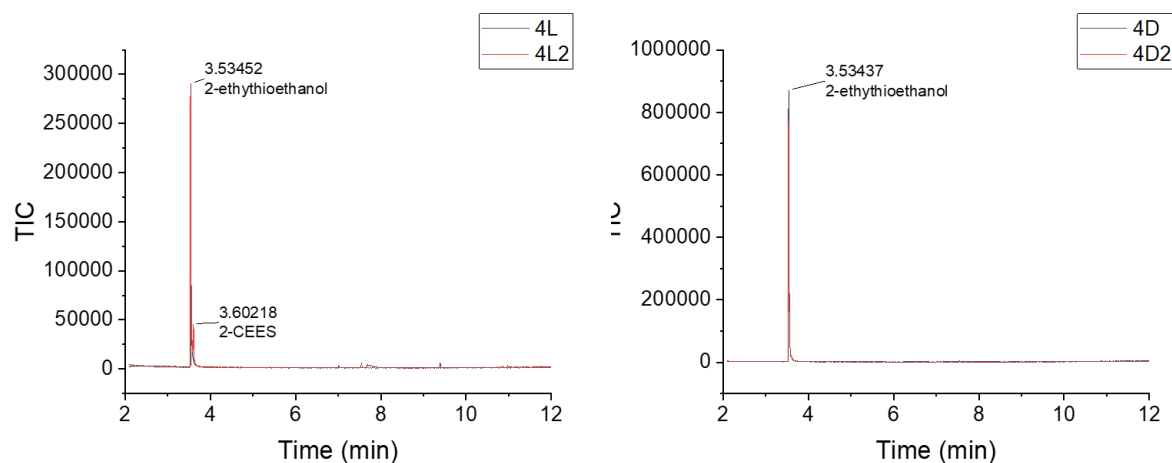


Figure 2.1.28. GC-MS chromatographs of 2-CEES 24 h assessment for JAB1261F (7 mg). The sample was assessed under light (A) and dark (B) conditions. Deposition of 2.07×10^{-6} mol of 2-CEES into the vial from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of dichloromethane.

In Figure 2.1.29, JAB1261G (TiN-SiO₂-Pd on Sm-TiO₂) demonstrated hydrolysis of 2-CEES in light and dark. No oxidation occurred in either condition.

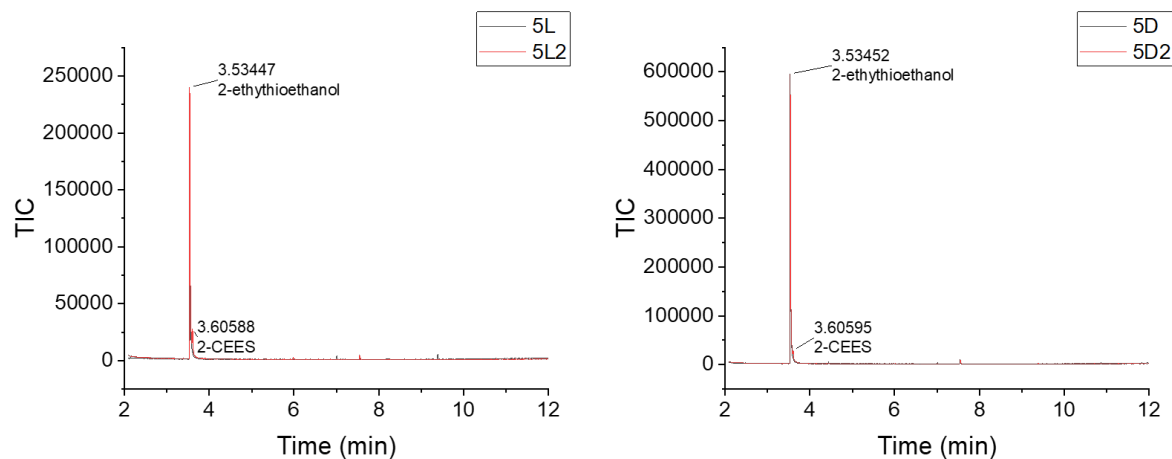


Figure 2.1.29. GC-MS chromatographs of 2-CEES 24 h assessment for JAB1261G (7 mg). The sample was assessed under light (A) and dark (B) conditions. Deposition of 2.07×10^{-6} mol of 2-CEES into the vial from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of dichloromethane.

In Figure 2.1.30, JAB1261H (TiN-SiO₂-Pt on Sm-TiO₂) demonstrated hydrolysis of 2-CEES in light and dark. No oxidation occurred in either condition.

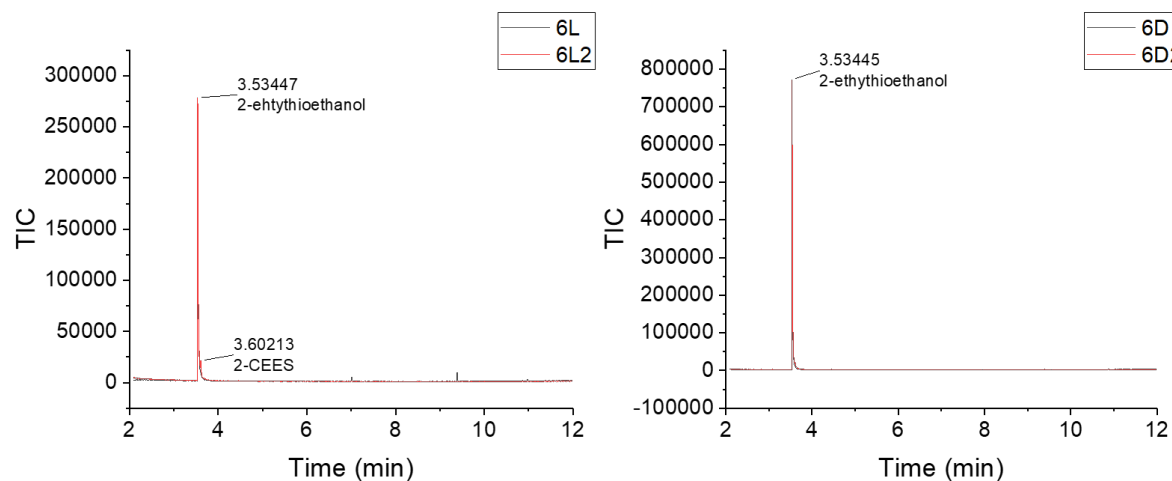


Figure 2.1.30. GC-MS chromatographs of 2-CEES 24 h assessment for JAB1261H (7 mg). The sample was assessed under light (A) and dark (B) conditions. Deposition of 2.07×10^{-6} mol of 2-CEES into the vial from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of dichloromethane.

In Figure 2.1.31, JAB1261A (TiN-TiO₂-Pd on TiO₂) is shown to result in hydrolysis of 2-CEES in light and dark with acetate formation, which again confirms the effect of Pd on 2-CEES oxidation. No photooxidation occurred in either condition. Note the presence of the remaining 2-CEES peaks in both chromatograms.

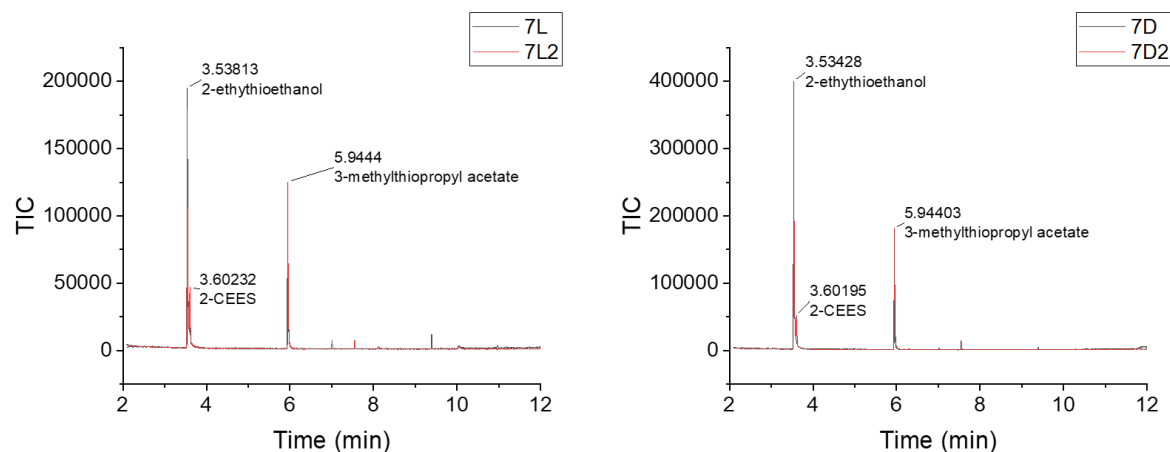


Figure 2.1.31. GC-MS chromatographs of 2-CEES 24 h assessment for JAB1261A (7 mg). The sample was assessed under light (A) and dark (B) conditions. Deposition of 2.07×10^{-6} mol of 2-CEES into the vial from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of dichloromethane.

In Figure 2.1.32, JAB1261B (TiN-TiO₂-Pt on TiO₂) is shown to result in hydrolysis of 2-CEES and acetate formation in light and dark as well. In this hybrid catalyst, the presence of Pt nanoparticles most likely caused 2-CEES oxidation to acetate. No effect of visible light was observed. There are also clearly observable 2-CEES peaks in both cases.

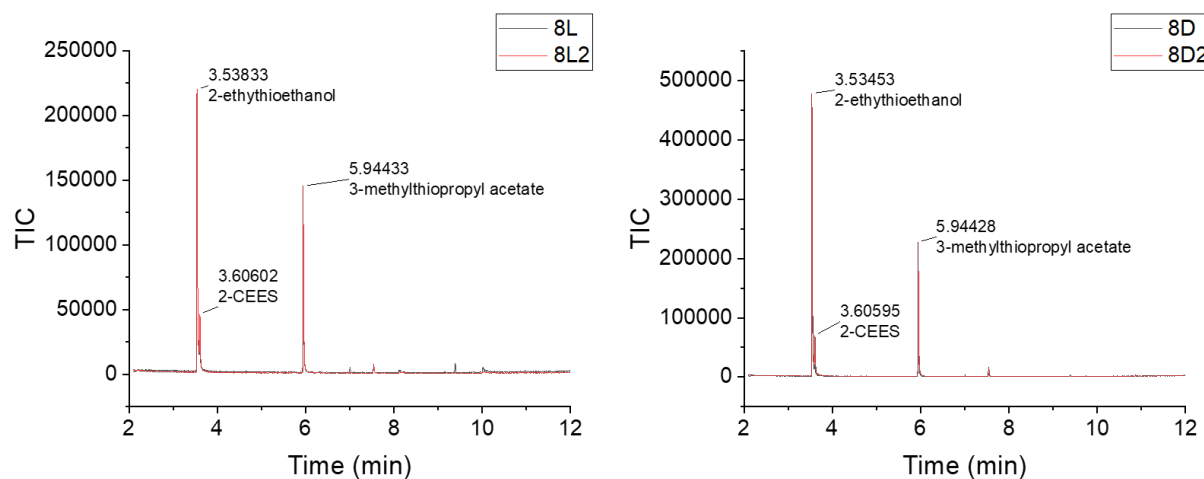


Figure 2.1.32. GC-MS chromatographs of 2-CEES 24 h assessment for JAB1261B (7 mg). The sample was assessed under light (A) and dark (B) conditions. Deposition of 2.07×10^{-6} mol of 2-CEES into the vial from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of dichloromethane.

In Figure 2.1.33, JAB1261C (TiN-TiO₂-Pd on Sm-TiO₂) is shown to result in hydrolysis of 2-CEES in light and dark accompanied by acetate formation. Contrary to previous scenarios, the ratio of 3-methylpropyl acetate to 2-ethylethanol peak favors formation of acetate. Again, there is no effect of visible light on 2-CEES decomposition.

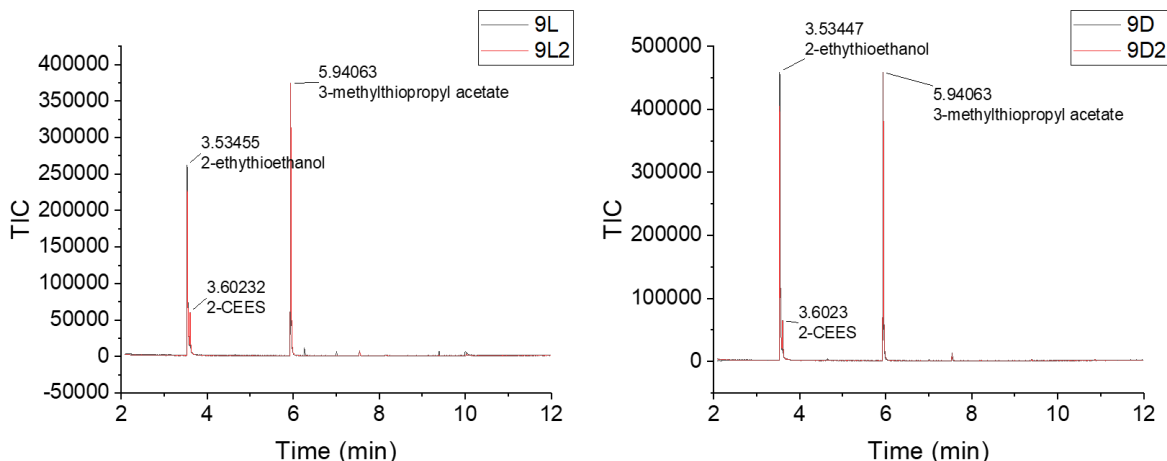


Figure 2.1.33. GC-MS chromatographs of 2-CEES 24 h assessment for JAB1261C (7 mg). The sample was assessed under light (A) and dark (B) conditions. Deposition of 2.07×10^{-6} mol of 2-CEES into the vial from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of dichloromethane.

In Figure 2.1.34, JAB1261D (TiN-TiO₂-Pt on Sm-TiO₂) is shown to result in hydrolysis of 2-CEES in light and dark and acetate formation. Again, this catalyst favors formation of acetate vs hydrolysis product.

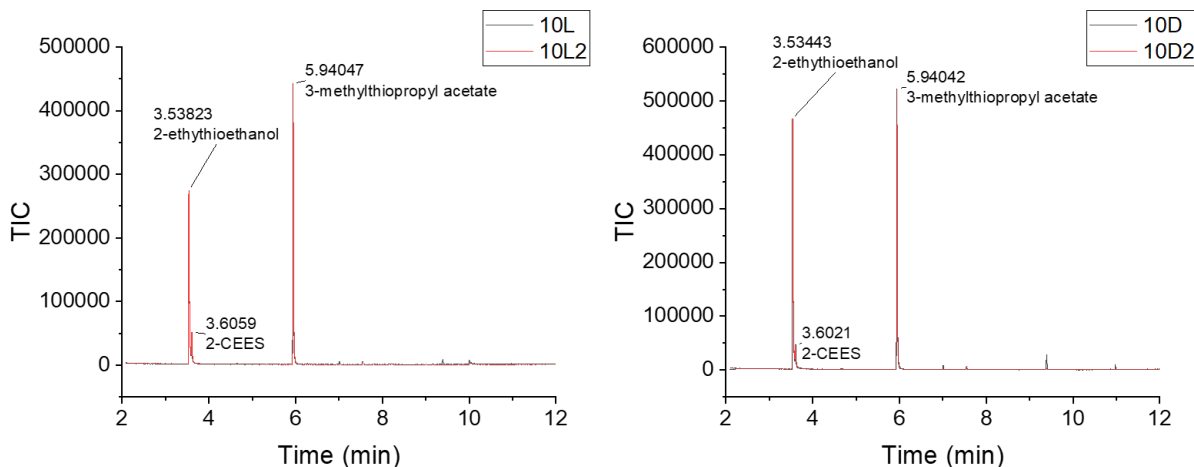


Figure 2.1.34. GC-MS chromatographs of 2-CEES 24 h assessment for JAB1261D (7 mg). The sample was assessed under light (A) and dark (B) conditions. Deposition of 2.07×10^{-6} mol of 2-CEES into the vial from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of dichloromethane.

Figure 2.1.35 presents the summary of the activity of all samples as measured by degradation percentage (right) and percent remaining (left). Significantly, near complete 2-CEES degradation (higher than 97.2 %) occurred in all hybrid plasmonic samples, in all conditions. Complete 2-CEES conversion to benign reaction products (mostly to 2-ethylethanol was observed for JAB1257A, JAB1257B, JAB1261F, and JAB1261H.

Sample	Dark		Light	
Replicate	1	2	1	2
1	100	100	100	100
2	100	100	100	99.9
3	99.2	98.3	100	99.2
4	100	100	100	98.3
5	100	98.5	100	98.7
6	100	100	100	99.1
7	100	97.7	99.8	98.2
8	99.1	97.2	98.9	98.9
9	98.7	97.2	98.7	97.7
10	98.9	97.9	98.7	98.0

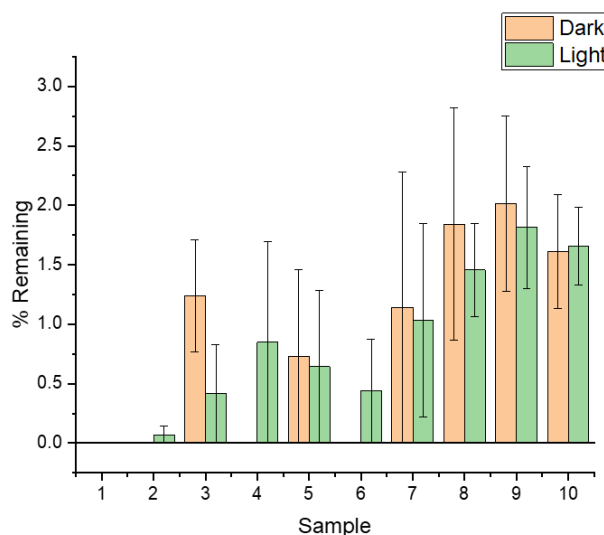


Figure 2.1.35. (Left) Summary of degradation percentages of all samples tested in this reporting period. (Right) Plot showing the average percent 2-CEES remaining in all samples tested.

In summary, all hybrid plasmonic samples exhibited activity towards decomposition of 2-CEES in dark conditions. The primary decomposition pathway for majority of the samples was hydrolysis. In addition to hydrolysis, formation of methylthiopropyl acetate was detected on the surface of the samples JAB1261E, JAB1261A, JAB1261B, JAB1261C and JAB1261D. Mechanism of acetate ether formation is being investigated. Most likely, Pt and Pd nanoparticles catalyze oxidation of -OH group of 2-CEES hydrolysis product to carboxyl group, which subsequently undergoes condensation reaction with by-product of 2-CEES decomposition. However, morphology of the nanoparticles and their interaction with TiO₂ support and SiO₂ shell may play an important role as well, as only one catalyst (JAB1261E, TiN-SiO₂-Pd on TiO₂) in the group of Pt- and Pt-containing nanoparticles demonstrated activity towards 2-CEES conversion to methylthiopropyl acetate. Under visible light exposure, only minor amounts of photooxidation to sulfoxide and some other products occurred on the surface of JAB1257A and JAB1257B (TiO₂ and Sm-doped TiO₂, respectively).

