Interface Engineering of Aluminum-Titanium Dioxide Nanomaterials for Plasmonic Photocatalysis

Design Day 2020

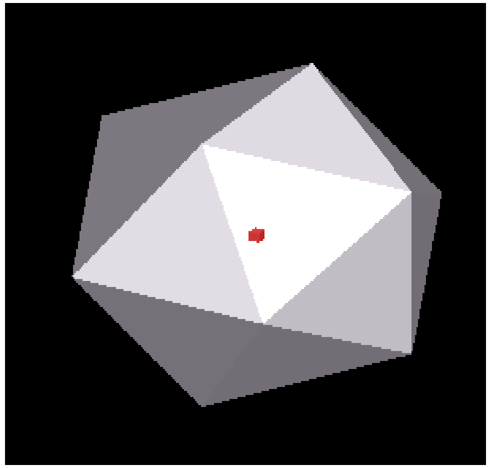
Johns Hopkins University Department of Electrical Engineering || Thon NanoEnergy Lab

Tina Gao, Mansi Gao, Sreyas Chintapalli, Yan Cheng, Kenneth Smith, Rachel Dziako, Art Bragg, Susanna Thon

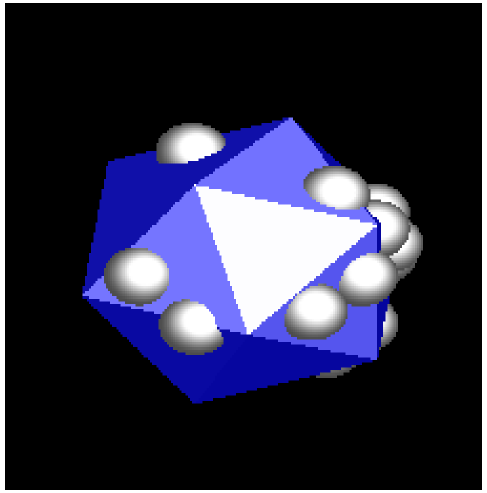
Introduction

PROJECT DESCRIPTION:

- Facilitate electron transfer between Al and titanium dioxide (TiO2) by creating a core-shell interface
- Tune the sizes and architecture of Al-TiO2 systems



