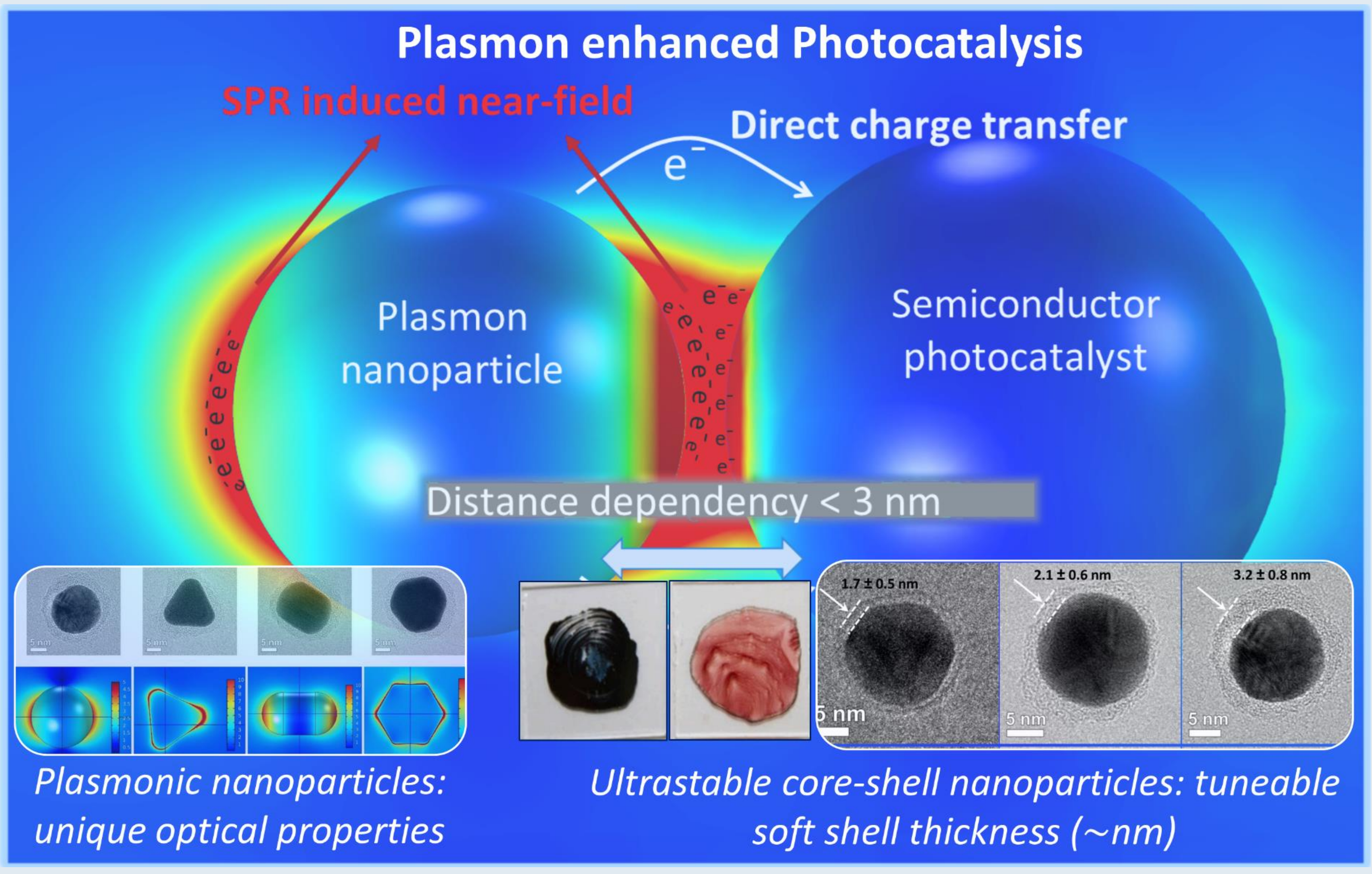

Mechanistic Study Of Plasmonic Photocatalysts Through Near-electric Field Simulations

Near-electric simulations are crucial to understand the charge transfer mechanism and provide vital insights for designing the nanostructures in plasmon-enhanced photocatalysis.

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Introduction

Near-electric field and hot electron transfer are the two major mechanistic pathways for semiconductor photocatalytic systems coupled with small size (dia. < 25 nm) plasmon nanoparticles[1].

In this work, we focus on elucidating the dominating mechanism of gold and silver plasmon-enhanced TiO_2 photocatalysis using polymer spacer layers for application in photocatalytic oxidation of acetaldehyde. The designed plasmonic photocatalytic system is shown in Figure 1.a, in which the semiconductor photocatalyst and the plasmon nanoparticle are separated by either an insulating or conducting spacer layer. The experimental results are compared with the near-electric field simulations by building FEM models of plasmonic photocatalysts using COMSOL Multiphysics®.