Time Dependent Catalytic Evaluation of Hybrid Plasmonic Nanoparticles

The results from our previous study on the catalytic destruction of 2-CEES a new product was observed from sample JAB1261E, JAB1261A, JAB1261B, JAB1261C, and JAB1261D (10, samples 3, 7, 8, 9, and 10, respectively). The new product, 3-methylthiopropyl acetate (3-MPA), was identified in all four samples both in light and dark environments. Further study on the formation of the products was performed to elucidate the mechanistic pathway. Following the same procedure, an hourly study was conducted where the products were extracted from the surface of the catalysts after 1, 4, and 8 h.

Reaction products from both environments at each time (1, 4, and 8 h) were identified using GC-MS. The products were identified at each hour to determine whether 3-MPA was produced through an established pathway or a new pathway.

Table 10. List of photocatalysts used throughout the experiment

Sample#	Name	Sample Group	Contents
3	JAB1261E	Hybrid Plasmonic NPS on nanoporous Titania TiN-SiO ₂ -Pt/Pd (1wt%) on TiO ₂ or Sm-TiO ₂	Pd-TiO ₂ , JAB1129L on JAB1260A
7	JAB1261A	Hybrid Plasmonic NPS on nanoporous Titania TiN-TiO ₂ -Pt/Pd (1wt%) on TiO ₂ or SmTiO ₂	JAB1258A on JAB1257A
8	JAB1261B		JAB1258B on JAB1257A
9	JAB1261C		JAB1258A on JAB1259B
10	JAB1261D		JAB1258B on JAB1257B

The reaction products from both light and dark environments for JAB1261E are displayed in Figure 2.1.36. 3-MPA and 2-ethylthioethanol (2-ETE) are observed at 1 h in both environments. As previously identified, the formation of 2-ETE indicates dissociation of C–Cl bond through hydrolysis. The presence of 3-MPA in light and in the absence of light indicates that visible light excitation of the catalyst is not needed for decomposition. As 2-CEES is consumed, both 2-ETE and 3-MPA are produced indicating that after the C-Cl bond breaks the two competing products are formed. There is a steady increase of both products throughout the study.

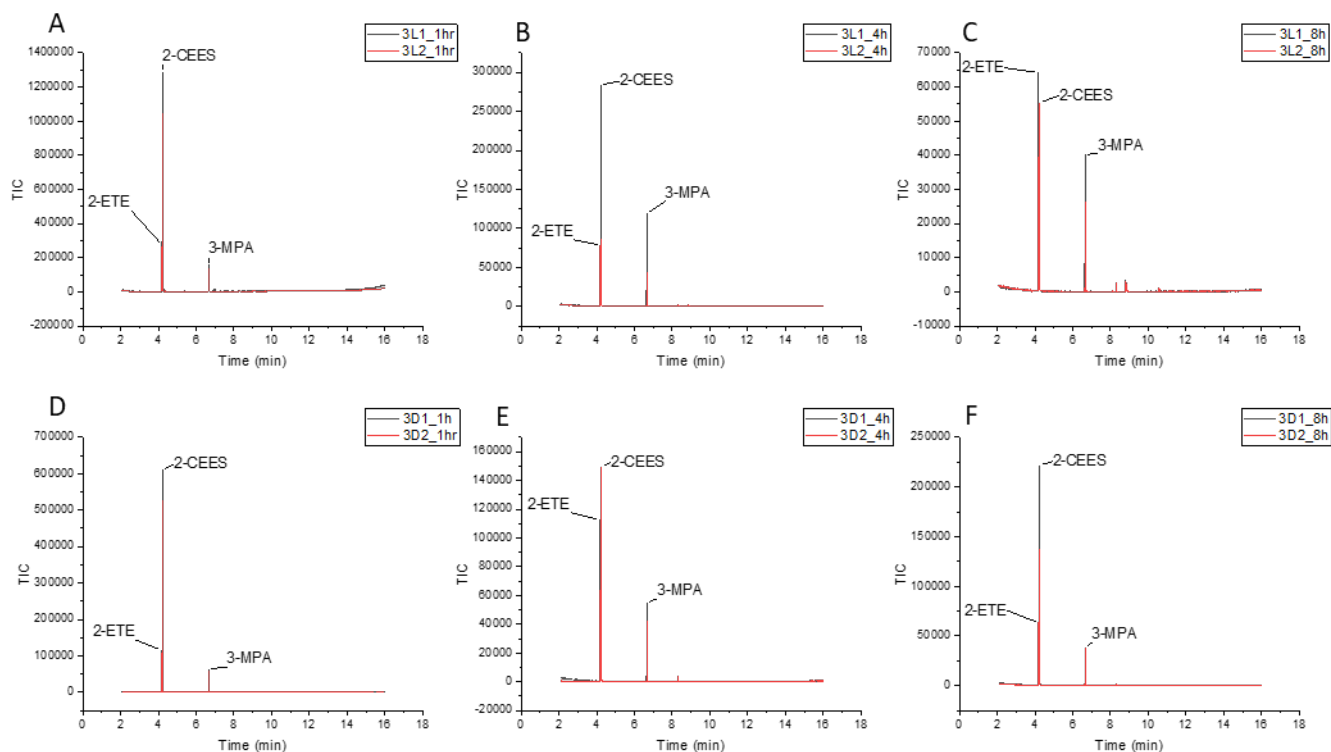


Figure 2.1.36. GC-MS chromatographs of 2-CEES 24 h assessment for Sample 3 (7 mg). The sample was assessed under light (A-C) and dark (D-F) conditions. Deposition of 2.07×10^{-6} mol of 2-CEES into the vial from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of dichloromethane

JAB1261A, JAB1261B, JAB1261C, and JAB1261D followed the same pattern of degradation as seen in Figures Figure 2.1.37-Figure 2.1.40. At 1 h, 2-ETE and 3-MPA are the extracted products from the

catalysts. As continued consumption of 2-CEES occurs both products are identified in similar observable ratio. The calculated ratio of both products are outlined in Table 11.

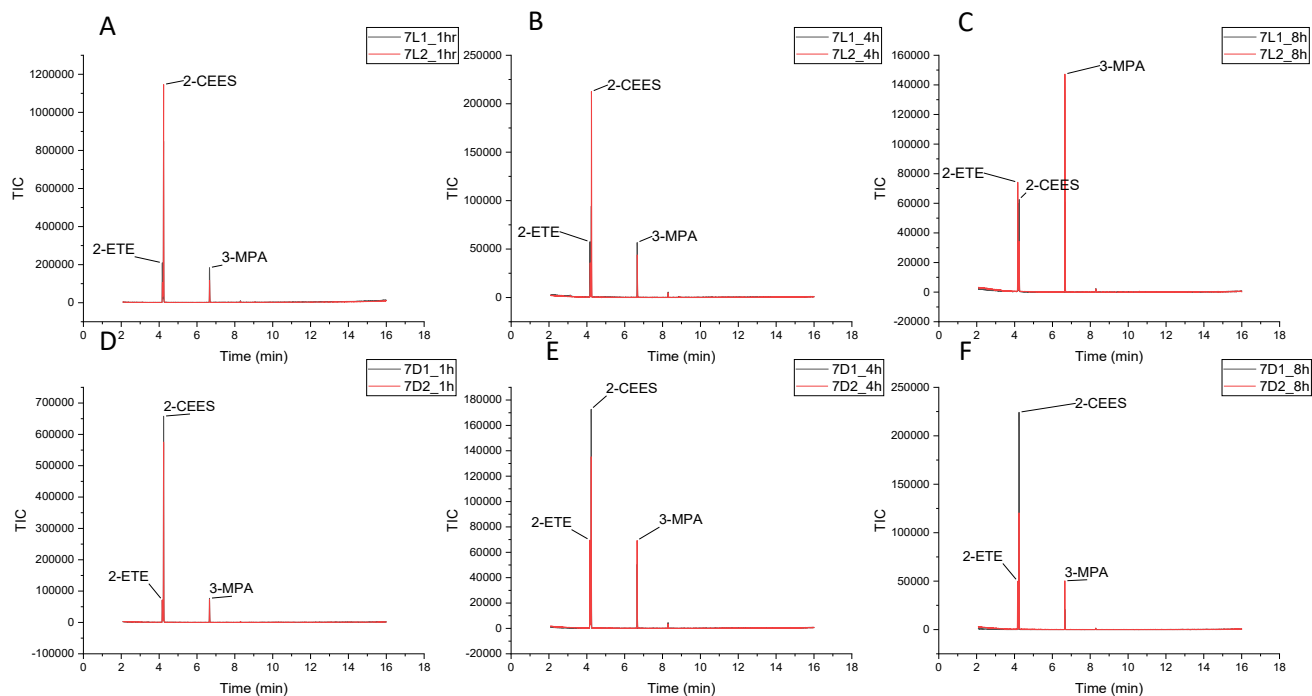


Figure 2.1.38. GC-MS chromatographs of 2-CEES 24 h assessment for Sample 7 (7 mg). The sample was assessed under light (A-C) and dark (D-F) conditions. Deposition of 2.07×10^{-6} mol of 2-CEES into the vial from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of dichloromethane.

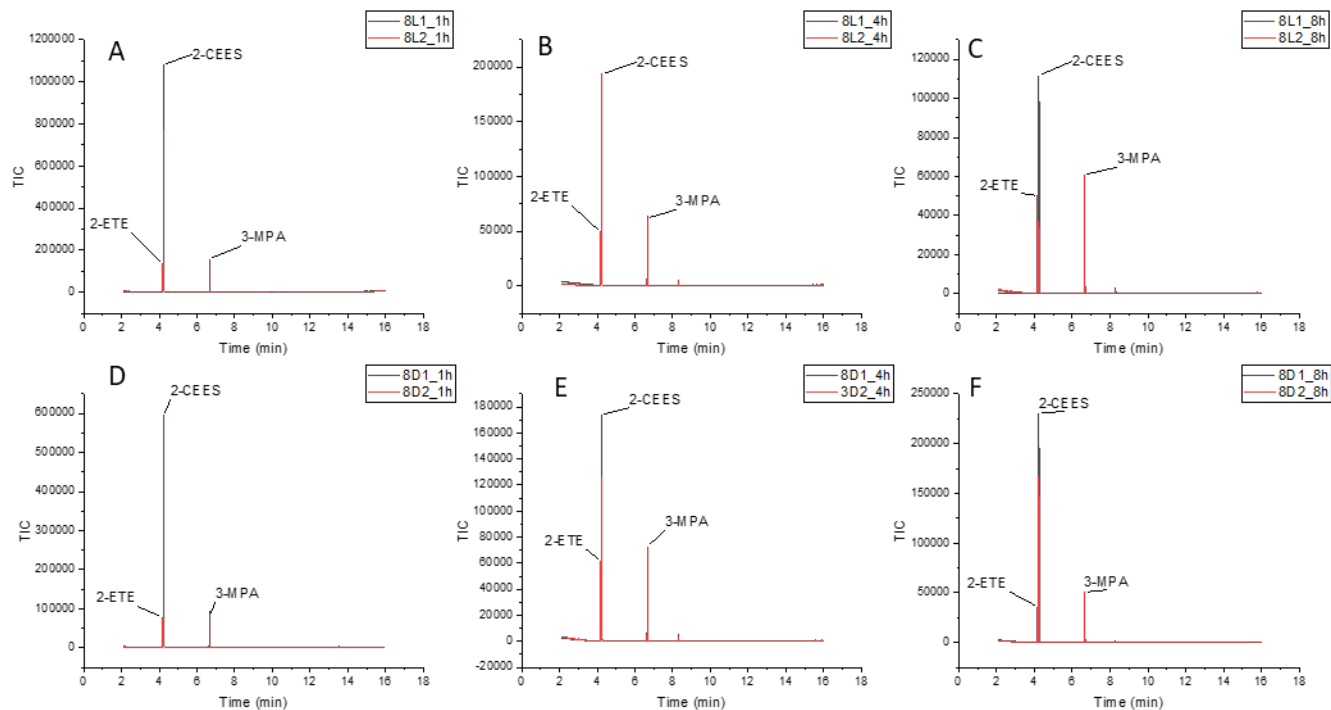


Figure 2.1.39. GC-MS chromatographs of 2-CEES 24 h assessment for Sample 8 (7 mg). The sample was assessed under light (A-C) and dark (D-F) conditions. Deposition of 2.07×10^{-6} mol of 2-CEES into the vial from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of dichloromethane.

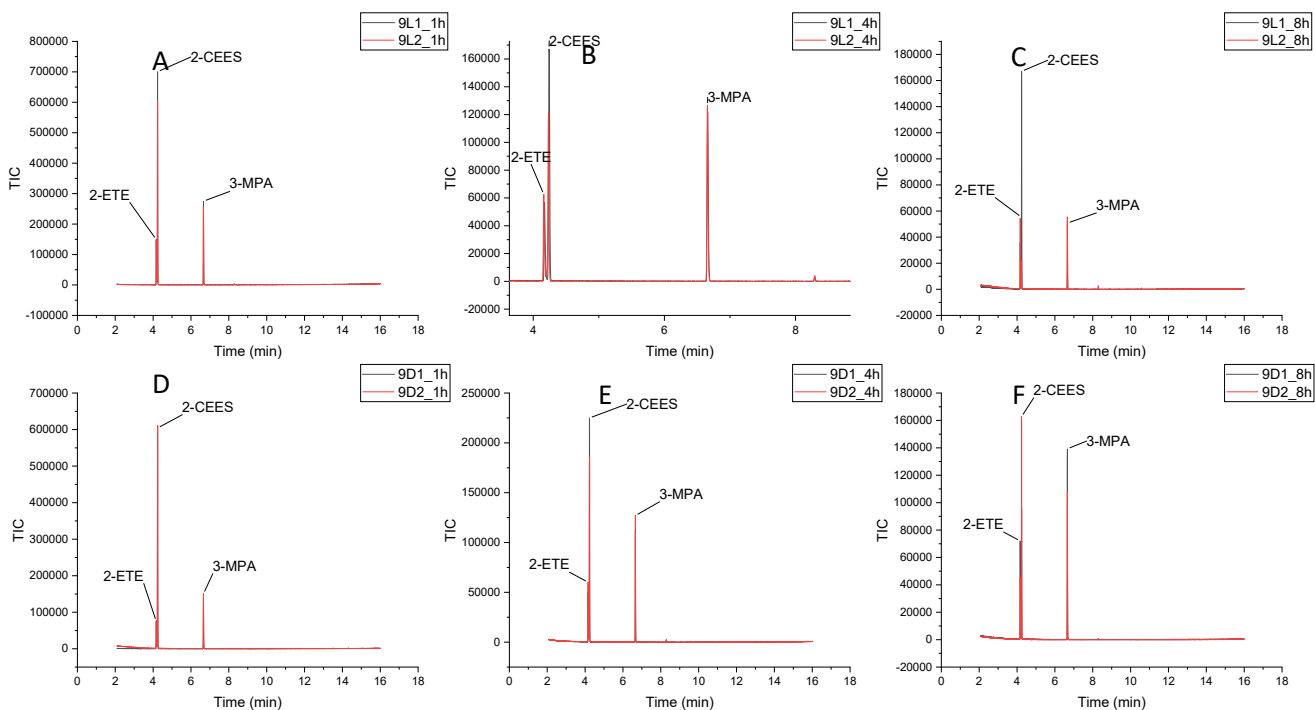


Figure 2.1.40. GC-MS chromatographs of 2-CEES 24 h assessment for Sample 9 (7 mg). The sample was assessed under light (A-C) and dark (D-F) conditions. Deposition of 2.07×10^{-6} mol of 2-CEES into the vial from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of dichloromethane.

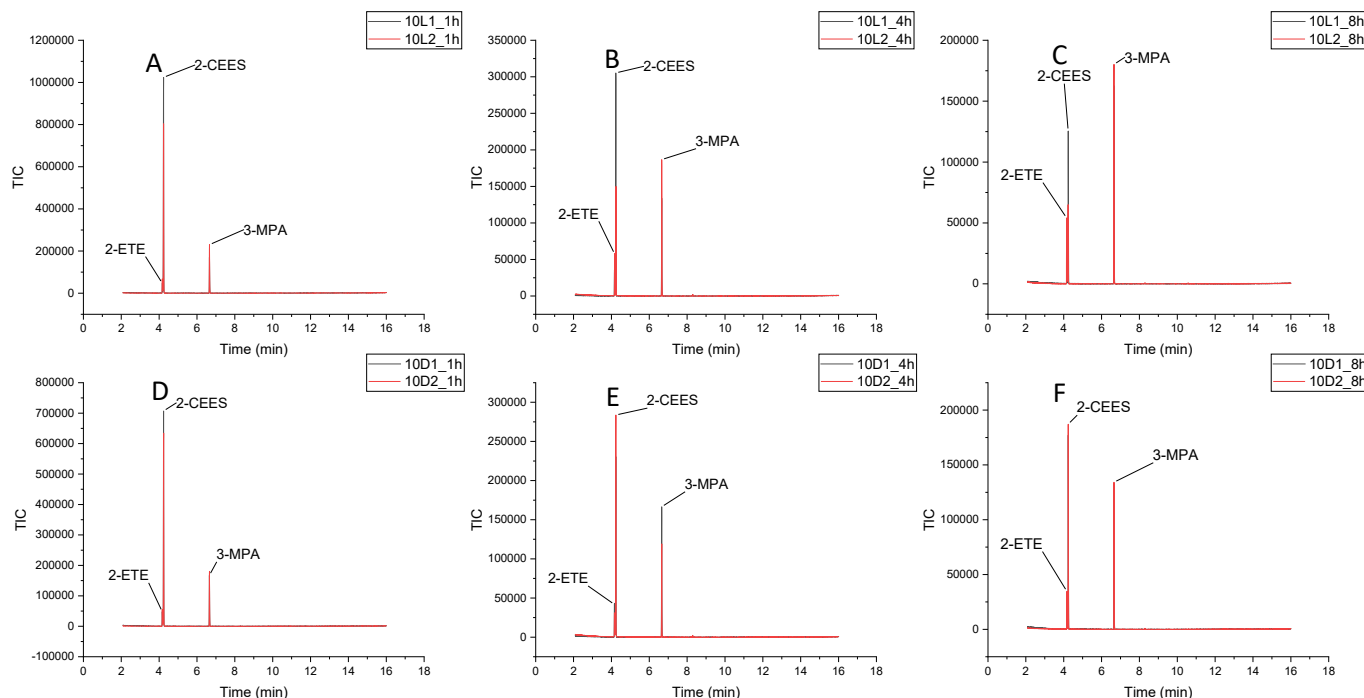


Figure 2.1.41. GC-MS chromatographs of 2-CEES 24 h assessment for Sample 10 (7 mg). The sample was assessed under light (A-C) and dark (D-F) conditions. Deposition of 2.07×10^{-6} mol of 2-CEES into the vial from 25 μ L of 2-CEES stock solution containing 19.25 μ L of 2-CEES in 2 mL of dichloromethane

Table 11. Calculated ratio of 3-MPA to 2-ETE throughout hourly study.