Goal for this Project: Icosahedron Al with TiO2 shell

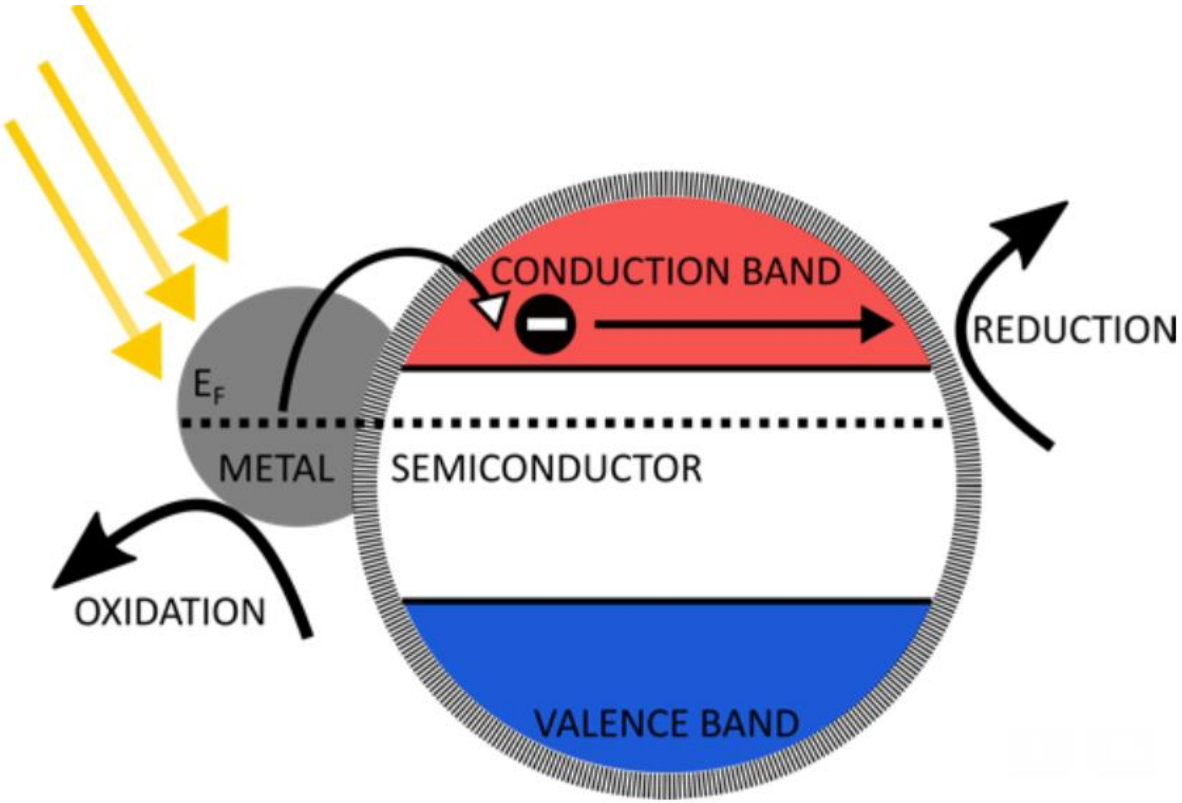


Other Potentially Interesting Architectures: Icosahedron Al with sparse TiO2 shell

Introduction

BACKGROUND

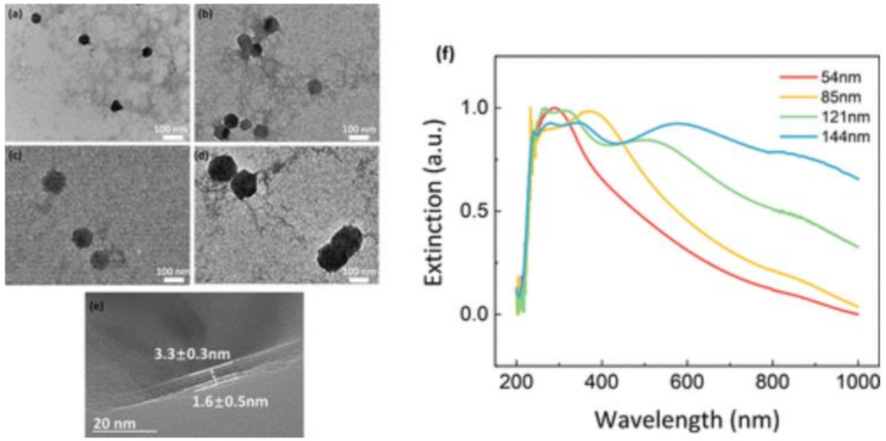
- Photocatalysts absorb light and transfer that energy into chemical reactions
    - Utilities include clean energy production and pollution treatment powered by sunlight
    - They operate by facilitating electron transfer from the valence band to the conduction band
- We want to utilize Al as a photosensitizer for TiO2 photocatalysis such that visible light will be absorbed
    - Increases efficiency because most sunlight that filters through Earth's atmosphere is visible light, not ultraviolet (UV)
    - Al is cost-effective and environmentally-friendly



