Near-Field FEM Simulations: A Vital Tool for Studying Silver-Based Plasmonic Systems

R. Asapu[1], S. W. Verbruggen[2], N. Claes[3], S. Bals[3], S.Denys[1], S. Lenaerts[1]

[1]Department of Bioscience Engineering, DuEL Research Group, University of Antwerp, Antwerp, Belgium
[2]Department of Bioscience Engineering, DuEL Research Group, University of Antwerp, Antwerp, Belgium; Center for Surface Chemistry and Catalysis, KU Leuven, Leuven, Belgium
[3]Department of Physics, EMAT Research Group, University of Antwerp, Antwerp, Belgium

Abstract

Silver nanoparticles are valuable in the field of plasmonics since silver has a higher field enhancement factor compared to other metals that possess plasmonic properties. They are highly useful in multiple fields of research in diagnostic and optical applications such as SERS1, biophotonics2 and photocatalysis3. The plasmonic properties of silver nanoparticles can be finely tuned to the incident light wavelength through their size, shape and dielectric environment. The main drawback associated with silver nanoparticles is the lack of long-term stability and formation of a diffuse silver oxide layer in oxidative atmosphere. Consequently, in this work an ultrathin polymer shell is deposited around the silver nanoparticles using the Layer-by-Layer method to provide additional stability. The effect of this polymer shell on the plasmonic properties is studied by building a finite element model (FEM) in COMSOL Multiphysics®. The near-field enhancement factor of these silver-polymer core-shell nanoparticles is studied as a function of the polymer shell thickness to determine the optimal shell thickness required for a given application. Comparison of the field enhancement simulations of the oxidized and the ultrastable silver-polymer core-shell nanoparticles corroborate the experimental results that unprotected bare silver nanoparticles are not viable for long term plasmonic applications (Figure 1). These ultrastable silver-polymer core-shell nanoparticles are further used in plasmon enhanced semiconductor (TiO2) photocatalysis. Simulating the interaction between silver and TiO2 is crucial to understand the mechanisms of near-field enhancement and charge transfer in plasmonic photocatalysis (Figure 2). Furthermore, these ultrastable silver nano-composites will be valuable in various plasmon-related applications that make use of hot spot effects of the plasmonic nanoparticles, which can be previewed using the FEM simulation. This will help identify the optimal arrangement of nano-arrays (Figure 3) and the required excitation wavelength depending on the application.

The near-field enhancement studies were done by finite element analysis using the Wave Optics Module of COMSOL. A plane wave polarized in the Z-axis direction and propagating along the X-axis direction was used for solving the scattered field of Maxwell's wave equations in a Wavelength Domain study. Figure 1 shows the normalized electric field enhancement (|E|/|E0|)2 emanating from the surface of a 18 nm bare silver nanoparticle,

this silver particle encapsulated by a polymer shell of thickness 1.4 nm and an oxidized silver particle encapsulated by a Ag2O shell of thickness 2 nm. The incident excitation wavelength of the monochromatic plane wave was always kept the same as the surface plasmon resonance wavelength of the respective core-shell nanoparticle system so that the maximal field enhancement is simulated after excitation at the SPR maximum. Additionally, theoretical calculations of the red shift in the surface plasmon resonance peak for core-shell nanoparticles performed in COMSOL were in good agreement with calculated extinction spectra from classical Mie theory equations and the experimental results.

This study exhibits how the FEM and field simulations using COMSOL Multiphysics® can act as a vital mechanistic tool to understand the plasmonic properties of silver nanostructures; and visualize their near-field enhancement which helps in more straightforward nano-engineering of dedicated plasmonic applications.

Reference

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Figures used in the abstract

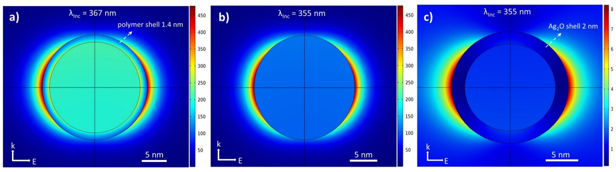

Figure 1: Near-field enhancement distribution maps of a) silver nanoparticle of dia. 18 nm encapsulated with 1.4 nm thick polymer shell, b) silver nanoparticle of dia. 18 nm and c) oxidized silver nanoparticle of dia. 16 nm with a 2 nm thick Ag2O shell.

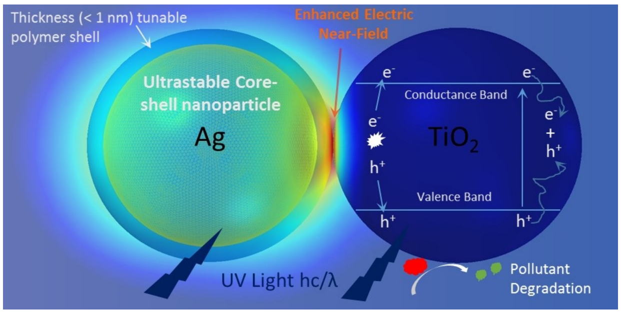

Figure 2: Scheme of Ag-polymer core-shell nanoparticle and TiO2 interaction as captured from COMSOL simulation and overlaid with textual description.

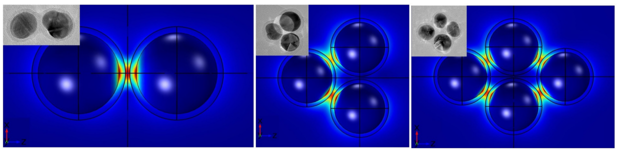

Figure 3: Dimer, trimer and tetramers of Ag-polymer core-shell nanoparticles exhibiting the hot spots generated because of surface plasmon resonance. Corresponding TEM images of core-shell nanoparticles are shown in the inset.