Sample#	Name	Environment	Ratio of 3-MPA : 2-ETE			
			1 h	4 h	8 h	24 h
3	JAB1261E	Dark	1 : 1.8	1 : 1.8	1 : 1.6	1 : 6.4
		Light	1 : 1.9	1 : 1.7	1 : 1.6	1 : 6.5
7	JAB1261A	Dark	1 : 1	1 : 1	1.1 : 1	1 : 2.7
		Light	1 : 1.1	1 : 1	1.5 : 1	1 : 1.7
8	JAB1261B	Dark	1.1 : 1	1.2 : 1	1.4 : 1	1 : 2.2
		Light	1.1 : 1	1.2 : 1	1.3 : 1	1 : 1.7
9	JAB1261C	Dark	1.9 : 1	2.1 : 1	2.1 : 1	1 : 1
		Light	1.8 : 1	2.1 : 1	1.5 : 1	1.4 : 1
10	JAB1261D	Dark	3.5 : 1	3.7 : 1	3.7 : 1	1.2 : 1
		Light	3.2 : 1	3.4 : 1	3.3 : 1	1.5 : 1

The ratio of each product remained relatively the same until 24 h. There is a significant increase in 2-ETE for Sample JAB1261E, JAB1261A, and JAB1261B. In samples JAB1261C and JAB1261D, 3-MPA was the initial favored product and then decreased relative to 2-ETE, which indicates hydrolysis as the main mechanism for decomposition. The MPA product was not stable and subsequently hydrolyzed to the alcohol. Analysis is still ongoing to determine the production pathway of 3-MPA. Analysis of 2-CEES conversion efficiency shows that *ca* 40% 2-CEES is converted to reaction products within 1 h in the dark (Figure 2.1.42), and 60-80% reacts within 4 h (Figure 2.1.42)

These results clearly demonstrate that JAB1261E, JAB1261A, JAB1261B, JAB1261C, and JAB1261D all rapidly and effectively decompose 2-CEES in dark aconditions. Among this sample set, degradation of 2-CEES resulted in the formation of two competing products, 2-ETE and 3-MPA, after

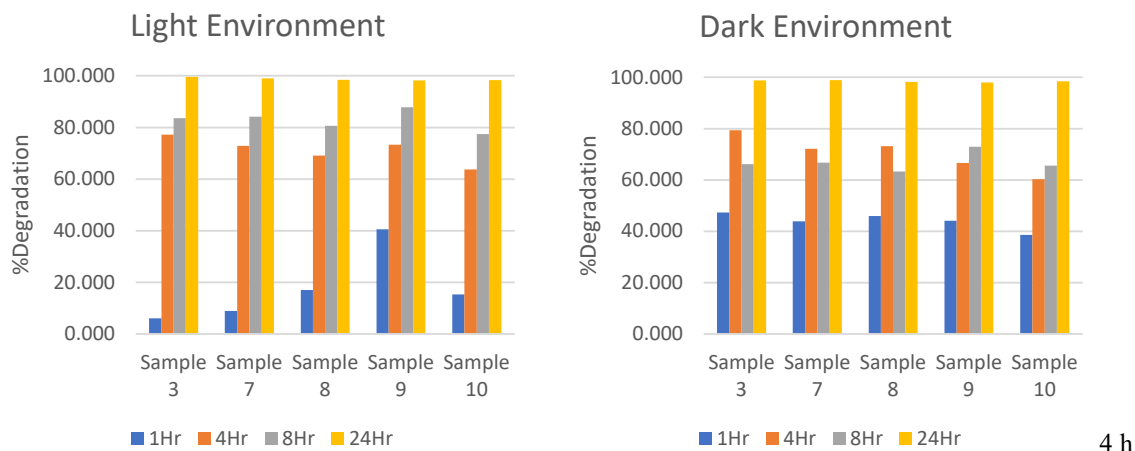


Figure 2.1.42. Degradation of 2-CEES at 1 h, 4 h, 8 h, and 24 h in light and dark environments.

cleavage of the C-Cl bond. The results suggest that 3-MPA is an unstable intermediate product that ultimately hydrolyzes to 2-ETE. The mechanism of formation of 3-MPA is currently under investigation.

Task 3. Sensing of CWA simulants decomposition products

Subtask 3.1 Feasibility of 2-CEES and 2-CEESO detection on a glassy carbon electrode in a three electrode electrochemical cell

We started electrochemical experiments with 2-CEES electrochemical identification due to a shortage of 2-CEESO. Electrochemical experiments were conducted in a three-electrode electrochemical cell. Mirror-polished glassy carbon served as a working electrode, and Pt mesh and Ag/AgCl served as a

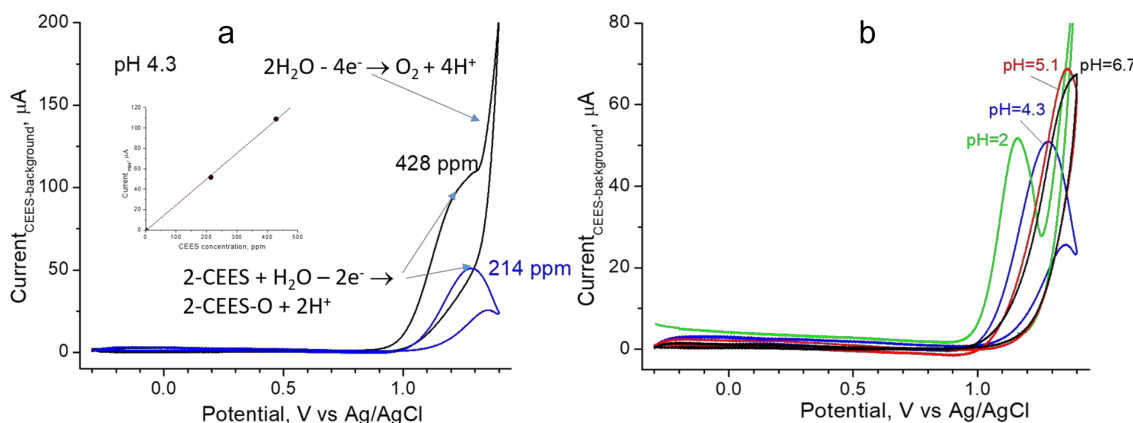
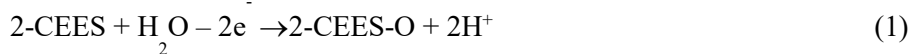


Figure 3.1.1. Corrected for background current vs. potential curves recorded on glassy carbon electrodes at 100 mV/s in 10% CH₃CN+0.1M Britton-Robinson buffer solution at (a) pH 4.3 and two different 2-CEES concentrations (214 and 428 ppm), and (b) different pH in the presence of 214 ppm 2-CEES. Inset Figure 1a shows correlation between the 2-CEES concentration and current at 1.25V.

counter and a reference electrodes, respectively. First, we demonstrated that 2-CEES can be oxidized electrochemically. Figure 3.1.1a shows current vs potential curves measured on glassy carbon electrodes in solutions of 10% CH₃CN+0.1M Britton-Robinson buffer solution at pH 4.3 in the presence of 214 and 428 ppm 2-CEES. The maxima at 1.25 V are presumably due to 2-CEES oxidation to 2-CEESO according to Eq. 1 below:



In order to prove that the currents peaked at 1.25 V in Fig. 1b are due to 2-CEES oxidation, the current was plotted as a function of 2-CEES concentration (see inset in Fig. 3.1.1). The linear relationship between the maximal current and 2-CEES concentration confirms that the peak at 1.25V is due to 2-CEES oxidation. Another important feature of the plots shown in Fig. 3.1.1 is the current increase with potential at $E > 1.4\text{V}$ for the higher 2-CEES concentration. The rising current branch is due to water oxidation reaction as shown below:



The overlap between reactions (1) and (2) can be minimized by adjusting the pH of Britton-Robinson buffer, as protons are involved in both reactions. The pH was adjusted by varying concentrations of NaOH, CH₃OH, H₃PO₄, and H₃BO₃ in Britton-Robinson buffers. Figure 3.1.1 b shows current vs potential curves measured in 10% CH₃CN+Britton-Robinson buffer solutions of different pH. One can see that the peak due to 2-CEES oxidation shifts to more negative potentials and becomes better separated from water oxidation branch with decrease in pH. Thus, pH 2 is an optimal pH for 2-CEES electrochemical identification. In addition to Britton-Robinson buffer in combination with CH₃CN, we tested it in combination with CH₃OH. We also explored lower pH regions (<2) by replacing Britton-Robinson buffers by 0.05 and 0.1M HClO₄. All the tested solution compositions are listed in Table 12. The best 2-CEES peak separation was observed for 10% CH₃CN+Britton-Robinson buffer at pH 2. The well-pronounced maximum at more positive potential of 1.3 V was also observed at pH 4.3. In addition to optimizing solution composition, we also attempted to optimize electrode material. The material of 2nd choice was nanostructured TiO₂ due to its activity towards 2-CEES oxidation under visible light excitation. However, experiments with thin-film TiO₂ electrodes did not produce promising results.

Table 12. Solution compositions utilized in electrochemical experiments

	Solution composition	Aqueous to non-aqueous phase ratio (v:v)
1	0.05 M HClO ₄ +CH ₃ OH	50:50
2	0.1M HClO ₄ +CH ₃ CN	90:10
3	0.1M HClO ₄ +CH ₃ CN	50:50
4	0.1M Britton-Robinson buffers (pH 1.86, 3.1, 4.0)+CH ₃ OH	50:50
5	0.1M Britton-Robinson buffers (pH 2, 3.6, 4.3, 5.1, 6.7)+CH ₃ CN	90:10

The simplest way to determine 2-CEES concentration electrochemically is known as amperometric detection, i.e. current measurement as a function of time at a certain applied potential. Then concentration of the analyte is determined from the calibration plot. In order to plot such calibration curve, we measured a series of current vs time curves in 10% CH₃CN+Britton-Robinson buffer solutions at pH 4.3 at applied

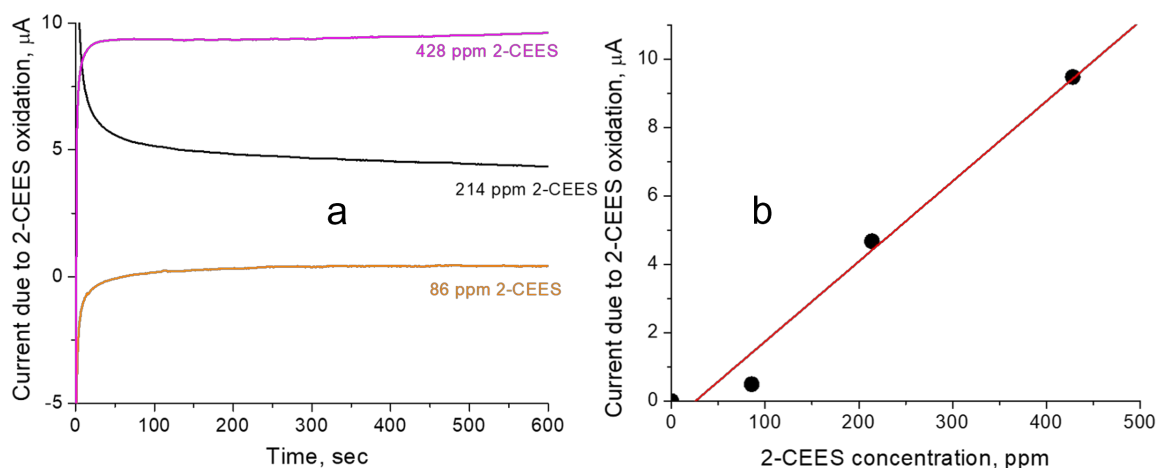


Figure 3.1.2. (a) Current transients measured at applied potential of 1.3 V in 10% CH₃CN+0.1M Britton-Robinson buffer solution at pH 4.3 on glassy carbon electrodes in the presence of 86, 214 ppm and 428 ppm CEES; (b) Current at t=200 sec in Figure 2a vs. CEES concentration.

potential of 1.3 V. Current vs time curves measured at three CEES concentrations are shown in Figure 3.1.2a. Currents plateau at 25 sec for 86 and 428 ppm CEES. For 214 ppm CEES, plateau is not as flat as for two other CEES concentrations likely due to the presence of some impurities on the electrode. Current measured at 200 sec in Figure 2a vs 2-CEES concentration displays linear correlation as is shown in Figure 3.1.2b. This confirms feasibility of 2-CEES electrochemical detection. We expect to obtain even better correlation at pH 2, which was found to be an optimal pH for separation of reactions of 2-CEES and H₂O oxidation.

After proving the feasibility of 2-CEES electrochemical detection, we moved to electrochemical characterization of 2-CEESO oxidation under conditions that were found to be optimal for 2-CEES

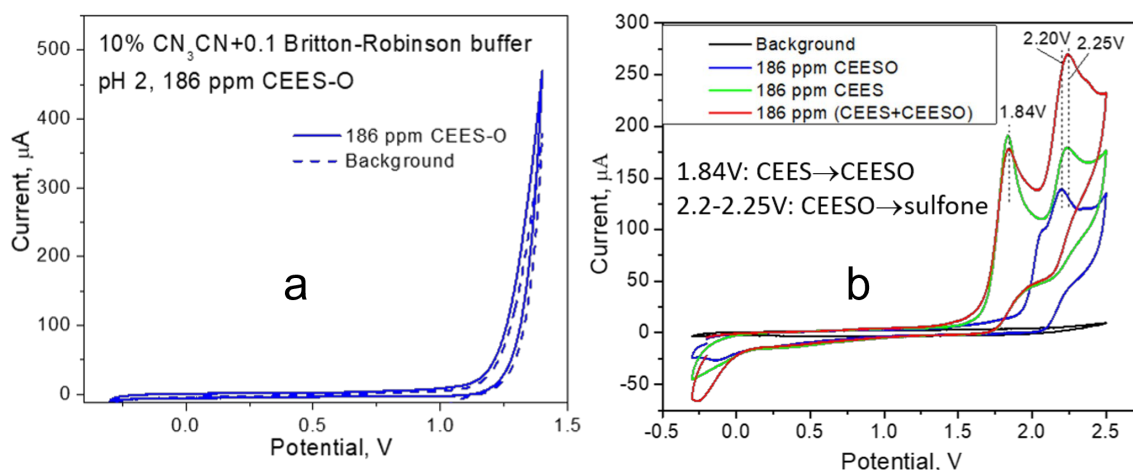


Figure 3.1.3. Current vs. potential curves recorded on glassy carbon electrode at 100 mV/s in (a) 10% CH₃CN+0.1M Britton-Robinson buffer solution adjusted to pH 2 in the presence of 186 ppm CEESO; (b) 0.1M TBAPF₆+CH₃CN in the presence of 186 ppm 2-CEESO (blue), 186 ppm 2-CEES (red) and the mixture of the two.

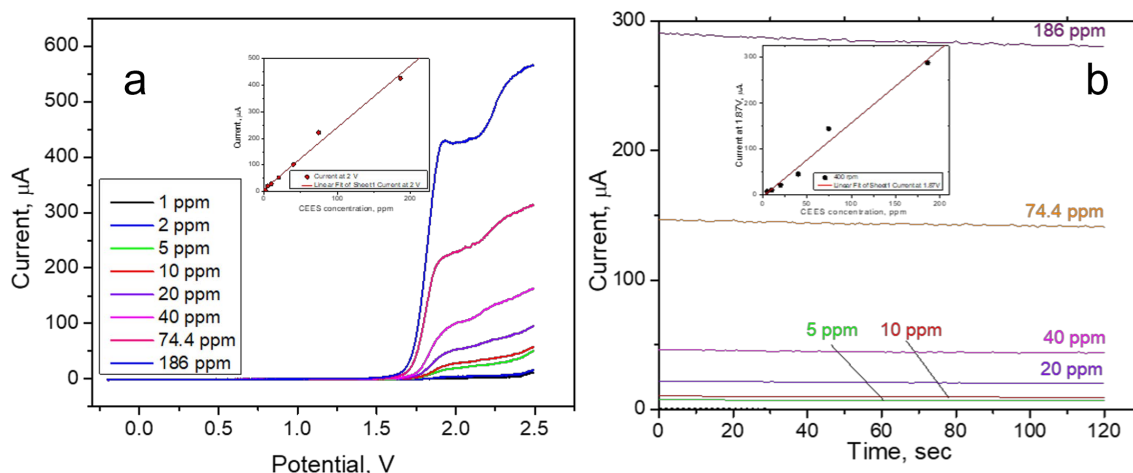


Figure 3.1.4. (a) Current vs. potential curves recorded at 100 mV/s in 0.1M TBAPF₆+CH₃CN solution at different 2-CEES concentrations. Inset shows currents measured at 2 V as a function of concentration; (b) Current vs. time curves measured at 1.87 V for different 2-CEES concentrations. Inset shows current measured at 20 sec as a function of CEES concentration. 0.1M TBAPF₆+CH₃CN solution, glassy carbon electrode, 400 rpm.

oxidation, i.e. in the presence of 10% CH₃CN+0.1M Britton-Robinson at pH 2. Figure 3.1.3 a shows cyclic voltammetry (CV) curve (solid blue line) measured in the presence of 186 ppm 2-CEESO vs background curve (dashed line). The rising branch at potentials above 1.2 V in the background curve is due to water oxidation. The curve measured in the presence of 2-CEESO share the same features with the background curve, which implies that CEESO oxidation occurs at potentials more positive than water oxidation. As such, 2-CEESO cannot be detected electrochemically in aqueous solvent, and an alternative solvent must be selected that have a broader potential window than H₂O. Acetonitrile seems to be a good choice, since its potential window can be extended up to 3V. Therefore, the next series of experiments was carried in 0.1M TBAPF₆+CH₃CN. The CV curves recorded on glassy carbon electrodes in the presence of 186 ppm CEES, 186 ppm CEESO and the mixture of 186 ppm CEES +186 ppm CEESO are displayed in Figure 3.1.3 b. It can be clearly seen that 2-CEES and 2-CEESO oxidation currents can be separated in CH₃CN. While the oxidation of 2-CEESO (blue line) occurs at 2.2-2.25 V, 2-CEES (green line) is oxidized at more negative potential of 1.84 V. Note the presence of the two peaks at 1.84 V and 2.25V on 2-CEES electrochemical oxidation curve. The peak at 2.25V is due to oxidation of 2-CEESO produced by CEES oxidation to a corresponding sulfone. In the mixture of 2-CEES+2-CEESO (red curve), two peaks can be clearly seen too. An important conclusion can be drawn from the arrangement of the curves shown in Figure 3.1.3b: 2-CEESO detection will be more complicated in the presence of 2-CEES, as the total 2-CEESO oxidation current needs to be corrected for the current of 2-CEESO oxidation produced by CEES.