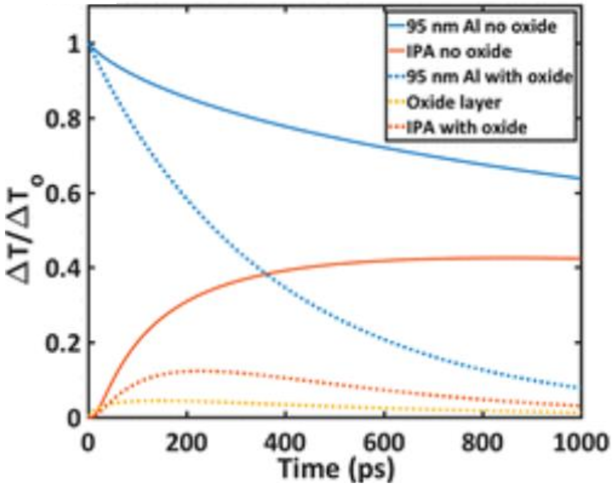
Depiction of photocatalysis

Summary of Past Work

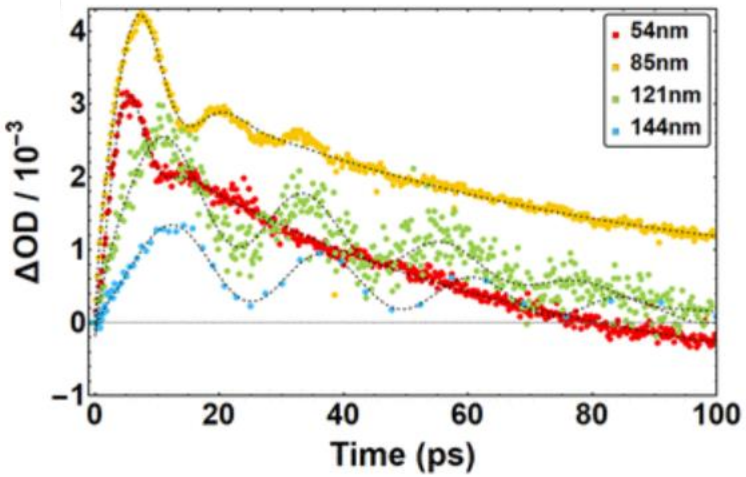
- Photothermal and photoacoustic properties of Al NPs are affected by particle size and surface components
  - Size-tuning:
    - Redshifted plasmonic peak with larger particles
    - Decreasing periods for phonon vibrations with smaller particles
  - Oxide layer
    - Oxide layer increases speed of heat-transfer



Al NPs with an oxide layer and organic ligand. Average diameters of 54nm, 85nm, 121nm, 144nm
LEFT: Transmission electron microscopy (TEM) , RIGHT: UV-Vis Spectra



Simulations of thermal energy transport



Time-dependent changes in near-IR extinction (integrated 1000–1075 nm) observed for particles of each size

Y. Cheng et. al., *Size- and Surface-Dependent Photoresponses of Solution-Processed Aluminum Nanoparticles*, American Chemistry Society Photonics, Vol. 7, Issue 3, pp. 637-645 (2020), https://doi.org/10.1021/acsphotonics.9b01170

K. Smith et. al., *Dynamics of Energy Transfer in Large Plasmonic Aluminum Nanoparticles*, American Chemistry Society Photonics, Vol. 5, Issue 3, pp. 805-813, https://doi.org/10.1021/acsphotonics.7b00932

Al-TiO2 Core Shell Synthesis

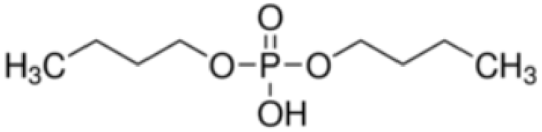
METHOD:

We based our TiO2 shell growth on Al NPs (~150 nm diameter) off of a three-step ligand exchange mechanism for gold (Au)-TIO2 core-shell synthesis. Procedures for Al-TiO2 core-shell synthesis is as follows:

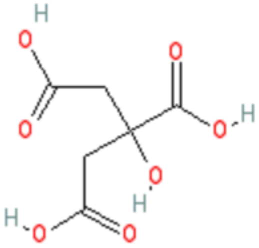
1. The Al NPs (1.8mL) are redispersed in chloroform and added with (3-mercaptopropyl)triethoxysilane (MPTS) (0.15mL) into the solution for 24 hours with stirring
2. Residual MPTS is removed through washing and dispersion with methanol.
3. To grow the TiO2 shell, the alcohol solution of Al cores was added 0.1ml of titanium isopropoxide (TTIP)and stirred for 2 hours.

