FDTD Investigation of Gap-Dependent LSPR in Ag Nanoparticles for Enhanced LIBS Sensitivity

Marcello Condorelli[1*], Luisa D'urso[1], Alessandro De Giacomo[2], Giuseppe Compagnini[1]

[1] Department of Chemical Sciences, University of Catania, Catania 95125, Italy
[2] Department of Chemistry, University of Bari, Via Orabona 4, 70126 Bari, Italy
*Corresponding author email: marcello.condorelli@unict.it

Plasmonic nanostructures offer unique opportunities to enhance light–matter interactions at the nanoscale, with significant implications for analytical techniques such as Laser-Induced Breakdown Spectroscopy (LIBS) [1]. To elucidate the role of localized surface plasmon resonances (LSPR) in signal amplification, we performed comprehensive numerical Finite-Difference Time-Domain (FDTD) [2] simulations of a 10 nm diameter silver (Ag) nanosphere on a dispersive plasma substrate modelled via the Drude formalism ($\varepsilon_\infty = 1$, $\omega_p = 1.37\times10^{16}$ rad/s eV, $\gamma = 3.34\times10^{13}$ rad/s).
A Total-Field–Scattered-Field (TFSF) plane-wave source and perfectly matched layer (PML) boundaries ensured precise excitation and absorption of electromagnetic fields, while a finely resolved local mesh (0.25 nm) around the nanoparticle and an extended substrate thickness (5 µm) effectively suppressed numerical artefacts [3]. We systematically studied both the near-field electric-field enhancement and the extinction cross-section as a function of the distance between the substrate and the Nanoparticle, moving this latter from 0 nm (contact with the substrate) up to 5 nm over the substrate.

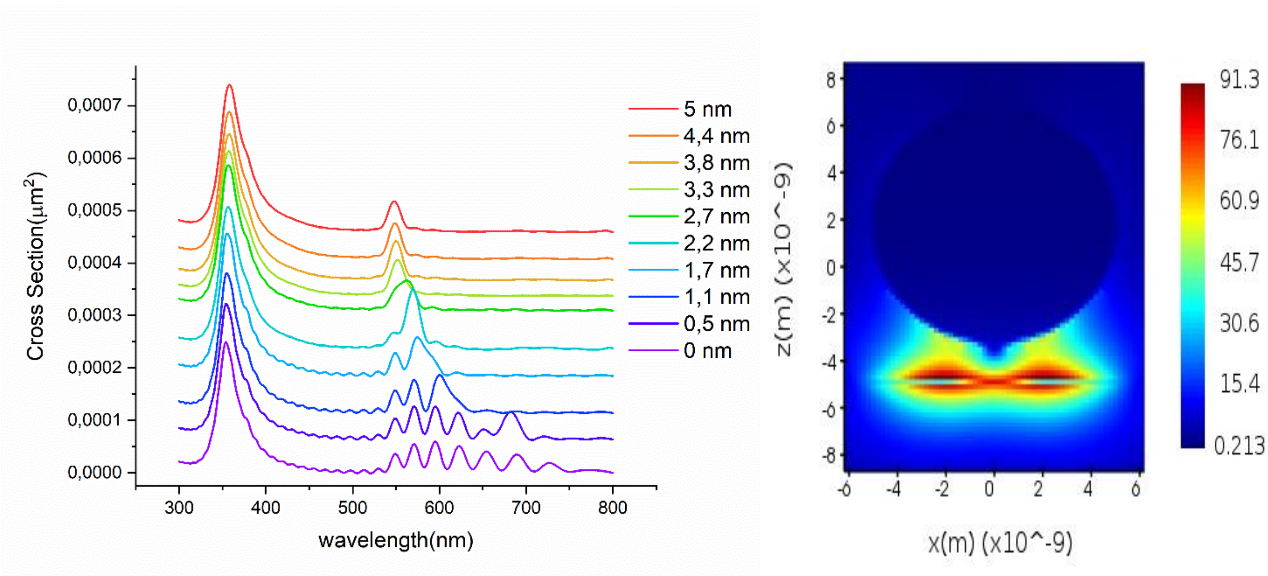

Figure 1: a) Calculated Extinction cross section of AgNPs on Plasma substrate with increasing gap b) Near Field at the interface AgNPs-Plasma with a gap of 1.7 nm

In Figure 1, the computed extinction spectrum reveals a dominant dipolar LSPR peak at ~ 380 nm due to the plasmon resonance of silver spherical nanoparticle and a secondary multipolar feature near 550 nm arising from particle–substrate coupling. Such coupling is also shown in the field-enhancement maps (Fig. 1b), which highlight a pronounced hot-spot in the gap region. In conclusion, Near-field amplification induced by the LSPR concentrates electromagnetic energy at the nanoparticle–substrate interface may lead to more efficient ablation and increased emission intensity of adsorbed species. These simulations provide a mechanistic foundation for the experimentally observed enhancement of LIBS signals when Ag nanoparticles are deposited on the measurement substrate.

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