Next, the 2-CEES detection limit was determined. The series of eight current-potential curves were measured at CEES concentration in the range of 1 ppm to 186 ppm (see Figure 3.1.4a). We start seeing deviation from the background current due to 2-CEES oxidation at concentrations of 1-2 ppm (e.g. 1.6 μA at 1 ppm). In order to enhance 2-CEES diffusion to the electrode surface and increase sensitivity, we used rotating electrode in these experiments. In a real device, we plan to use a cell with the flowing electrolyte in order to optimize 2-CEES diffusion conditions. One can see from Fig. 3.1.4a, that 2-CEES oxidation current increases with 2-CEES concentration. This is an expected behavior that confirms that the current is due to 2-CEES oxidation. Quantitative analysis shows that the current at a fixed potential grows with 2-CEES concentration in a linear fashion as shown in the inset in Figure 3.1.4a.

To prove that CH₃CN-based electrolyte can be used for amperometric 2-CEES detection, we conducted a series of experiments at potentiostatic conditions, when working electrodes were held at a constant potential in the region of 2-CEES oxidation, i.e.1.87 V, as shown in Figure 3.1.4b. One can see

that the current decreases slightly with time for each 2-CEES concentration. However, this change is not significant, which implies that 2-CEES oxidation products do not contaminate the electrode surface.

In a following step, current vs 2-CEES concentration plot was constructed to ensure that linear correlation is observed (see inset in Figure 3.1.4b). The linear relationship can serve as a calibration plot for 2-CEES electrochemical detection. 2-CEESO detection limit will be determined in a similar fashion. Next, we plan to validate the results of experiments in electrochemical cell in a flow cell that utilizes a commercial screen-printed electrode.

Subtask 3.2. Feasibility of CEES electrochemical identification using commercial carbon screen-printed electrodes (SPEs)

After proving feasibility of 2-CEES and 2-CEESO electrochemical detection in a three-electrode electrochemical cell, we moved to evaluation of a CEES electrochemical response in a more practical

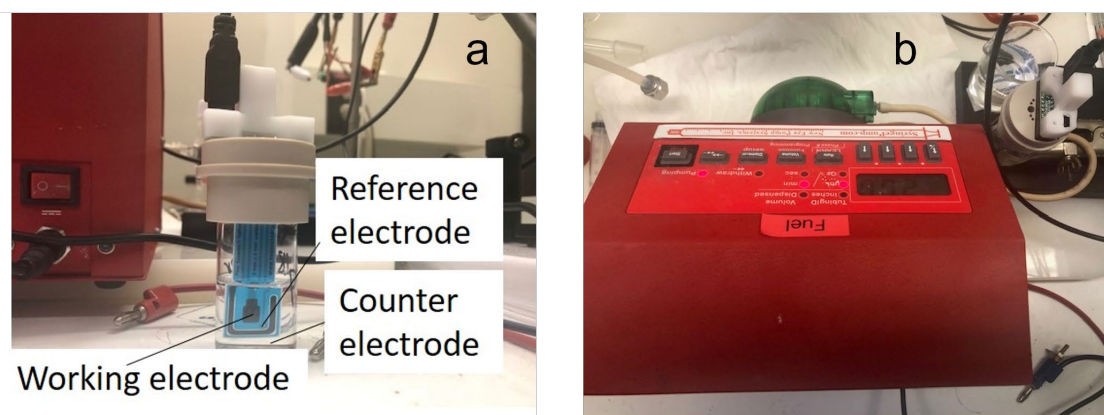


Figure 3.2.1. (a) Carbon SPE (Pine Research) immersed in 10 vol% $\text{CH}_3\text{CN}+0.1\text{M}$ Britton-Robinson buffer solution adjusted to pH 2; (b) Peristaltic pump connected to electrochemical cell utilizing SPE (top view)

setting. Screen-printed electrodes (SPEs) immersed in a vial with an electrolyte were examined as an alternative to a conventional electrochemical cell. Figure 3.2.1a shows commercial (Pine Research) carbon SPE immersed in solution of 10 vol % $\text{CH}_3\text{CN}+0.1\text{M}$ Britton-Robinson buffer solution adjusted to pH 2. The advantage of using the SPEs instead is in minimizing the cell and electrolyte volume. Because SPE's availability and low price, they can be used as a disposable option. One can see from the Figure 3.2.1a

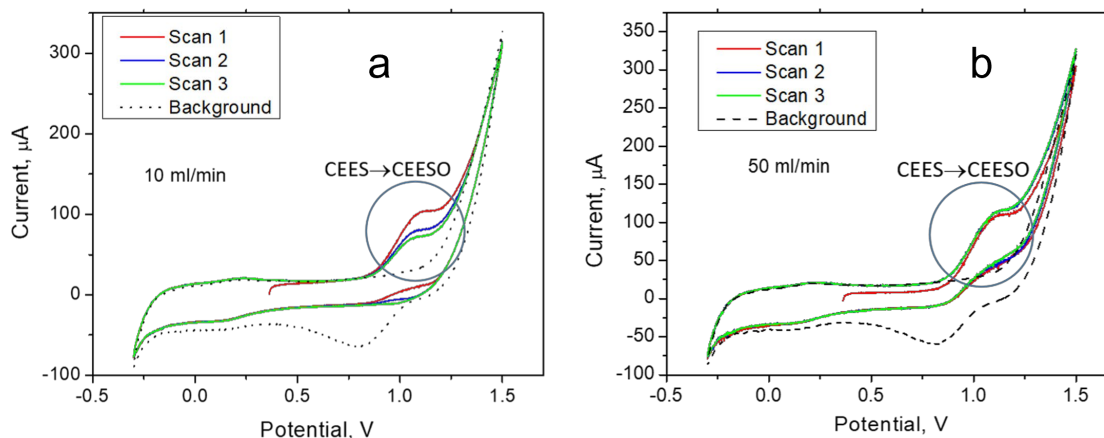


Figure 3.2.2. Current vs. potential curves recorded on carbon SPE at 100 mV/s in 204 ppm CEES + 10 vol % $\text{CH}_3\text{CN}+0.1\text{M}$ Britton-Robinson buffer at pH 2 at (a) 10 and (b) 50 ml/min flow rate. Dashed curve represents 10 vol % $\text{CH}_3\text{CN}+0.1\text{M}$ Britton-Robinson buffer.

that all three electrodes (working, counter and reference) are printed on the in the plate in a close proximity to each other. Reference electrode is a tiny Ag/AgCl round spot located between the working and counter electrodes. Both working and counter electrodes are made of carbon black printed on a conductive polymer subbstrate. Because this electrode is not suitable for experiments in non-aqueous electrolytes, all experiments were conducted in 10 vol % CH_3CN +0.1M Britton-Robinson buffer aqueous solutions. Prior to carrying out electrochemical experiments, SPEs were activated by potential cycling in 0.05 M H_2SO_4 . Our initial experiments demonstrated that electrolyte stirring was critical for obtaining a reproducible 2-CEES oxidation signal. Electrolyte was pushed through the cell by peristaltic pump shown in Figure 3.2.1b. The cell (20 ml vial) was modified by adding the in- and out-ports to enable connection to the pump. In order to optimize an electrolyte flow rate through the cell, a series of cyclic voltammetry curves (CVs) were measured. Figure 6a shows a series of cyclic voltammetry curves measured at a flow rate of 10 ml/min. One can see that current increases at potentials around 1.12 V due to 2-CEES oxidation to 2-CEESO. Current due to 2-CEES oxidation decreases with each successive scan, prior to acquiring a consistent value. Current decrease is likely due to 2-CEES depletion near the surface due to slow 2-CEES diffusion. As one would expect, increase in a flow rate leads to an increase in the current. Indeed, at a flow rate of 50 ml/min initial current due to 2-CEES oxidation is greater than that at 10 ml/min and, in addition, it is not affected by successive potential scanning (see Figure 3.2.2b). This is likely due to better diffusion of 2-CEES molecules to the electrode surface provided by a flowing electrolyte. In order to explore the effect of the electrolyte flow rate in more detail, cyclic voltammetry curves were measured at different flow rates as shown in Figure 3.2.3a. An increase in the flow rate from 1ml/min to 50 ml/min leads to a significant increase in a current of 2-CEES oxidation. This effect can be better visualized after correction of the currents measured in the presence of 2-CEES by the background current, as shown in Figure 3.2.3b. The peaks at *ca.* 1.12V are due to CEES oxidation. The peak height increases with an increase in a flow rate due to an enhanced 2-CEES diffusion to the surface. A dramatic 4X increase in a peak current in observed for 50 ml/min vs 1 ml/min.

To prove that carbon SPEs can be used for amperometric 2-CEES detection, we conducted a series of experiments at potentiostatic conditions, when working electrodes were held at a constant potential in the region of 2-CEES oxidation, i.e. 1.12 V, as shown in Figure 3.2.3c. The flow rate varied from 1 to 50 ml/min. One can see that the current (1) increases with a flow rate; and (2) decreases slightly with time for a given flow rate. However, this change is not significant (within 10% for 1, 20 and 50 ml/min), which implies that 2-CEES oxidation products do not accumulate on the electrode surface in significant extent.

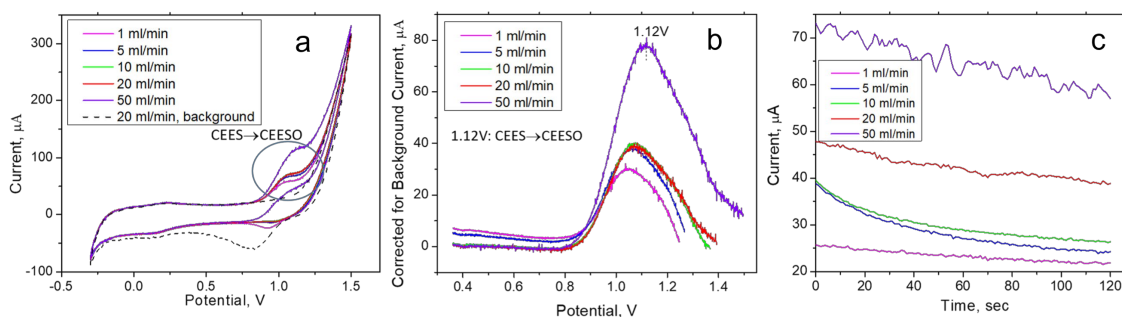


Figure 7. (a) Current vs. potential curves recorded at 100 mV/s on carbon SPEs in 204 ppm CEES + 10 vol % CH_3CN +0.1M Britton-Robinson buffer at pH 2 at different electrolyte flow rates; (b) Background-corrected currents from Figure 7a; (c) Current vs time curves recorded while holding potential of the working electrode at 1.12V. Flow rates vary

Higher flow rates obviously have advantage due to higher currents that provide better sensitivity.

In addition to carbon SPE, Au SPE was tested in order to promote 2-CEES oxidation rate. However, Au electrode appeared to be active towards CH_3CN oxidation.

In conclusion, carbon SPEs can be utilized for 2-CEES electrochemical detection from 10 % $\text{CH}_3\text{CN} + 0.1\text{M}$ Britton-Robinson buffer aqueous solutions, if peristaltic pump is used for optimization of 2-CEES diffusion.

2-CEES electrochemical detection using commercial boron-doped diamond SPEs

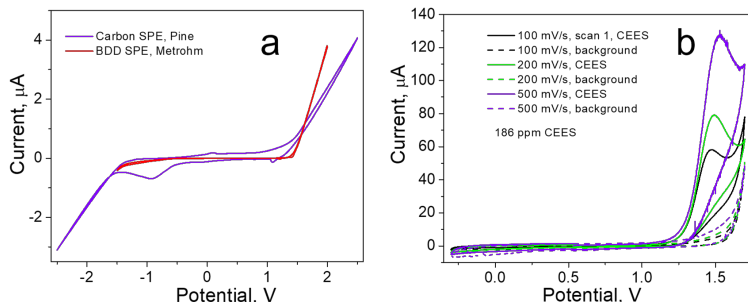


Figure 3.2.4. Current vs potential curves measured on (a) BDD (red) and carbon (violet) SPEs at 100 mV/s in 50 mM H_2SO_4 , and (b) BDD SPEs immersed in solution of 204 ppm 2-CEES + 10 vol % $\text{CH}_3\text{CN} + 0.1\text{M}$ Britton-Robinson buffer at pH 2 at scan rates of 100, 200, and 500 mV/s.

In order to optimize CEES electrochemical detection on commercially available screen-printed electrodes (SPEs), we utilized boron-doped diamond (BDD) SPEs (Metrohm). The advantages of these electrodes are in (1) a broader stability window in aqueous electrolytes vs carbon, i.e. lower activity towards water oxidation; (2) lower double layer capacitance (i.e. lower background

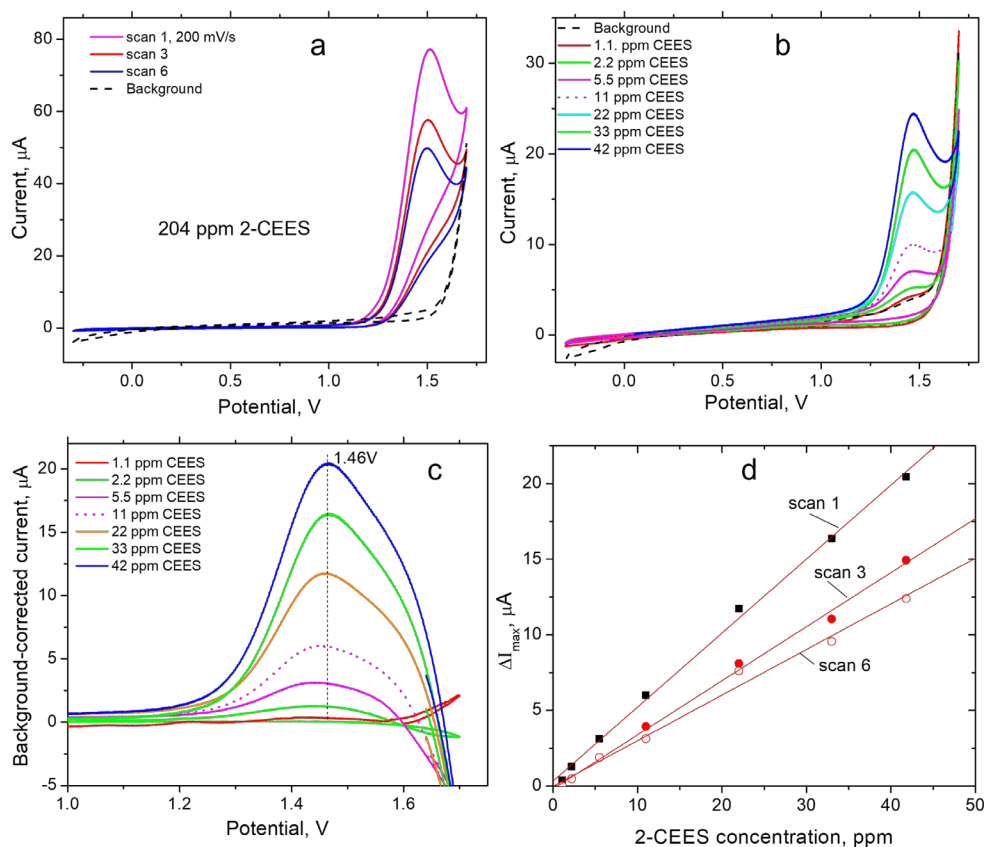


Figure 3.2.5. Current vs potential curves measured on BDD SPEs immersed in solutions of (a) 204 ppm 2-CEES + 10 vol % $\text{CH}_3\text{CN} + 0.1\text{M}$ Britton-Robinson buffer at pH 2 and (b) 2-CEES + 20 vol % $\text{CH}_3\text{CN} + 0.1\text{M}$ Britton-Robinson buffer at pH 2, scan 1 is shown. (c) Background-corrected currents shown in Figure 9b vs potential; (d) maximal background-corrected current vs 2-CEES concentration (calibrations plots) deduced from scans 1, 3, and 6. Dashed curves in Figure 9 a and b represent background currents. Scan rate 200 mV/s

current); and (3) lower activity towards adsorption of organic molecules in comparison to carbon. Prior to

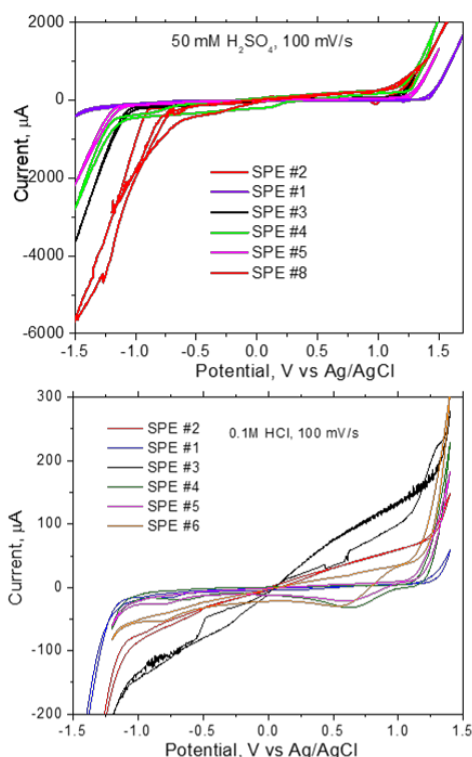


Figure 10. CV curves recorded on BDD SPEs immersed into 0.05 M H_2SO_4 and 0.1M HCl solutions. The curves shown in the top panel were collected from the older batch of electrodes. Scan rate 100 mV/s

number of CV scans necessary to achieve reproducible results. In particular, the following parameters have been selected for optimization: (1) scan rates of 100, 200, and 500 mV/s; (2) cathodic vertex potentials of -0.3; 0.2; 0.5; and 1.0V; (3) anodic vertex potentials of 1.5; 1.6; and 1.7V; and (4) number of CV scans equal to 1, 3 and 6.