(*) Temperature: 70 C

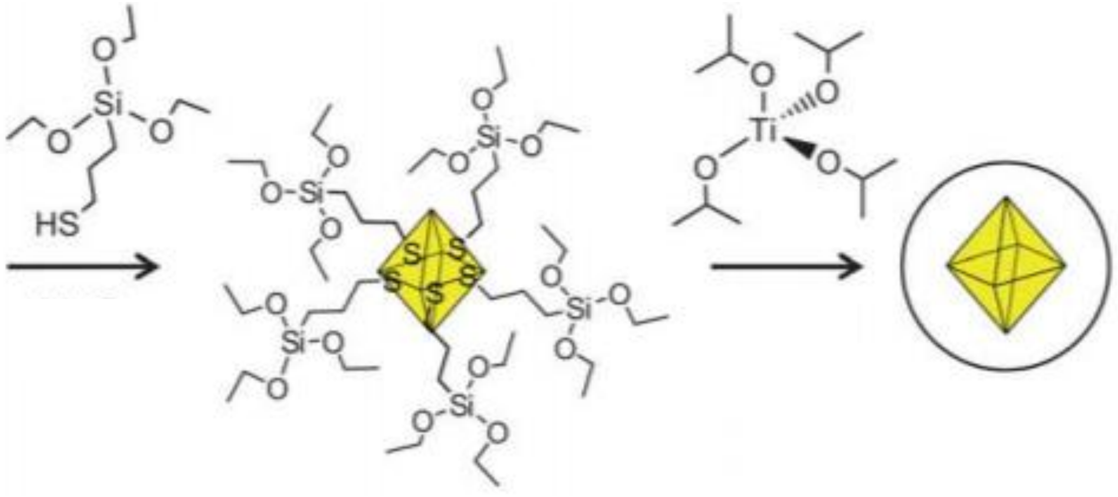
(*) Humidity: 50%



Dibutyl Phosphate – surface ligand of our just-synthesized Al NPs



Citric Acid – surface ligand of the Au-NPs that we based our ligand exchange method off



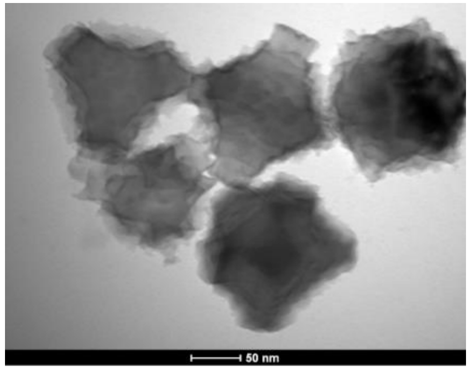
Ligand exchange method for growing TiO2 on Al NCs

W. Liu et. al., *The influence of shell thickness of Au@TiO2 core–shell nanoparticles on the plasmonic enhancement effect in dye-sensitized solar cells*, NanoScale Vol. 5, Issue 7953 (2013), DOI: 10.1039/c3nr02800c

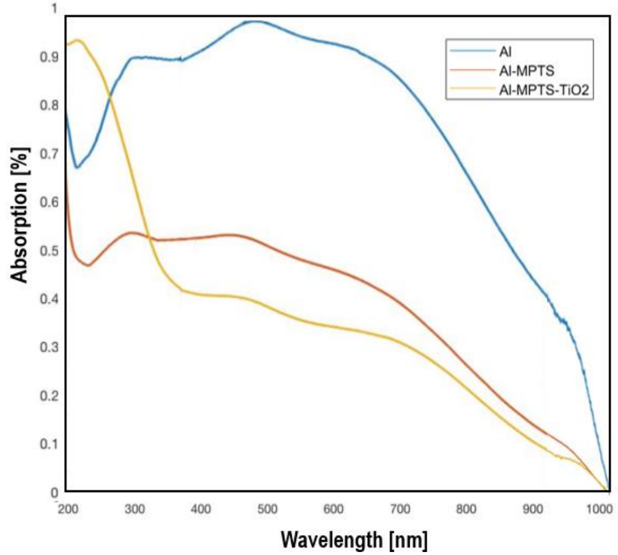
Al-TiO2 Core Shell Synthesis

RESULTS:

