

Optimizing the Spectral Response of Plasmonic Aluminum Nanoparticles

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Abstract

Motivation

Aluminum nanoparticles (Al NPs) are of interest due to their ability to increase the efficiency of photocatalysts. Aluminum is of specific interest due to its natural abundance in Earth's crust. In addition, the plasmon resonance of aluminum nanoparticles can be tuned across the visible spectrum through changes in size and shape. Al NPs can act as solar antennas for light to enhance common photocatalysts such as titanium dioxide (TiO₂). Optimizing the spectral response of these NPs to better match the solar spectrum offers a pathway for renewable and efficient photocatalytic materials.

Methods

Lumerical FDTD: Aluminum nanoparticles were simulated using the finite-difference time-domain method to solve Maxwell's equations. The NPs were simulated as regular icosahedra with a 4 nm native oxide shell.

Air-free Synthesis: Care must be taken to minimize the O₂ and H₂O levels during the synthesis process. Prior to the synthesis, all solvents should be dehydrated and degassed. Solvents are subsequently stored in a glove box. The synthesis is completed on a Schlenk line under inert atmosphere.

UV-Vis Spectroscopy: Experimental absorption spectra for the Al NPs were obtained using a Cary 5000 UV-Vis-NIR Spectrophotometer.

TEM Imaging: Transmission electron microscopy images of the Al NPs were obtained using a Tecnai TF-30.

Introduction

- Al NPs increase photocatalytic efficiency through localized electric field enhancement
 - Caused by localized surface plasmon resonance (LSPR)
- Incident light hits a NP, the electric field of the light causes the valence electrons of the NP to oscillate coherently
 - These collective oscillations are a plasmon
- Plasmons are confined to the metal-dielectric interface
 - Interface is between the Al NP and the native Al₂O₃ formed after colloidal synthesis
 - Localized surface plasmons cause electric field enhancement near the NP surface
- The LSPR corresponds to the maximum extinction value, so the spectral response can be tuned through the modification of the LSPR
 - Achieved by changing the size or shape of the NP
 - Extinction is comprised of a scattering and absorbance contribution
 - $\sigma_{ext} = \sigma_{abs} + \sigma_{scat}$
- Extinction cross sections are measurable via spectrophotometry
 - Beer-Lambert Law: $A(\lambda) = C \cdot l \cdot \sigma_{ext}$
 - A is the total light attenuation, as a function of wavelength
 - C is the number density
 - l is path length through the sample

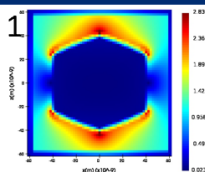


Figure 1: Electric field profile for an Al NP with Al₂O₃ shell



Figure 2: Cuvette of Al NPs suspended in 2-propanol

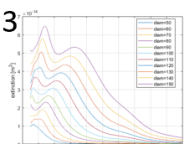
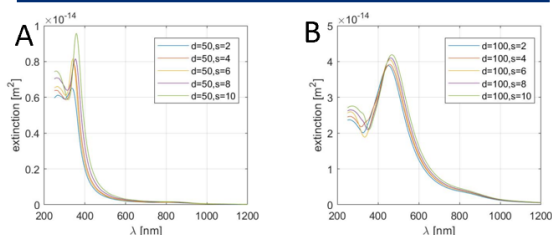
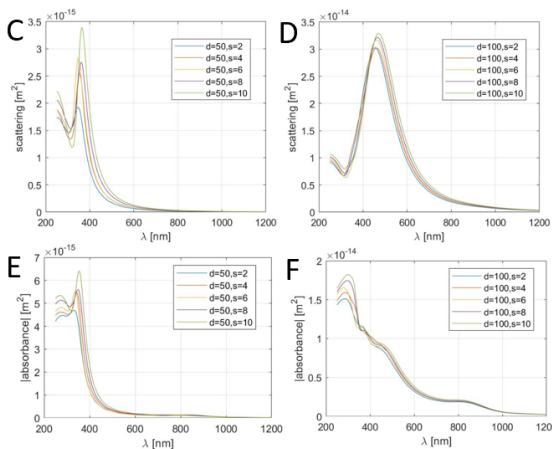


Figure 3: FDTD simulations of an Al NP with 4nm of oxide. As the particle size increases, we observe a noticeable redshift of the LSPR

FDTD Simulations



Graphs A-F show the results of a simulation of an Al NP with a TiO₂ shell. In the legends, *d* is the diameter of the Al NP and *s* is the thickness of the TiO₂ shell, both in nm. Graphs A, C, and E are the extinction, scattering, and absorbance cross sections, respectively, for a 50 nm NP. Graphs B, D, and F are the extinction, scattering, and absorbance cross sections for a 100 nm NP. These graphs show a red-shift of the maximum extinction with increasing particle size, illustrating the ability to optimize the spectra through modification of particle size.



Graph G shows the extinction cross section for a simulation of a 150 nm Al NP surrounded by a shell of isopropyl alcohol (IPA). The thickness of the IPA shell varies from 0 to 150 nm. IPA is the final solvent used after the cleaning process, so this simulation shows how solvent remaining on the NP would affect the spectral response.

Nanoparticle Synthesis

- Solvents are degassed using the Freeze-Pump-Thaw method and dehydrated with molecular sieves
- The synthesis takes place on a Schlenk line

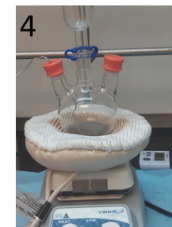
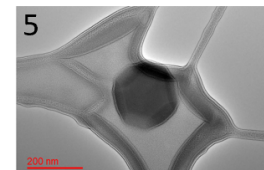


Figure 4: Experimental set up for the Al NP synthesis



Figures 5 and 6: TEM micrographs of an Al NP. Figure 3 shows a single Al NP. Figure 4 shows part of the same particle with higher magnification. This shows the presence of an ~4 nm native aluminum oxide layer which forms after the synthesis.

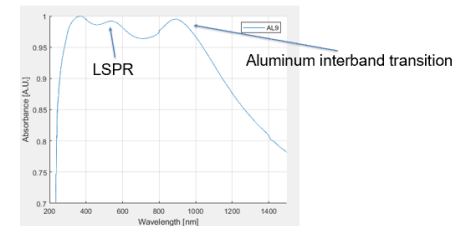


Figure 7: Experimental UV-Vis-NIR Spectrogram of a batch of Al NPs.

References

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