Figure 3.2.4b illustrates the effect of scan rate on the 2-CEES oxidation current for 2-CEES concentration of 204 ppm. One can see that the current in maximum increases from 58 μA to 126 μA with increase in the scan rate from 100 to 500 mV/s. However, 200 mV/s was selected as an optimal scan rate (*ca* 80 μA maximal current), considering that the current range of electrochemical reader is 200 μA . Regarding the cathodic and anodic vertex potentials they were set to -0.3 and 1.7 V, respectively. Figures 3.2.5 a and b show a representative series of CV curves measured at 200 mV/s in the potential range from -0.3 to 1.7V. In Figure 3.2.5 a, three out of six consecutive CV scans are shown, which clearly demonstrate that 2-CEES oxidation current decreases with every consecutive scan. In order to determine the optimal number of scans, necessary to reliably determine 2-CEES concentrations, six consecutive CV scans were measured for each 2-CEES concentrations in the range from 1.1 to 42 ppm. Each of CV curves displayed in Figure 3.2.5 b corresponds to scan 1. Similar series of CVs were plotted for scans 3 and 6 (not shown in the Figure). In order to eliminate contribution from background current, all currents in Figure 3.2.5 b were corrected for such current. The resulting currents (i.e. currents due to 2-CEES oxidation) are shown in Figure 3.2.5 c. To determine if there is a linear correlation between the maximal current and 2-CEES concentration, calibration plots were derived from the curves shown in Figure 3.2.5 c and similar curves obtained for scans 3 and 6. The resulting calibration curves are shown in Figure 3.2.5 d. Obviously, the best

carrying out 2-CEES electrochemical oxidation, electrodes were activated in 0.1M HNO_3 by applying 800 μA for 60 sec. Figure 3.2.4a compares cyclic voltammetry (CV) curves recorded on the BDD and carbon SPEs. One can see that water oxidation starts at more positive potential on BDD SPE than on carbon (1.42 V vs 1.2 V for BDD vs carbon, respectively). In addition, the BDD electrode demonstrates lower double layer charging current in the potential region between 0 V and 1.4 V. The advantage of Metrohm's SPEs is in that they can be integrated with the Metrohm's electrochemical reader, a very simple hand-held potentiostat, that can run only a few basic electroanalytical techniques, such as cyclic voltammetry, square wave voltammetry, etc. Cyclic voltammetry has several advantages over amperometry that had been explored at an earlier stage of our program. First, cyclic voltammetry provides stronger signal due to the fact, that 2-CEES oxidation current (proportional to 2-CEES concentration gradient) can be controlled by the rate of changing the applied potential (i.e. scan rate). Second, this method provides a shorter response time. For example, it takes only 40 sec to run CV in potential range of 2V at a scan rate of 100 mV/s, while current stabilization in amperometry requires $\sim$ 120 sec. However, prior to utilizing it for 2-CEES detection, this method needs to be optimized in terms of scan rate, cathodic and anodic vertex potentials, and the

linear correlation ($R^2=0.997$) and the highest currents were obtained for scan 1. Therefore, only one CV scan is necessary to determine 2-CEES concentration from electrolyte solution.

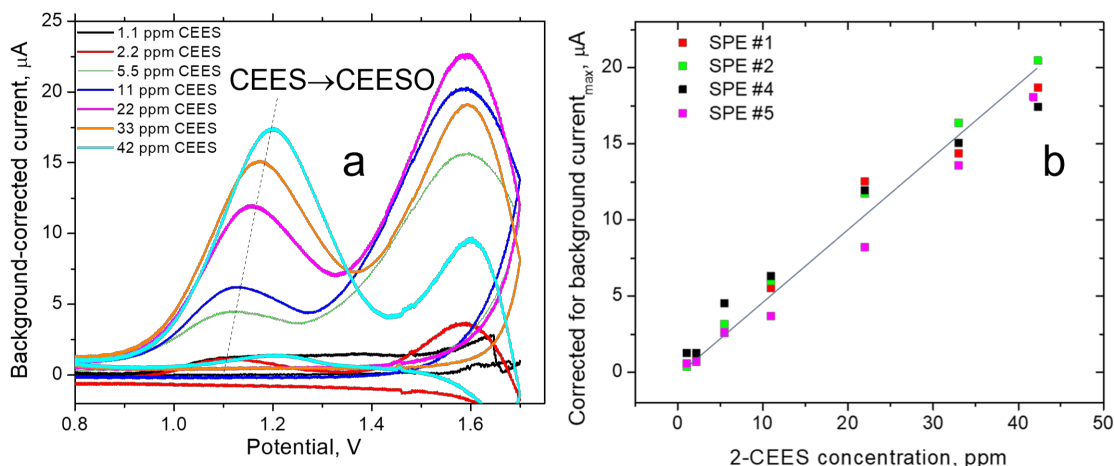


Figure 11. (a) Corrected for background CV curves recorded on the BDD SPE immersed in solutions of 2-CEES in 20 vol % $CH_3CN+0.1M$ Britton-Robinson buffer at pH 2, scan rate 200 mV/s, 1st scan is shown; (b) Corrected-for-background maximal current of 2-CEES oxidation vs 2- CEES concentrations measured for four different SPEs.

Next, reproducibility of commercial BDD SPEs was assessed. Fifteen SPEs from two different batches were tested (9 electrodes from one batch, and six electrodes from another one). First, their performance was assessed in inert electrolytes such as 0.05M H_2SO_4 and 0.1M HCl . We expected to observe low current in the wide potential region (*ca* 3V) due to low activity of BDD electrodes towards water reduction and oxidation. However, as one can see from Figure 3.2.6, not all SPEs act according to our expectations. Only one electrode out of six (SPE #1, old batch, violet curve) in Figure 3.2.6 a demonstrates an ideal behavior. For this electrode, low current is observed within potential window of 3V (from -1.5 to 1.5V). The performance of the SPEs from a newer batch shown in Figure 3.2.6 b appears to be more reproducible, with the three electrodes out of six (SPEs #1, #4, and #5) showing similar performance. Being aware of this issue, Metrohm discontinued manufacturing the BDD SPEs.

Next, four electrodes with similar performance were selected for evaluation of 2-CEES electrochemical oxidation and construction of calibration curves. CV curves were measured in solutions of 20 vol% $CH_3CN+0.1M$ Britton-Robinson buffer (pH 2) in the presence of different 2-CEES concentrations. Figure 3.2.7 a shows a representative series of corrected-for background curves. The peak at *ca* 1.2 V is due to 2-CEES electrochemical oxidation. On other electrodes (not shown in the Figure), potential at which maximal current was observed varied between 1.15 and 1.45V. Figure 3.2.7 b shows maximal background corrected currents of 2-CEES oxidation as a function of 2-CEES concentration for four SPEs. Although there is discrepancy between the points, they fall on the straight line that can be used to determine 2-CEES concentration. This discrepancy is due to inconsistency in the surface properties of different electrodes.

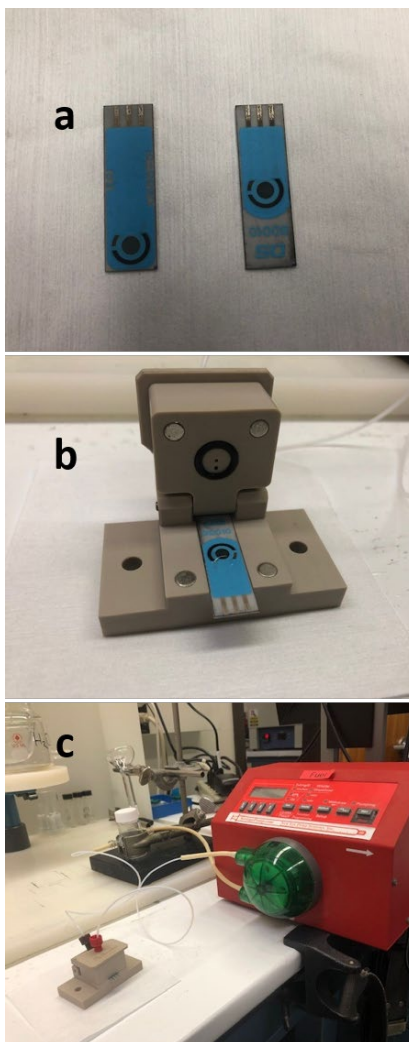


Figure 3.2.8. (a) BDD SPEs (Metrohm); (b) BDD SPE mounted in electrochemical cell; (c) electrochemical cell connected to peristaltic pump.

Interestingly, even though potentials of maximal currents of 2-CEES oxidation are not the same, currents remain almost the same for a given 2-CEES concentration.

Assessment of a miniature flow cell for 2-CEES detection

In order to miniaturize electrochemical setup for 2-CEES detection, we assessed performance of a commercial miniature flow cell, provided by Metrohm. The flow of electrolyte is provided by peristaltic pump. Commercial BDD SPEs, flow cell, and flow cell connected to a peristaltic pump are shown in Figure 3.2.8 a, b and c, respectively. Electrolyte enters and leaves the cell through two ports located at the top of the cell. Two magnets installed in the top and bottom parts of the cell keep the cell sealed. The volume of electrolyte in the cell is *ca* 50 μl . Figure 3.2.9 a shows the CV curve recorded in solution of 20 v% CH_3CN + 0.1M Britton-Robinson (pH 2) buffer in a miniature cell in comparison to that in an electrochemical cell (i.e. 20 ml vial). The two CVs are in a good agreement. Next, the series of CVs curves was collected in the flow cell in the presence of 1, 2, 5 and 10 ppm 2-CEES. Fig. 3.2.9 b and c compares CV curves recorded in the presence of different 2-CEES concentrations. Surprisingly, no peaks of 2-CEES oxidation is observed even at concentrations as high as 10 ppm 2-CEES. Also, in our previous experiments we observed increase in current with increase in 2-CEES concentration at potentials of 2-CEES oxidation (i.e above 1.2 V). Unfortunately, this is not the case. For instance, at 1.5 V current drastically increases with increase in 2-CEES concentration from 1 to 2 ppm, and then drops with further increase in concentration to 5 and 10 ppm. To explore further this phenomenon, we measured CVs in the presence of higher concentrations of 2-CEES (20, 30 and 38 ppm, Figure 3.2.9c). The CVs are characterized by a

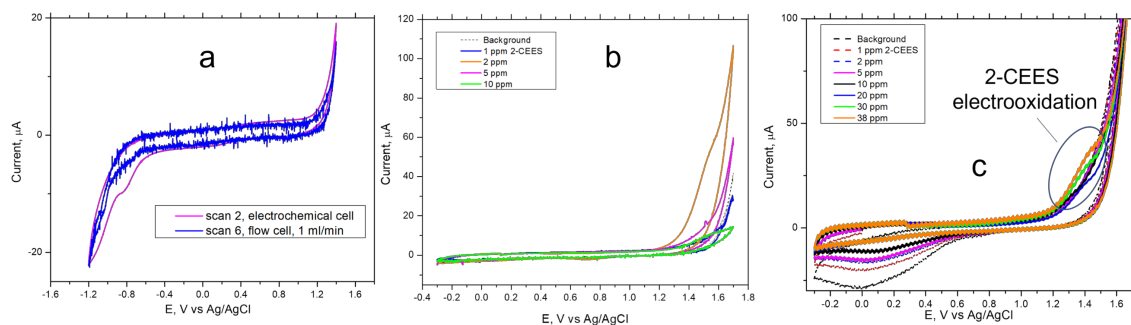


Figure 3.2.9. CV curves, recorded on BDD SPEs at (a) 100 mV/s in electrochemical cell (magenta) and flow cell (blue) at 1 ml/min. Solution – 20 v% CH_3CN + 0.1 M Britton-Robinson buffer (pH 2); (b) 200 mV/s in the presence of 1, 2, 5, and 10 ppm 2-CEES in the flow cell; (c) 200 mV/s in the presence of 1-38 ppm 2-CEES in the flow cell. Electrolyte solution in b and c: 20 v% CH_3CN + 0.1M Britton-Robinson buffer (pH 2).

shoulder at *ca.* 1.4 V due to 2-CEES oxidation. However, the effect is rather small in comparison to our previous experiments. Noticeable current increase in Fig. 3.2.9 c is observed at 2-CEES concentration exceeding 20 ppm (vs 2 ppm in our previous experiments). Such unexpected behavior can be caused by a leak in the cell. We also experienced another inconvenience while working with the flow cell. The electrodes kept developing cracks thus creating leaks in the cell. Eventually, we came to conclusion that a miniature glass electrochemical cell would be a better solution for working with the fragile SPE electrodes in comparison to the Metrohm's flow cell.

Feasibility of 2-CEES electrochemical detection from gas phase

In the battlefield CWAs are present in a vapor phase, which means that the method needs to be developed to generate simulant in a vapor phase and introduce it in electrolyte solution. Following that,

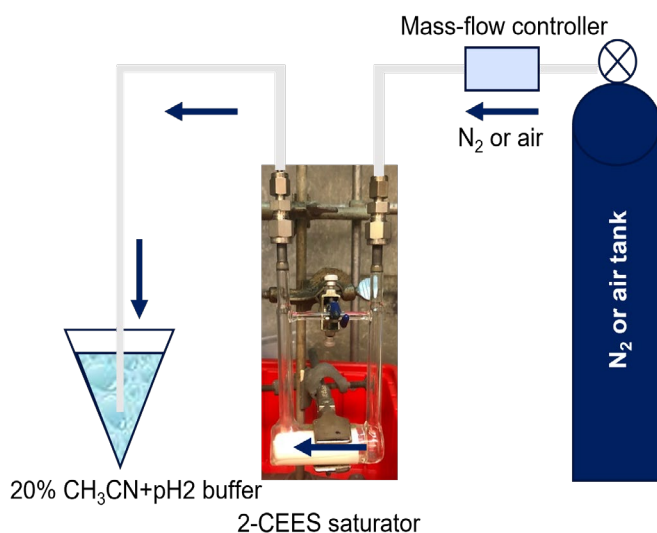


Figure 3.2.10. Schematic of the setup for introduction of 2-CEES vapors into liquid electrolyte. Balance UHP N_2 or synthetic air were used. Flow rate of 5 and 10 ml/min were tested

feasibility of 2-CEES electrochemical detection needs to be assessed. A commercial saturator (Glassblowers, Inc) shown in Figure 3.2.10 was used to generate 2-CEES vapors. Approximately 1/3 of the saturator was filled with liquid 2-CEES. In a saturator, a wick inserted inside the horizontal glass tube, absorbs liquid 2-CEES, and balance gas (N_2 or air) flowing through the wick carries 2-CEES vapors to the flask filled with electrolyte solution. The duration of N_2 or air purge was varied from 1 min to 63 min to determine minimal time necessary to observed 2-CEES signal. The flow of balance N_2 was controlled by a mass flow controller. First, N_2 flow rate was optimized. Figure 3.2.11 compares CV curves measured in electrolyte solutions purged with 2-CEES in balance N_2 flowing at 5 and 10 ml/min.

One can see that at 5 ml/min, the peak of 2-CEES oxidation at *ca.* 1.5 V (Fig. 3.2.11 a, green curve) becomes noticeable only after 5 min exposure to 2-CEES vapors. The CVs measured after purging electrolyte with 2-CEES vapors for shorter time intervals (1 and 2 min) do not reveal any oxidation peaks. On the contrary, when the electrolyte is purged with 2-CEES at a higher rate of 10 ml/min (Fig. 3.2.11 b), a clearly pronounced oxidation peak is observed after 2 min purge. Moreover, the peak current measured after 2 min purge is a factor of two higher than the one observed after purge at 5 ml/min (3.6 μA vs 1.8 μA). The peak current increases with time at $t > 2$ min in Fig. 2b, implying that more 2-CEES from vapor phase dissolves in electrolyte. At 1 and 2 min, the currents measured at 1.5 V are almost identical. However, the shape of the peak becomes more defined with longer purge. Therefore, in all the following experiments 10 ml/min balance gas flow rate was utilized.

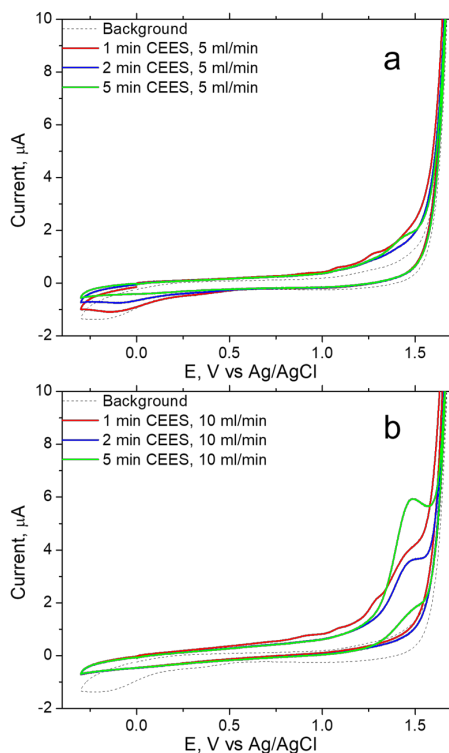


Figure 3.2.11. CV curves measured in solutions of 20 v% CH_3CN +0.1M Britton-Robinson (pH2) buffer purged by 2-CEES in N_2 for 1, 2 and 5 min. Flow rates: (a) 5 ml/min; (b) 10 ml/min. Scan rate 200 mV/s. Electrolyte volume 10 ml

In electrolyte, purged with 2-CEES carried by air, 2-CEES oxidation peak is also observed at *ca* 1.5 V (Figure 3.2.13 b). In a similar manner, the peak current increases in magnitude at $t > 2$ min. At shorter exposure times (1 and 2 min), there is no significant differences between the two currents. However, the more defined maximum is observed safter 2-min exposure. Interestingly, the peak height increases in the presence of oxygen (N_2 vs air, Figure 3.2.13 a vs Figure 3.2.13 b) in the carrier gas. To make a qualitative comparison, we calculated 2-CEES concentrations from the peak currents shown in Figs 3.2.13 a and b. The results of such calculations are presented in Fig. 3.2.13c. 2-CEES concentrations in electrolyte purged with 2-CEES in balance air almost doubles that in balance N_2 . We attribute this effect to promotion of 2-CEES oxidation to 2-CEES-O by molecular oxygen. Another important conclusion that can be drawn from analysis of the CV curves shown in Fig. 3.2.13 is that the sensor response time is expected to be on the order of 1-2 min.

Next, we established correlation between 2-CEES concentrations in balance N_2 and electrolyte solution. This task was accomplished by our informal collaborator from Code 6882 Dr. Keith Perkins utilizing residual gas analysis (RGA)

Figure 3.2.12 shows more data on the effect of purging time on 2-CEES oxidation current (which is proportional to 2-CEES concentration). The CV after 63 min purge was measured to determine whether the 2-CEES peak current reaches a plateau with time, i.e. electrolyte solution becomes saturated with 2-CEES. The inset in Figure 3.2.12 shows that this is not the case. Although the data presented in the inset in Fig. 3.2.12 are not sufficient to claim a linear relationship between the peak current and time, one can conclude that the peak current increases with time in a monotonic manner. This implies that even after prolonged purge of electrolyte solution with 2-CEES, saturation has not been reached. In the next steps, we focused attention on short 2-CEES exposure times, being driven by desire to reduce sensor response time.

Because in the battlefield vapors of CWAs are dispersed in air, which consists of oxygen and nitrogen, in our next series of experiments we compared electrochemical response of 2-CEES introduced in balance air and nitrogen (Figure 3.2.13).

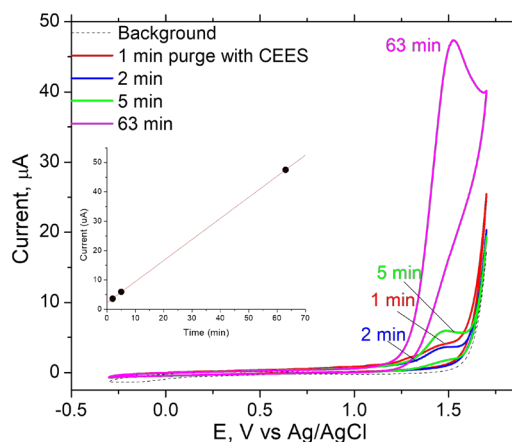


Figure 3.2.12. CV curves measured in solutions of 20 v% CH_3CN +0.1M Robinson (pH2) buffer purged by 2-CEES in N_2 for 1, 2, 5, and 63 min. Flow rate 10 ml/min; scan rate 200 mV/s; electrolyte volume 10 ml.