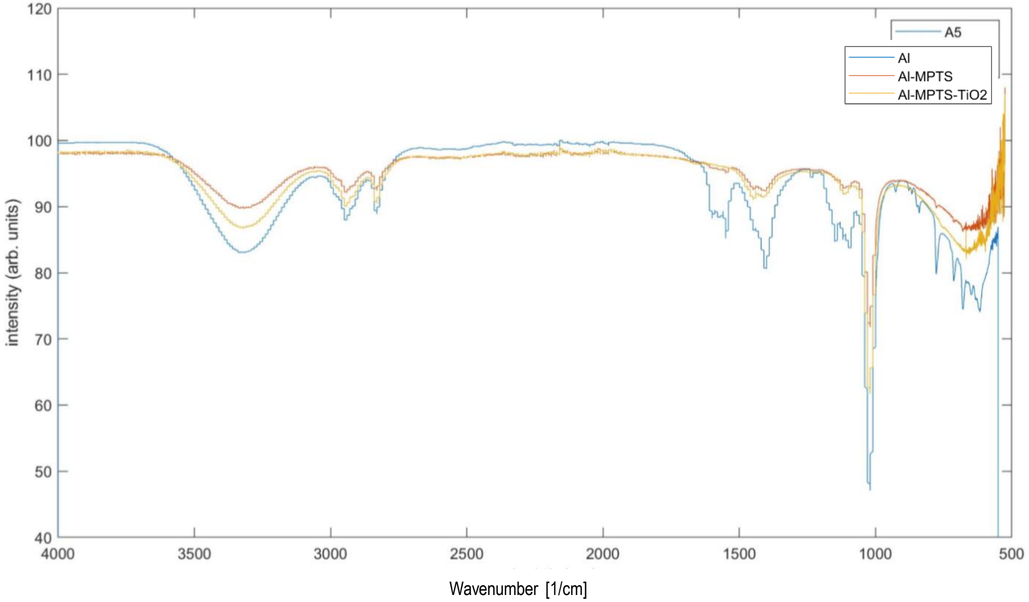
- TEM
  - Icosahedron facets
  - ~150 nm diameter
- UV-Vis
  - ~300 nm – quadrapole
  - ~550 nm – plasmonic resonance
  - ~800 nm – transition band
- FTIR
  - ~3200 cm^-1, ~2900 cm^-1, ~2700 cm^-1, ~1400 cm^-1, ~100 cm^-1 are dips associated with IPA
  - ~500 cm^-1, ~750 cm^-1 are from Al-O