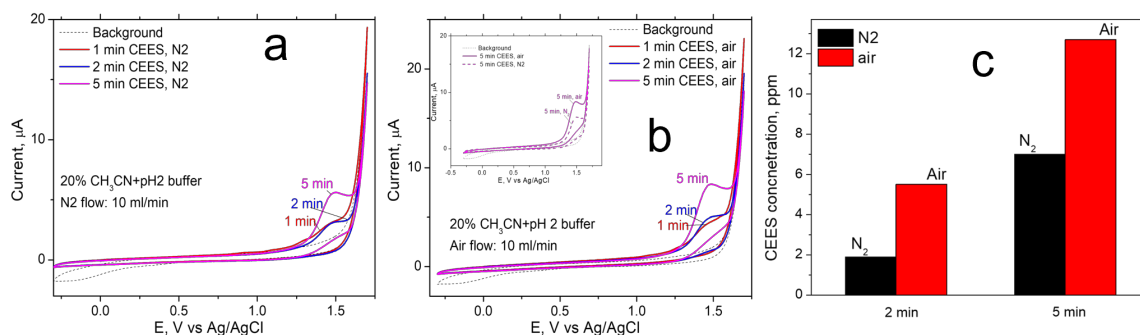


Figure 3.2.13. CV curves measured in solutions of 20 v% CH₃CN+0.1M Robinson (pH2) buffer after purging them with 2-CEES in (a) N₂ and (b) air for 1, 2, and 5; (c) Comparison of 2-CEES concentrations in electrolyte solutions purged with 2-CEES in balance N₂ and air for 2 and 5 min. Flow rate 10 ml/min; scan rate 200 mV/s

Using RGA, intensities of 2-CEES breakdown products can be measured and correlated to 2-CEES concentrations using Kintek permeation tube system. 2-CEES vapors were delivered to residual gas analyzer by N₂ flowing at 10 ml/min through the saturator shown in Figure 3.2.10. Prior to entering the analyzer, the 2-CEES in N₂ was further diluted by dry N₂ flowing at 90 ml/min. Monitoring of 2-CEES

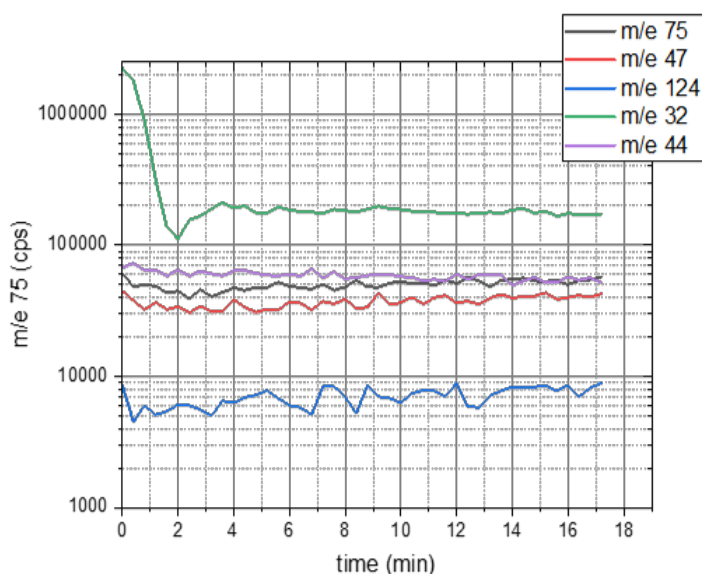


Figure 3.2.14. Intensities of 2-CEES decomposition products (m/e 75, 47 and 124) measured by RGA. m/e 32 and 44 refer to residual O₂ and CO₂ in the system

maintained in balance air.

decomposition began immediately after closing vapor line. Figure 3.2.14 displays intensities of 2-CEES decomposition products observed over the course of 17 min. Remarkably, these intensities remained stable within 15 min. Masses 75, 47, and 124 were assigned to 2-CEES. In addition, residual O₂ and CO₂ were detected in the system. Unfortunately, it was impossible to calibrate 2-CEES signals, as Kintek 2-CEES permeation tube concentration, 2 ppb, was too low for analyzer. However, Dr. Perkins was able to provide an estimate (100 ppm) for the lower limit of 2-CEES concentration in the saturator. Although this experiment was carried out in balance N₂, we expect that the same 2-CEES concentration (> 100 ppm) will be

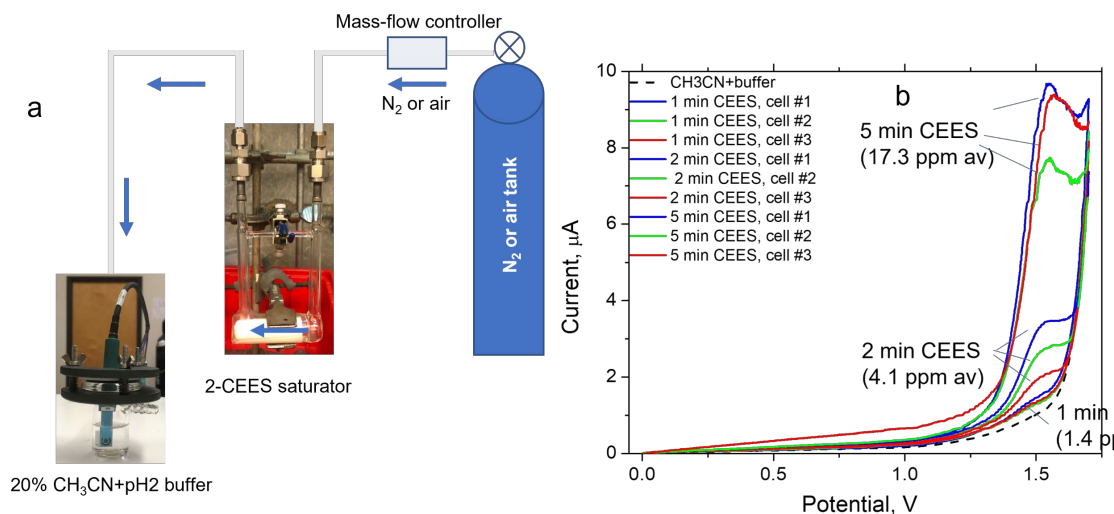


Figure 3.2.15. (a) Schematic of apparatus used for detection of 2-CEES introduced from vapor phase in an electrochemical cell. Balance air; flow rate 10 ml/min. (b) CV curves measured in solutions of 20 v% $\text{CH}_3\text{CN}+0.1\text{M}$ Robinson (pH2) buffer purged by 2-CEES in N_2 for 1, 2, and 5 ml/min; scan rate 200 mV/s. Three trials for each time interval represent measurements in three different cells.

In parallel to establishing correlation between 2-CEES concentration in gas (from the saturator) and liquid (in electrochemical cell) phase, we attempted to re-design a sensor prototype. Instead of using earlier discussed commercial (Metrohm) electrochemical flow cell (see Fig. 3.2.8b), we came up with the idea of using a miniature electrochemical cell made of glass. The cell design was proposed, discussed, and the order was executed by Glass Technologist, Inc. The cell consisted of a glass body, a teflon lid with the opening for the SPE, a clamp, and a port for introduction of 2-CEES vapors, as shown in Figure 3.2.15 a. With such cell in hands, 2-CEES can be monitored online using an apparatus shown in Figure 3.2.15 a. In such configuration, 2-CEES vapors generated in saturator flow directly into the cell, where they can be electrochemically detected by SPE. Three cells were custom-made, and each of them was consecutively tested. Each cell was filled with 10 ml of 20 v% $\text{CH}_3\text{CN}+0.1\text{M}$ Britton-Robinson buffer solution and purged with 2-CEES in balance air flowing at 10 ml/min for 1, 2 and 5 min. Following 2-CEES exposure, its electrochemical response was measured, as shown in Figure 3.2.15 b. Three traces for each exposure time correspond to three trials carried out in different cells. Only a small shoulder is observed on CVs at *ca* 1.5V due to 2-CEES oxidation after 1-min purge. The shoulder becomes more pronounced after longer (2-min) purge, and converts into a well pronounced peak after 5 min purge. The differences in the current magnitudes for traces measured in different cells are likely due to differences in the porosities of frits at the end of gas dispersing tubes. On average, 2-CEES concentration in solution was found to be 1.4, 4.1, and 17.3 ppm after purging the cells for 1, 2, and 5 min, respectively.

2-CEES electrochemical identification using commercial carbon SPEs

In a quest for other SPEs that could replace discontinued BDD SPEs in the sensor prototype, we evaluated carbon SPEs from two different companies: Conductive Technologies and Pine Research. Representative electrodes are shown in Figure 3.2.16 a. BDD SPE is shown for comparison in the same Figure. Both carbon SPEs have carbon working and carbon counter electrodes, while their reference electrodes are different. Pine SPE has

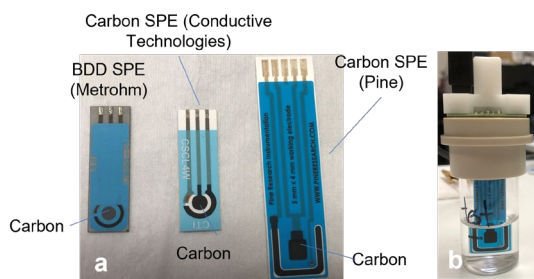
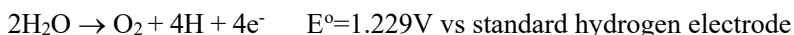


Figure 3.2.16. (a) BDD (Metrohm) and carbon SPEs manufactured by Conductive Technologies and Pine Research, and (b) – electrochemical cell.

Ag/AgCl reference (grey dot in the lower right corner, while SPE from Conductive Technologies has Ag film (silver sector from the left side) as a reference electrode. The SPE electrodes were mounted into electrochemical cell as shown in Figure 3.2.16 b. Figure 3.2.17 shows cyclic voltammetry (CV) curves measured in the presence of 2-chloroethyl ethyl sulfide (2-CEES) in electrolyte solution on a (a) BDD, (b) carbon (Pine) and (c) carbon (Conductive Technologies) SPEs. Obviously, sensitivity of carbon SPEs is significantly lower than that of BDD SPEs. While a noticeable current increase due to 2-CEES oxidation is observed on the BDD SPEs at 10 ppm (well-pronounced shoulder at *ca* 1.5V in Figure 3.2.17 a), no current due to 2-CEES oxidation is observed on the Pine SPEs (Figure 3.2.17 b) up to 38 ppm. Given that the current of 2-CEES oxidation is clearly seen at 204 ppm 2-CEES, the detection limit for these electrodes falls between 38 and 204 ppm. Similar behavior is observed for the SPEs from Conductive Technologies. A very broad shoulder due to 2-CEES oxidation appears on the CV curve at 2-CEES concentration as high as 204 ppm at *ca* 1.4V. The reason for lower sensitivity of carbon SPEs toward 2-CEES oxidation vs BDD electrodes is in their higher activity towards water oxidation:



Comparison of activities of the BDD and Carbon SPEs toward water oxidation is provided in Figure 21d. One can see an increase in current at $E > ca$ 1V on carbon SPEs in the absence of 2-CEES due to water oxidation. On the contrary, the current of water oxidation is nearly zero on BDD electrodes. That explains why small currents of 2-CEES oxidation at concentrations as low as 5 ppm can be observed on BDD,

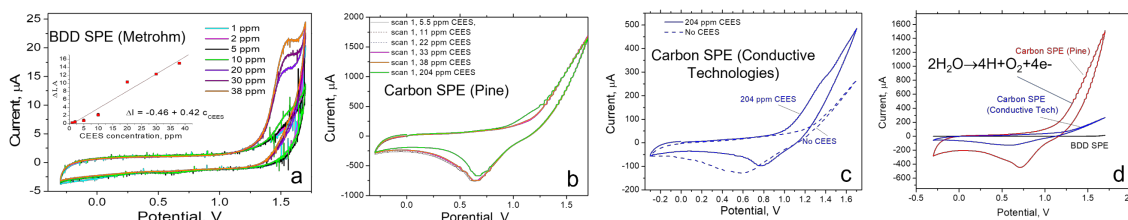


Figure 3.2.17. Cyclic voltammetry (CV) curves measured on the (a) BDD SPEs (Metrohm), (b) Carbon SPEs (Pine), and (c) Carbon SPEs (Conductive Technologies) in 20% CH₃CN+0.1M Britton Robinson buffer at pH 2 in the presence of 2-CEES. Figure 2d shows CV curves measured on the three electrodes in the absence of 2-CEES.

SPEs. Due to low activity of BDD SPEs toward the water oxidation, they are successfully used for oxidation of organic molecules in waste water treatment. In the future, we plan to take advantage of NRL expertise in making thin boron-doped diamond-like films to make BDD SPEs in reproducible manner.

2-CEES electrochemical detection using electrochemical reader

Metrohm electrochemical reader was used at the final stage of the program for detection of 2-CEES



Figure 3.2.18. Electrochemical reader (Metrohm) connected to BDD SPE electrode immersed in solution of 20 v % CH₃CN+Britton-Robinson buffer at pH 2 in the presence of 42 ppm 2-CEES. The reader shows 15.7 ppm 2-CEES.

concentration in liquid phase. Using built-in calibration curve, the reader is capable of detection of analyte concentration after running cyclic voltammetry curve with pre-installed parameters (scan rate, initial and final potentials, and electrode pre-treatment time). The reader is activated by pressing the button. Analyte concentration pops up on the monitor as soon as CV measurements is completed. The electrochemical reader connected to the BDD SPE immersed in electrolyte solution (42 ppm 2-CEES + 20 v% CH₃CN+Britton-Robinson buffer at pH 2) is depicted in Figure 3.2.18. For 42 ppm 2-CEES, we expect to see the corresponding reading in the reader's monitor. However, the reader's display shows 15.7 ppm. To determine the origin of such inconsistency, two series of cyclic voltammetry (CV) curves were measured using Autolab potentiostat, as shown in Figure 3.2.19 (a, b). One can see a typical series of CVs, demonstrating increase in

2-CEES oxidation currents with increase in 2-CEES concentration. The currents peak at *ca.* 1.43 and 1.47 V for CVs measured in solutions of the three highest 2-CEES concentrations (22, 33 and 42 ppm 2-CEES). The peak potential for the previous series of CV curves used for deriving calibration plot was 1.47 V, as illustrated in Figure 3.2.20 a. However, the peak current measured for 11 ppm 2-CEES was higher (10 μ A, Figure 3.2.20 a) than the one measured for 11 ppm CEES (6.9 μ A) in Figure 3.2.19(a, b). Calibration plots derived from the latter plots are compared with the curve used by the electrochemical reader in Figure 3.2.20 b. The lines derived from the CV series shown in Figure 3.2.19 (a,b) are consistent with each other, but not with the plot derived

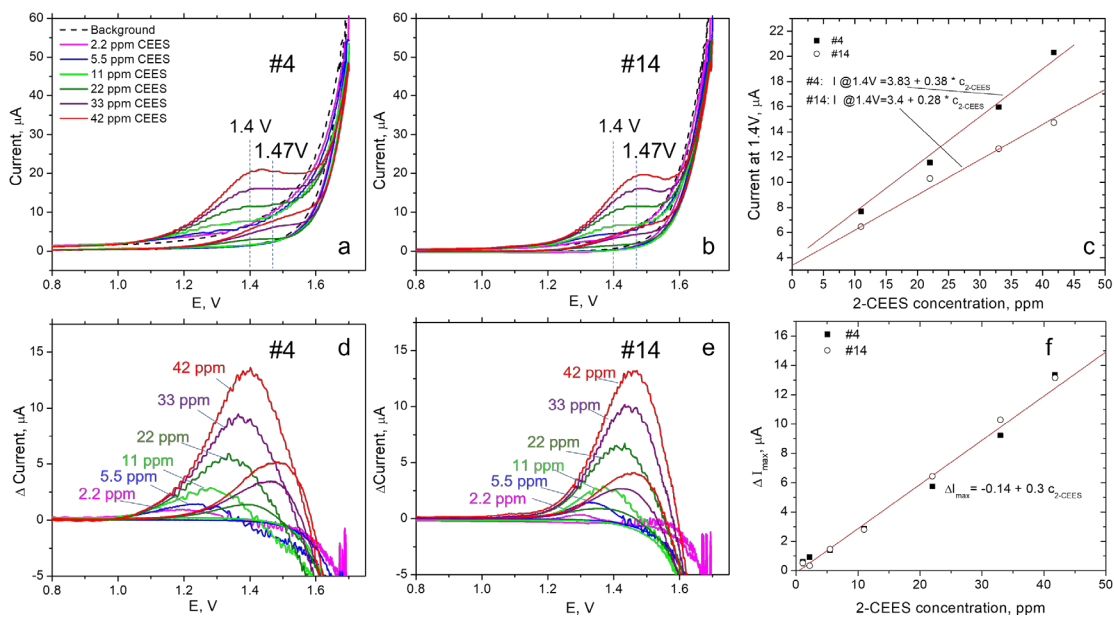


Figure 3.2.19. (a,b) Cyclic voltammetry (CV) curves measured on two different BDD SPEs (Metrohm) at 200 mV/s, first scan is shown; (c) calibration plots derived from currents measured at 1.4V; (d, e) background-corrected CVs shown in Figure 21 (a,b); (f) calibration plot derived from the corrected-for-background peak currents. Solution: 20% CH₃CN+0.1M Britton Robinson buffer at pH 2 +2-CEES.

earlier. However, even using linear correlation $I@1.47V = 4.48 + 0.48 c_{2-CEES}$ we expected to obtain concentration of 33.45 ppm for current equal to 20 μ A, not 15.7 ppm displayed by the reader. We attempted to discuss this issue with the manufacturer, but were unable to obtain any clear answer. Note the detection limit

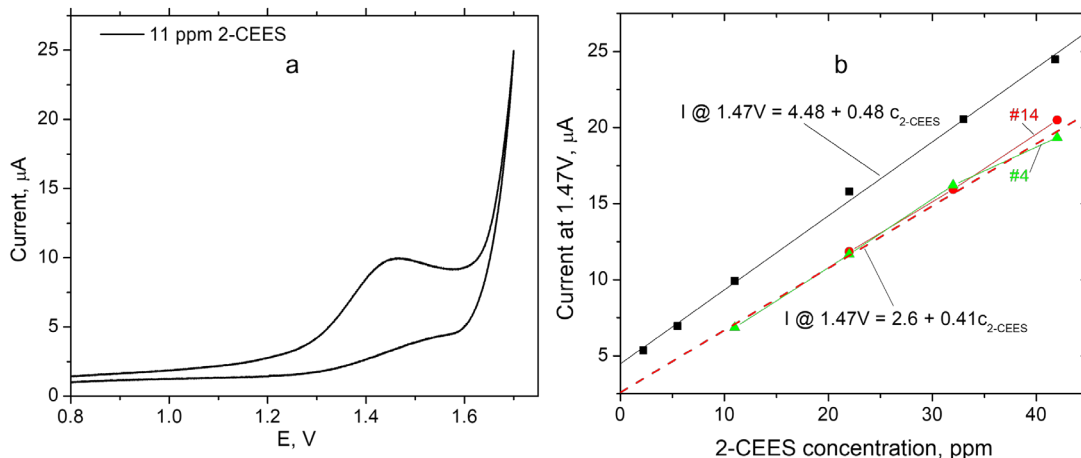


Figure 3.2.20. (a) An example of CV curve from a previous series of measurements used for construction of the calibration plot and (b) calibration curve incorporated into electrochemical reader (solid squares) vs two experimental curves obtained from two series of CVs shown in Figure 24. Current collected at 1.47 V was used to derive the calibration plot

for the calibration curves shown in Figure 3.2.19 (a,b). The reason for that is that the CV curves measured at lower 2-CEES concentration fall on background curves at 1.47V. In order to increase detection limit, we derived calibration curves for the two series of CVs shown in Figure 3.2.19 (a,b) using currents measured at 1.4V (see Figure 3.2.19c). Indeed, the detection limit was increased to 10 ppm. The problem is that the two calibration curves shown in Figure 3.2.19c are not consistent with each other.