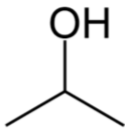
TEM: Al NPs after TiO2 growth



UV-Vis: Al NPs in different stages of the ligand exchange and TiO2 growth



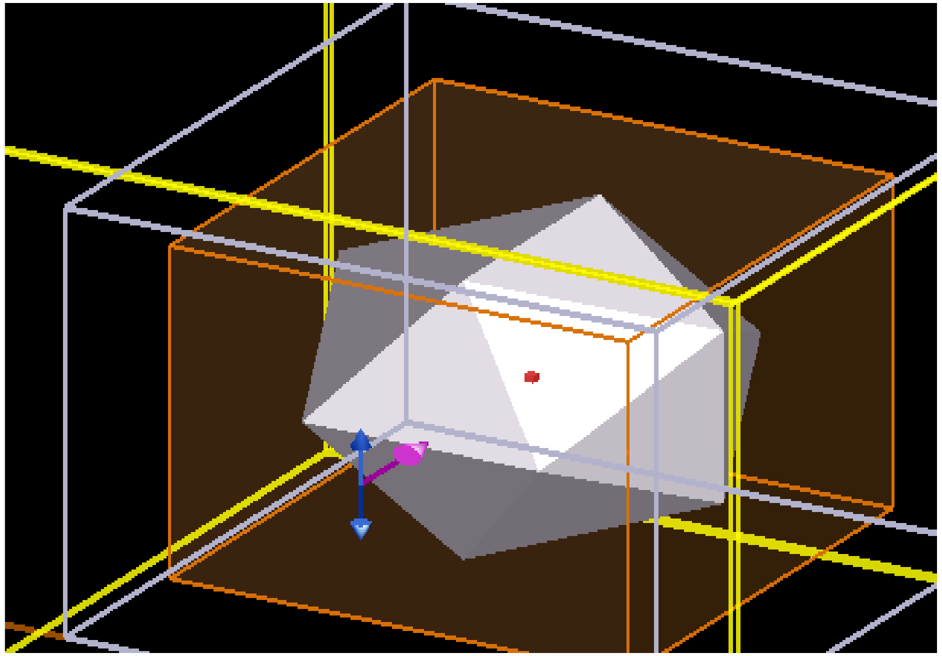
FTIR: Al NPs in different stages of the ligand exchange and TiO2 growth



IPA: Solvent molecule

V. Zeitler et. al., *THE INFRARED SPECTRA OF SOME Ti-O-Si, Ti-O-Ti AND Si-O-Si COMPOUNDS*, American Chemistry Society, Vol. 61, Issue 9 (1957), https://doi.org/10.1021/j150555a010