Another way to more precisely determine 2-CEES concentration involves deriving calibration curves from the background-corrected peak currents (i.e. currents, measured in the absence of 2-CEES (dashed black lined in Figure 3.2.19 (a,b)). Corrected-for-background currents are shown in Figure 3.2.19 (d,e). Corresponding calibration curves are displayed in Figure 3.2.19 f. The symbols corresponding to peak currents corrected for background fall on a straight line, extending the detection limit to 2 ppm CEES. Unfortunately, Metrohm electrochemical reader does not have capability to perform background correction. There are, however, more complicated versions of hand-held potentiostats available on the market that can perform such corrections. An example is Sensit wireless potentiostat (PalmSens) that is run by the software installed in Android cell phone.

2-CEES electrochemical detection using Sensit BT miniature potentiostat

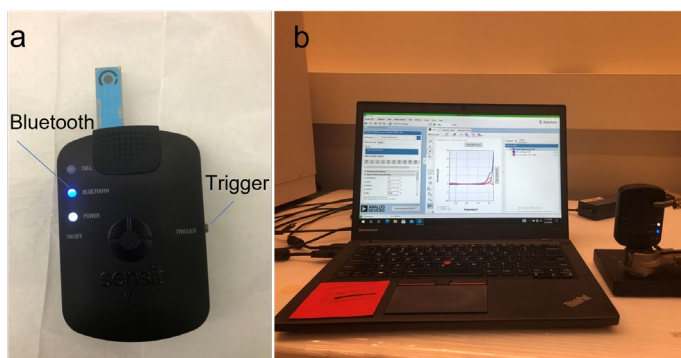


Figure 3.2.21. (a) Sensit BT (PalmSens) miniature potentiostat connected to BDD SPE; (b) Sensit BT connected to laptop via Bluetooth, running cyclic voltammetry curve on BDD SPE immersed in solution of 11 ppm 2-CEES+20% CH₃CN+0.1M Britton-Robinson buffer at pH 2. Both cyclic voltammetry curve and background-corrected curves are shown

Sensit BT is a more advanced version of potentiostat in comparison to the previously discussed Metrohm's electrochemical reader. This potentiostat can be controlled by either Android cell phone or laptop. For the cell phone, PStouch application needs to be installed. Communication between the potentiostat and laptop (or cell phone) is established either via USB cable or Bluetooth. Another advantage of using Sensit BT potentiostat is in that the software performs correction for background current, thus enabling higher sensitivity. Figure 3.2.21 shows Sensit BT potentiostat connected to BDD SPE, and the same potentiostat carrying out electrochemical experiment on BDD SPE immersed in solution of 10 ppm 2-CEES+20%

CH₃CN+0.1M Britton-Robinson buffer solution. The connection between the potentiostat and laptop is established via Bluetooth.

In the series of experiments carried out by Sensit BT potentiostat, we utilized both step-by-step procedures and scripts comprised the sequence of steps. The results of both experiments were consistent with each other. Figure 3.2.22 a displays a representative set of curves recorded for each of 2-CEES concentration. In addition to recording 2-CEES oxidation current (black curve), the software calculates a background-corrected current (red curve) and determines the height and position of the peak. The calibration plot derived from the

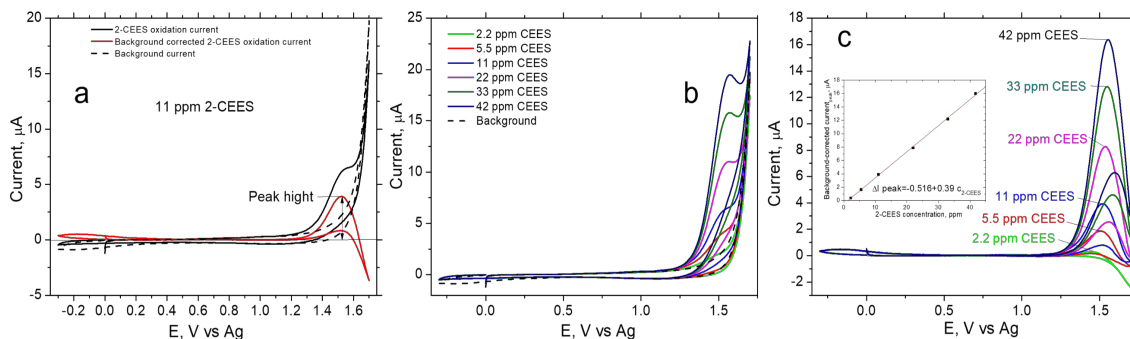


Figure 3.2.22.(a) CV and background-corrected curves recorded using Sensit BT potentiostat on BDD SPE in the presence of 11 ppm 2-CEES in electrolyte solution. Background curve is shown as a reference; (b) series of CV curves measured in the presence of different 2-CEES concentrations; (c) background-corrected curves. Inset shows correlation between the peak height and 2-CEES concentration. Scan rate 200 mV/s, electrolyte solution 20% CH_3CN +0.1M Britton-Robinson buffer at pH 2.

peak currents is shown as an inset in Figure 3.2.22 c. The peak heights form linear relationship with 2-CEES concentrations with the good correlation coefficient of $R^2=0.999$. As it was mentioned earlier, the measurements were carried out both using (a) step-by-step process, consisting of (1) collecting CV curves using Blanks; (2) defining peak heights using “Define peaks” option, and (3) saving the data; and (b) scripts. The script consisted of the sequence of the same steps listed above. After executing the script, an output file was generated that listed parameters of each peak, such as height, positions, width, and area. If 2-CEES concentration is unknown, it can be determined from the calibration curve using the peak height provided in the file.

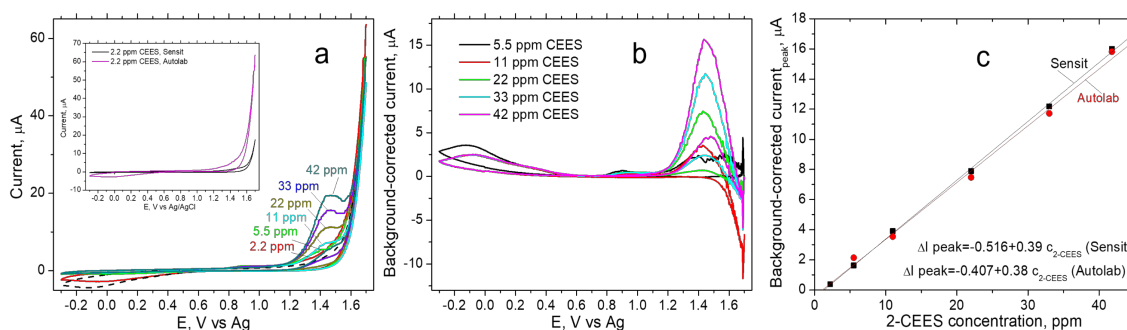


Figure 3.2.23. (a) CV and (b) background-corrected curves recorded using Autolab potentiostat on BDD SPE in the presence of different 2-CEES concentrations in electrolyte solution. Background curve in Figure 3.2.23 a is shown as a reference. Inset in Figure 3.2.23 a compares CV curves measured using Sensit BT (black) and Autolab (magenta) potentiostats. (c) calibration curves derived from background-corrected curves measured using Sensit and Autolab potentiostats. Scan rate 200 mV/s, electrolyte solution 20% CH_3CN +0.1M Britton-Robinson buffer at pH 2.

The script described above was written using PSTrace software provided by PalmSens. This script can be executed either from an open PSTrace window or laptop’s command line. Another option is to trigger experiments by a “Trigger” button located from the right side of the potentiostat (see Figure 3.2.21 a). In the latter case, the “Trigger” button is configured in such a way that each push starts a measurement and stores the measured data on the on-board storage. The “Trigger” button can be activated by the script. However, this particular option is not supported by PSTrace software and need to be written manually.

To ensure that the new Sensit BT potentiostat produces reliable results, we compared the results obtained with Sensit BT to those from more traditional Autolab. Figure 3.2.23 (a,b) shows the series of CV curves and background-corrected CVs in the presence of different 2-CEES concentrations recorded using Autolab potentiostat. Although qualitatively the curves shown in Fig 3.2.23 (a,b) and Fig 3.2.22 (b,c) agree with each other, there is a difference in absolute current values (see inset in Fig. 3.2.23 a). However, after correction for background, very close peak currents in Fig. 3.2.22 c and 3.2.23 b are observed. As a result, calibration plots (Fig.3.2.23 c) derived from background-corrected currents measured on the two instruments look almost identical. Therefore, experimental results obtained with Sensit BT potentiostat can be used for electrochemical 2-CEES detection from electrolyte solution.

Task 4. Integration of individual parts into a sensor prototype (*Art Webb, NRL*)

The goal is to design and fabricate a self-contained device which will 1) perform selective photooxidation using visible light of 2-chloroethyl ethyl sulfide (CEES), hereby designated as “material” and 2) determination of the concentration of photooxidized CEES using electrochemical detection via the employment of a commercial electro chemical cell employing screen printed electrodes. The final product will be a self-contained, field portable, battery operated device capable of being operated with minimal training.

During this period, initial designs were made in order to ascertain the incorporation all the required elements necessary to produce an effective system that can be employed in the field. At the present time a rough setup for a prototype or “benchtop” system been laid out in order to effectively evaluate the system performance and where necessary, changes in design and or reconfigurations will be made to provide an effective system capable of the require operation requirements.

At the present time the basic design consists of two major components; they are

- 1) The visible light oxidation cell
- 2) Electrochemical cell for measuring potential of oxidized material

The visible light oxidation cell is where the material will be oxidized, oxidation of the material will take place using a chip on board (COB) LED. The LED is capable of being operated at 12V and thus can be battery operated. The oxidation cell will consist of 1) the cell base, 2) active substrate 3) visible light LED and 4) a cover to seal the components in the cell. The cell will be gas tight and capable of withstanding nominal vacuum during operation. The key component of the cell is item 2 comprising of photocatalytically active nanoparticles on a suitable substrate. At present, the prototype design will consist of the photocatalytically active nanoparticle substrate mounted in a 3D printed rectangular cell with an internal serpentine path. The concept of oxidation cell is demonstrated in Figures 4.1-4.4. The serpentine path is designed to maximize the time the material resides within the cell and exposed to visible light.

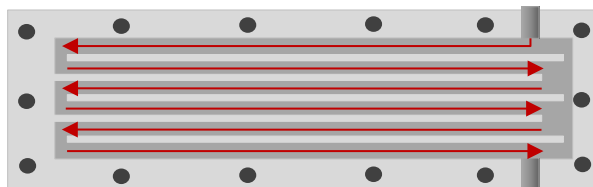


Figure 4.1. Concept of oxidation cell showing serpentine path and outlet ports

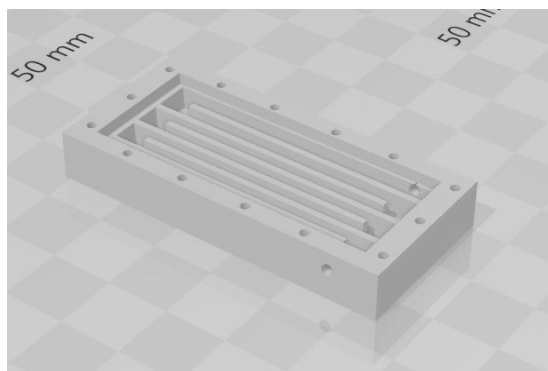


Figure 4.2 CAD design of cell prior to 3D printing

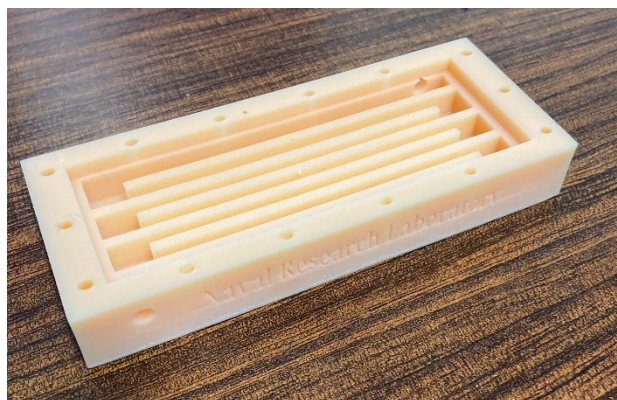


Figure 4.3 3D printed cell complete with serpentine path and inlet and outlet ports

Currently the cell is currently designed to incorporate a standard dimension microscope slide which will be the substrate for the photocatalytically active nanoparticles.



Figure 4.4. Standard dimension microscope slide employed as base for photocatalytically active nanoparticles

The visible light source will be a 12V COB LED array. The array will be mounted on the reverse side of the oxidation cell thus allowing the light to pass through the material as the material flows over the photocatalytically active nanoparticle substrate. The current COB LED to be employed is approximately 2,500 lumens.



Figure 4.5 Standard dimension microscope slide employed as base for photocatalytically active nanoparticles

Figure 4.6 illustrates the general schematic of the photooxidation cell system. The system consists of the following:

- 1) Photooxidation cell
- 2) Vacuum pump
- 3) Bubble chamber
- 4) Peristaltic pump
- 5) Electrochemical cell
- 6) Potentiostat

The system will operate by material (in gas phase) being drawn into the oxidation cell via a vacuum pump. Oxidized material (again in gaseous phase) will exit the oxidation chamber and will pass into a bubble chamber filled with electrolyte. Once the oxidized material has been bubbled into the electrolyte, the electrolyte will be transferred via a peristaltic pump to the electrochemical cell where potential will be read. The amount of electrochemical potential will represent the concentration of the oxidized material. Important factors that will be addressed using this arrangement are the required residence time of the material in the oxidation chamber to assure complete oxidation. This may require adjustment to oxidation cell configuration and or size and it may also require a feed-back loop such that a given volume of the material will be recirculated through the oxidation cell multiple times to effect complete oxidation. The other factor is the duration the material will need to be bubbled through the electrolyte before passing on to the electrochemical cell. This and other factors will be determined using the benchtop prototype.

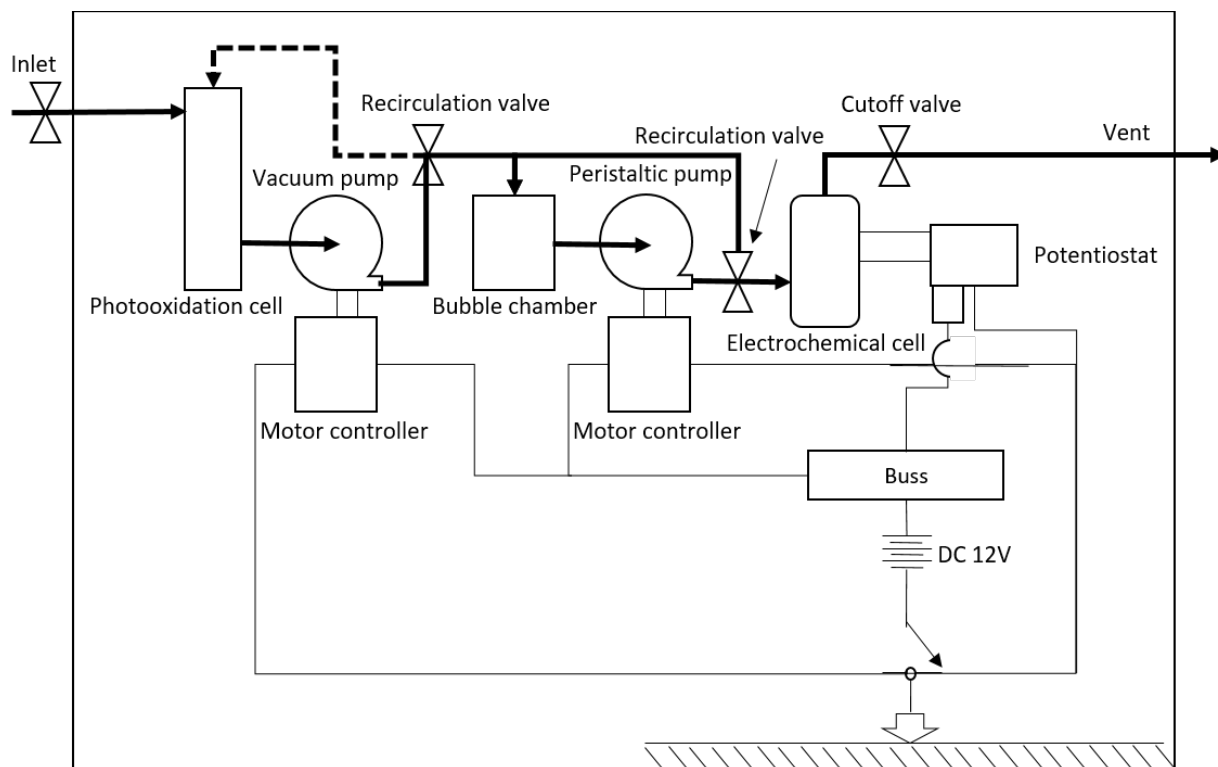


Figure 4.6 Schematic of system configuration

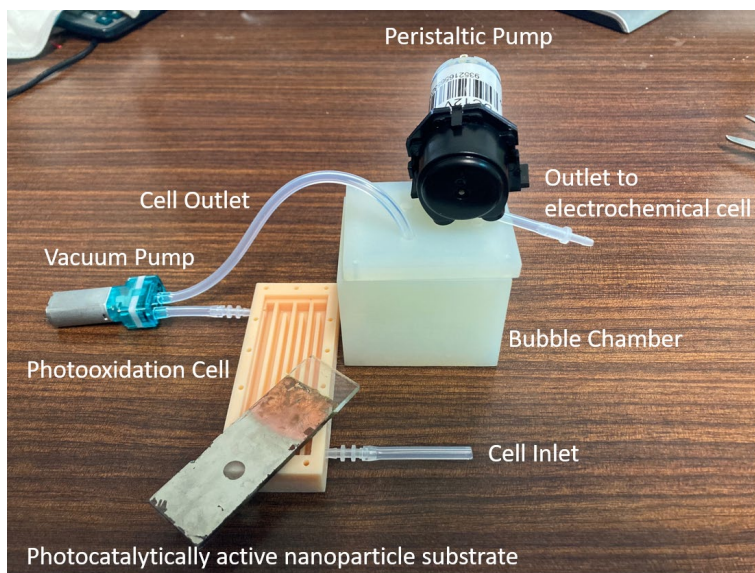


Figure 4.7. Basic components of photooxidation system. Cell pictured is for fitment purposes only as actual cell will have a glass bottom window. Electrochemical cell is not included in the picture

Photooxidation system basic components are illustrated in Figure 4.7.

After discovery of 2-CEES direct electrochemical oxidation, we shifted focus to a simpler design, illustrated in Figure 4.8. Now the basic components of sensor prototype include sampling pump, electrochemical cell, and a miniature potentiostat.. 2-CEES concentration is determined after running CV curve by a potentiostat. The current peak on CV curve due to 2-CEES oxidation is converted into concentration using built-in calibration

curve. A miniature electrochemical cell for a sensor prototype was custom-made by Glass Technologist. A 12 volt peristaltic pump, variable speed motor controller, and a switchable 6 AA battery pack were

packaged together in order to deliver 2-CEES in air into electrochemical cell. Calibration of the sampling pump was carried out according to the basic scheme illustrated in Figure 4.9.

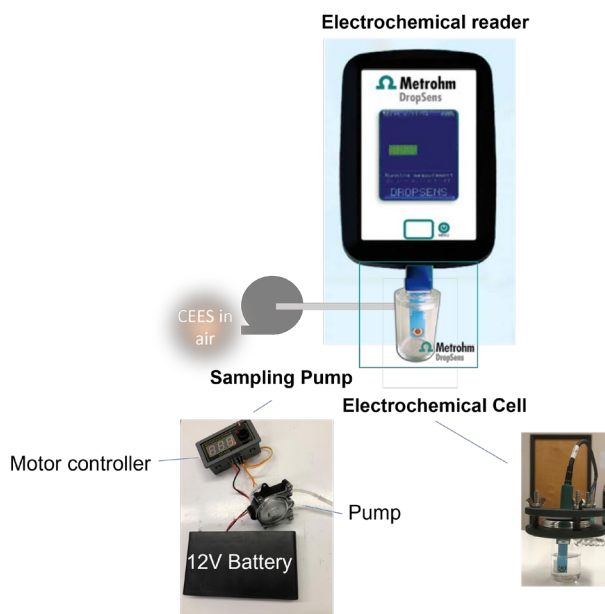


Figure 4.8. General scheme of sensor prototype

switched off to stop the motor. When switched back on, the motor will resume the same speed unless the variable speed controller setting is changed. A sampling pump was calibrated to obtain flow rates in the range of 4-22 ml/min

Calibration of flow rate using variable speed motor controller and gas tight syringe

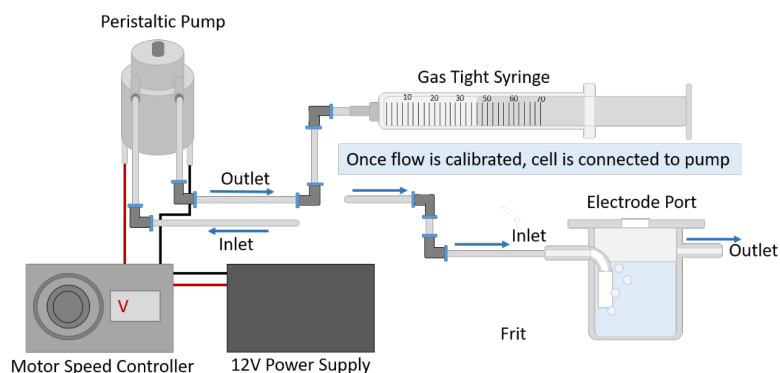


Figure 4.9. Calibration of flow rate

due to more advanced design and capability to make correction for background-corrected current. PalmSens BT potentiostat, however, requires an Android cell phone or laptop that can communicate with PalmSens BT via Bluetooth. The sensor prototype detects 2-CEES in electrolyte solution. with 2-ppm low detection limit and 2 min response time.

Calibration consisted of connecting the peristaltic pump to a digital variable speed motor controlled which is powered by a 12 volt battery operated power supply. The pump outlet is connected to a gas tight syringe and the motor controller switched on. The voltage to the motor is increased until the pump begins to operate. The desired flow rate can be adjusted using the motor controller. The flow rate volume is read directly off of the gas tight syringe. Once the proper flow volume is achieved the, outlet from the pump can then be connected to the electrolytic oxidation cell. The pump inlet can then be employed to draw in the gaseous vapors which will then be passed through the frit in the electrochemical cell. The power supply can be

After calibration, motor controller, peristaltic pump, motor controller and 12V battery were assembled in a box shown in Figure 4.10. The size of this box can be significantly reduced if AA batteries are replaced by lighter Li-ion batteries.

In the final design, Metrohm's electrochemical reader was replaced by a miniature PalmSens BT potentiostat



Figure 4.10. Pump, motor controller and a 12V battery packaged together

CONCLUSIONS

1. *Materials synthesis and modeling*

In our investigation into coating TiN NPs with Au via pALD, we found that under the pALD conditions studied, it was possible to decorate the TiN NPs with Au nanoparticles but not possible to coat the TiN NPs with thin continuous Au shells. Maintaining a stationary drum (no rotation) in the pALD reactor in order to carry out conventional ALD, we developed a recipe for ALD of Au using $\text{Me}_3\text{AuPMe}_3$, O_3 , and H_2O in the pALD reactor. According to ellipsometry measurements, 50 ALD cycles yielded Au islands on a TiN-coated Si wafer. This is consistent with our results from our experiments with Au ALD using $\text{Me}_2\text{Au}(\text{S}_2\text{CNET}_2)$ in a conventional ALD reactor, which suggested that an Au film thickness greater than ~ 20 nm (at least ~ 200 ALD cycles) is required for a percolating Au film on TiN (see Supplemental Information). For 50 ALD cycles using $\text{Me}_3\text{AuPMe}_3$ in the pALD reactor, the Au mass deposition per cycle was equivalent to ALD of an Au thin film at ~ 0.08 - 0.12 Å/cycle, with the higher end of that range achieved on a wafer positioned near the drum opening, closer to the pALD chamber inlet. Similarly, in preliminary studies of Au pALD on TiN NP powder, we found that Au deposition could be enhanced by positioning the powder near the chamber inlet: an Au pALD recipe that resulted in no apparent deposition on TiN NP powder in the back of the rotary drum (where powder is generally located during rotation) resulted in deposition of Au NPs (clearly visible via TEM) on TiN NP powder located in a weigh boat adjacent to the inlet. The Au NPs, however, were distributed nonuniformly throughout the powder, and many TiN NPs were not decorated at all. We were able to deposit Au NPs on TiN NP powder in the rotary drum by significantly increasing the $\text{Me}_3\text{AuPMe}_3$ dose (by both using a N_2 carrier gas flow and increasing the number of pulses per cycle), but the deposition remained nonuniform despite the powder stirring/agitation provided by the rotary drum, suggesting that a further increase of the $\text{Me}_3\text{AuPMe}_3$ dose may be required to obtain uniform deposition. However, deposition uniformity aside, thin continuous Au shells appear to be very difficult to achieve due to the fundamental challenge presented by Au's tendency to form islands/NPs on a TiN surface.

In our investigation into coating open-frame TiO_2 supports with Au via pALD, we found that this is a promising route toward plasmon-enhanced photocatalysis that circumvents the continuous Au shell challenge. Using Au pALD recipes similar to those developed for Au deposition on TiN NPs, we first deposited Au NPs on commercial P25 TiO_2 NP powder located in a weigh boat adjacent to the chamber inlet, producing Au-decorated TiO_2 NPs that exhibited plasmonic absorption peaking around 550 nm. We enhanced the Au deposition, and thereby enhanced the plasmonic absorption, by precoating the TiO_2 NPs with a thin layer of Al_2O_3 via Al_2O_3 pALD prior to Au pALD. Like the Au NPs deposited on TiN NPs, however, the Au NPs deposited on TiO_2 NPs were distributed nonuniformly, with some TiO_2 NPs remaining undecorated. In order to improve uniformity and transition to Au deposition on high-surface-area ($200 \text{ m}^2/\text{g}$) ARL-synthesized open-frame TiO_2 supports, we developed a TiO_2 powder agitation procedure based on vibration and slow rotation: the rotary drum was vibrated to minimize powder adhesion to the wall, and the drum was rotated at 5 rpm rather than the typical ~ 100 rpm to minimize powder escape from the drum. Using this approach, we deposited Au NPs on ~ 75 mg of ARL-synthesized open-frame TiO_2 support powder ($\sim 15 \text{ m}^2$ total surface area) and attained an Au-coated TiO_2 nanopowder mass yield of approximately 80%. UV-vis revealed plasmonic absorption peaking near 550 nm, and TEM images (along with the uniform color change of the powder) suggested spatially uniform Au deposition throughout the TiO_2 powder. Over a series of Au pALD runs, however, we observed decreased Au deposition over time, which may be due to $\text{Me}_3\text{AuPMe}_3$ degradation, and so a new batch of $\text{Me}_3\text{AuPMe}_3$ should be used in future experiments. Additionally, we have modified the rotary drum, partially filling it with glass so that the TiO_2 powder is located closer to the chamber inlet, which we expect will enhance Au deposition on the TiO_2 powder and produce more consistent results in future experiments.

Highly efficient TiO_2 and Sm-doped TiO_2 photocatalysts were synthesized by Pajarito Powders using sacrificial support method. These materials are characterized by a highly porous structure that provides efficient light absorption, high surface area (220 - 250 m^2 BET surface area), and *ca* 5 nm TiO_2 crystallite

size. For comparison, Degussa P25 TiO₂ which serves as a standard in photocatalysis, is characterized by *ca* 21 nm TiO₂ particle size, and 50 m²/g BET surface area.

Although TiO₂ is wide-band semiconductor absorbing light in UV region, it can absorb light in the visible region in the presence of large number of defects on the surface. We observed significant visible light absorption by Pajarito's samples, while for commercial P25 TiO₂ it was nearly zero. Effects of multiple factors on the visible light absorption and photocatalytic activity such as annealing temperature, sacrificial support, Ti precursor, and dopants have been investigated. The most impressive improvement in photocatalytic activity and selectivity was observed for Sm-doped TiO₂. After Pajarito's departure, we attempted to reproduce synthesis of both materials. However, the photocatalytic activity of the newly synthesized materials was less impressive than the ones made by Pajarito.

Plasmonic ZrN nanoparticles were successfully synthesized in-house by Jonathan Boltersdorf. This is a very challenging task due to a strong affinity of Zr to oxygen. Although ZrN demonstrated stronger plasmonic response vs TiN nanoparticle, in agreement with the theoretical prediction, it was not as strong as predicted due to agglomeration of ZrN nanoparticles, which cannot be avoided during high-temperature synthesis.

Au, Cu, TiN, and ZrN plasmonic nanoparticles were deposited on open-frame TiO₂ supports by a variety of wet chemistry methods to promote TiO₂ activity in the visible region. Although the strongest plasmonic response was demonstrated by Au/TiO₂, it varied depending on the synthesis method utilized for deposition of Au nanoparticles. Au nanoparticles deposition method on TiO₂ was found to be detrimental for achieving high selectivity and activity of the Au/TiO₂ photocatalyst.

A series of hybrid nanoparticles comprising TiN core, SiO₂ or TiO₂ shell, and Pt or Pd islands were synthesized. Addition of SiO₂ shell and Pd and Pt clusters led to damping and red-shifting of plasmonic resonance, in agreement with the modeling prediction.

In parallel to experimental work, optical properties of nanoparticles with TiN or ZrN core and Au shell, as well as TiN-SiO₂(TiO₂)-Pt/Pd hybrids were modeled by Ohio team led by Prof. Alexander Govorov

The Ohio Team has carried out an extended set of computational tasks for hybrid nanocrystals listed above. The simulations were done in a solution using the COMSOL software for the nano-cuboid multi-layer geometries. The computed properties included: absorption, scattering, rate of generation of high-energy electrons, and phototemperature. Overall, we conclude that the hybrid nanostructures of interest show enhanced photophysical and photochemical properties due to the combination of two metals in a single nanostructure. Our calculations described well the experiments on the photo properties of one-component nanocrystals (Au, TiN, ZrN) performed at NRL. We are also ready to compare our calculations with the experimental data for the hybrids (TiN-Pt and TiN-Pb) when the data become available after the clearance.

Some of the main conclusions from our theory on the hybrids of interest - **(1) TiN-Au hybrid:** [a] Since the TiN-Au hybrid is composed of two plasmonic materials and gold is much more optically active, the gold properties start to dominate rapidly by increasing the shell; [b] the Au shell strongly amplifies optical responses, including the absorption signal, due to the optical antenna effect; [c] thicker Au shells lead to strong scattering that is not preferable for photochemistry; [c] the core-shell TiN-Au and ZrN-Au nanocubes behave in similar ways; [d] we concluded that thin Au shells could work as optical and photochemical amplifiers due to their plasmonic antenna effect. Simultaneously, the TiN and ZrN cores can work as supports and additional absorbers made of inexpensive materials. **(2) TiN-SiO₂-Pt/Pd hybrids:** (a) Our hybrid is composed of two metallic materials (TiN/ZrN and Pt/Pd), which interact optically. However, the plasmonic metal (TiN/ZrN) dominates the optical response, while the photocatalytic metal (Pt/Pd) is less optically active; (b) we observe the effect of damping of the TiN/ZrN plasmons due to the Pt/Pd shells. This effect happens because Pt and Pd are very resistive; (c) overall, the TiN/ZrN-based cubes strongly amplify optical responses, including the absorption and electromagnetic signals, due to the optical antenna effect.

(d) TiN demonstrates lower plasmonic amplification coefficients than ZrN; (e) we show that the TiN/ZrN cubic cores can be used in photochemistry as optical amplifiers due to their strong plasmonic antenna effect. Simultaneously, these TiN and ZrN core cubes work as support materials, which hold expensive photochemical components (Pt- and Pd-shells). Notably, the above materials (TiN and ZrN) are inexpensive; **(3) TiN-SiO₂-Pt/Pd hybrids for the hot electron generation:** (a) TiN-Pt/Pd hybrids are excellent generators of hot electrons in the Pt/Pd shells, and these electrons can be used for surface photochemistry of CWAs; (b) The HE production efficiencies grow in the visible and red intervals due to the amplification of the plasmonic effects in these spectral intervals; (c) simultaneously, the Pt/Pb shells tend to create the damping of the plasmon resonances of the TiN/ZrN components; (d) the hybrids TiN/ZrN-Pt/Pb have two sources of generation of HEs: the Pt/Pb-water interface and TiN/ZrN-SiO₂ interface. The first one (i.e., Pt/Pb-water interface) is critical for our application since it provides HEs for the surface catalysis; (e) overall, the triple-material hybrids – a plasmonic core (TiN/ZrN) --- a catalytic metal - (Pt/Pd) deserve further investigations and show interesting photophysical behaviors as HE generators; (f) since the thermal conductivity of the components (TiN/ZrN, SiO₂, Pt/Pd) is high and the absorption in the TiN/ZrN-core is strong, our hybrids efficiently generate photo-temperature that should be taken into account for designing chemical sensors.

2. Photocatalytic activity evaluation

We demonstrated that some of the synthesized open-frame TiO₂ materials exhibited high photocatalytic activity towards 2-CEES photooxidation to 2-chloroethyl ethyl sulfoxide (2-CEES-O) and sulfone under visible light excitation. Nearly complete 2-CEES oxidation was observed within 4 h of exposure to visible light. The same procedure performed with commercial P25 TiO₂ resulted in very minor 2-CEES photooxidation, which highlights the effect of morphology on the photocatalyst's activity. We discovered that photooxidation occurs in parallel to hydrolysis pathway (hydrolysis of C-Cl bond resulting in formation of 2-(ethylthio)-ethanol as a major byproduct). As such, our effort was focused on suppression of hydrolysis and promotion of selective photooxidation to 2-CEES-O. Significant improvement in suppression of hydrolysis was achieved by Sm-doping of TiO₂ support and utilizing Au plasmonic nanoparticles to further promote catalysts' selectivity towards 2-CEES-O production. To the best of our knowledge, it was the first demonstration of plasmonic effect on 2-CEES photocatalytic oxidation confirmed by analysis of reaction products by GC-MS analysis.

Incorporation of other plasmonic nanoparticles such as TiN and Cu did not result in a significant shift of the reaction pathway towards 2-CEES-O production. The reason for that is that both TiN and Cu promote 2-CEES hydrolysis due to the presence of oxide layers on the surface.

Addition of Pt and Pd nanoparticles to TiN-SiO₂/TiO₂ hybrids led to promotion of the catalysts' activity in the dark with formation of hydrolysis and oxidation products (2-(ethylthio)-ethanol and methylthiopropyl acetate, respectively). No significant visible light effect was observed. From 60% to 80% 2-CEES was converted to reaction products within 4 h challenge for 8 synthesized catalysts.

Photocatalysts synthesized within the program can be successfully used for surfaces decontamination.

3. Sensing of 2-CEES

Feasibility of 2-CEES-O detection on glassy carbon electrodes in solutions of 20 v% CH₃CN+0.1M Britton-Robinson buffer at pH 2 was demonstrated in the program. However, while experimenting with 2-CEES, we discovered, that 2-CEES also can be detected electrochemically. Then the focus of the program was shifted to direct electrochemical detection of 2-CEES. To optimize conditions for 2-CEES detection, electrolyte solution, electrode material, and parameters of cyclic voltammetry technique were identified and optimized. Our experiments demonstrated that 2-CEES can be detected on screen printed doped diamond electrodes (BDD SPEs, Metrohm) with sensitivity of 2 ppm and response time on the order of 2 min. In a parallel series of experiments, we proved that sufficient for electrochemical detection 2-CEES concentration can be generated in electrolyte after purging it for 2 min with 2-CEES flowing in air at 10

ml/min. 2-CEES concentration in the balance air was correlated to 2-CEES concentration in the electrolyte solution. The major issues we experienced in this part of the program is in that Metrohm discontinued production of BDD SPEs

4. Integration of individual parts into a sensor prototype: 2-CEES direct electrochemical detection

All the necessary parts have been assembled and prepared for a final demonstration. Sampling pump was designed and calibrated to obtain flow rates in the range of 4-22 ml. A miniature electrochemical cell was custom-made by Glass Technologist, Inc. There was a couple of issues with the Metrohm's electrochemical reader due to (1) 2-CEES incorrect concentration calculation, and (2) inability to correct for background curve (i.e. curve measured in the absence of 2-CEES in electrolyte solution), which led to a decrease in 2-CEES detection limit from 2 to 20 ppm. However, both issues were resolved by a replacement of an electrochemical reader by a more advanced miniature Sensit BT (PalmSens) potentiostat. The potentiostat can be controlled by an Android cell phone via Bluetooth or USB cable.

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