Al-TiO2 Shell Simulations

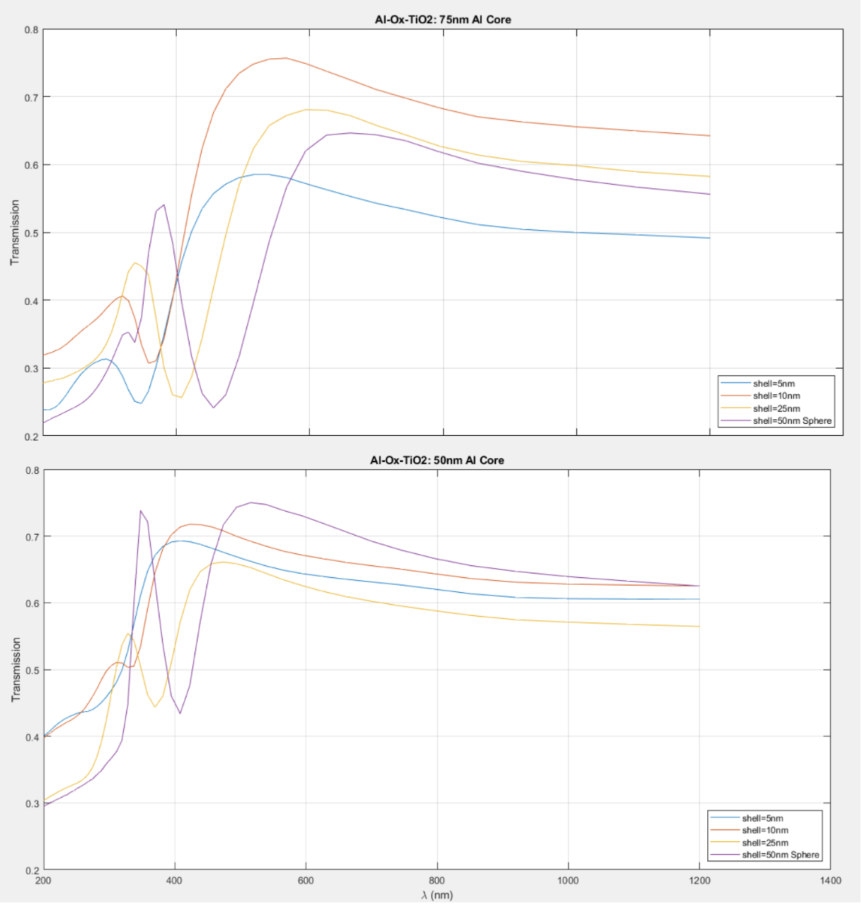


Al-Ox-TiO2 with surrounding simulation region and mie source

SET-UP

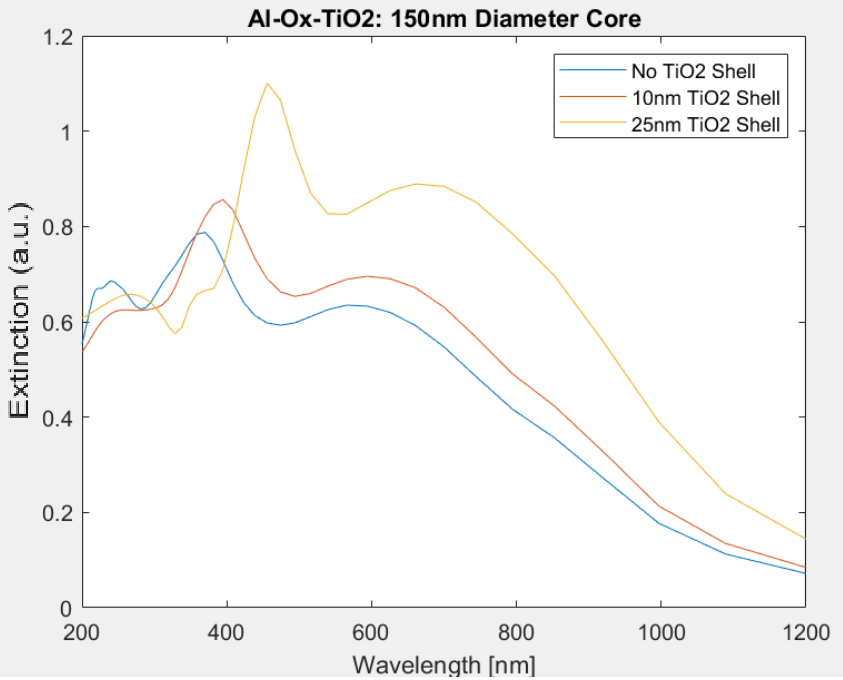
- Finite-Difference Time Domain (FDTD) simulations
  - Solves Maxwell's equations through time and space
- Parameters
  - Al diameters: 50nm, 75nm, 150nm
  - Oxide layer: 5nm
  - Total particle diameter with TiO2 thickness: 50nm, 10nm, 25nm, 50nm

Al-TiO2 Shell Simulations



Transmission spectra of Al NPs with a 5nm oxide layer and varying TiO2 shell thicknesses (5nm, 10nm, 25nm, 50nm)

TOP: 75nm diameter. BOTTOM: 50nm diameter.



Transmission spectra of Al NPs with a 5nm oxide layer and varying TiO2 shell thicknesses (5nm, 10nm, 25nm, 50nm)

RESULTS

- An increase in Al NP core size and an increase in TiO2 thickness results in a red shift
- The simulation of 150nm-diameter particles has its plasmon peak at ~650nm while our experimental Al NPs (average diameter 150nm) is at ~550
  - Discrepancy comes from lack of mono-dispersity in experimental results

Conclusion

In conclusion, the goal of this project was to explore Al-TiO2 nanomaterials for photocatalysis. Although we are still working on our synthesis method for creating an Al-TiO2 core-shell particle, we have utilized FDTD simulations to note a redshift with increasing TiO2 layers. In our previous projects, we have also characterized the size and oxide effects on Al photothermal and photoacoustic effects.

Acknowledgements

Thanks so much to the co-authors!

- Mansi Gao
- Sreyas Chintapalli
- Yan Cheng
- Kenneth Smith
- Rachel Dziako
- Art Bragg
- Susanna Thon

Thanks for the funding!

- Petroleum Research Fund

ACS PRF

Thon NanoEnergy Lab