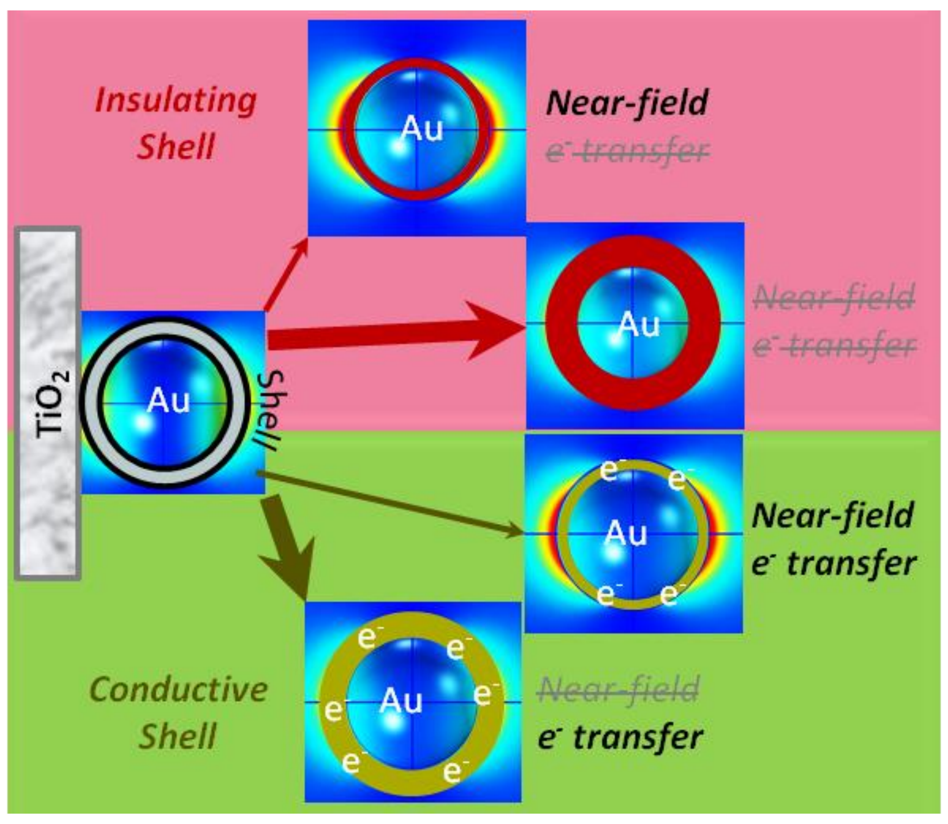

Figure 1.a) Schematic representation of plasmonic photocatalytic system design to study the effect of near-electric field

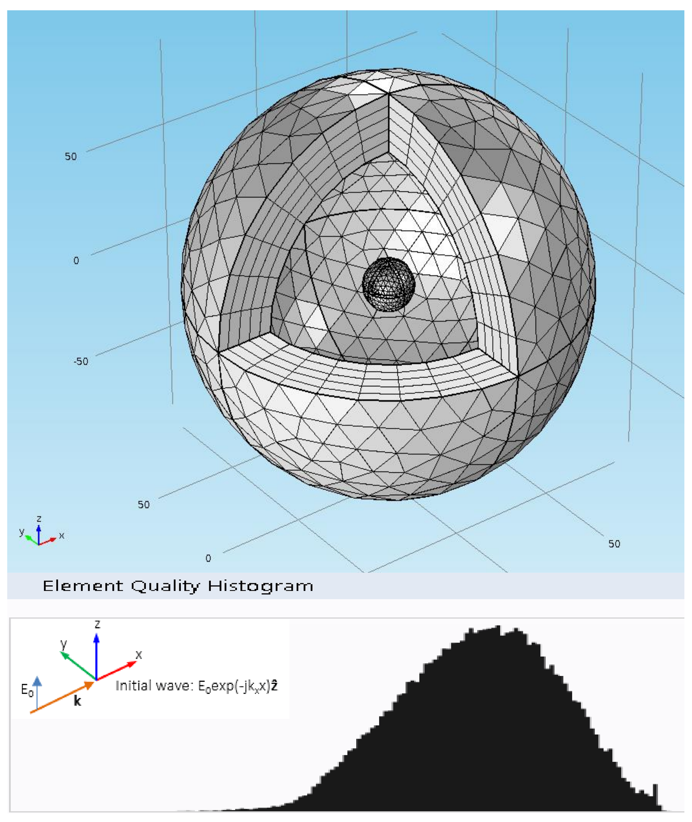

Figure 1.b) 3D models with meshing and a histogram of element quality

Methodology

In the near-electric field modeling studies, Maxwell's wave equations are solved with respect to the scattered electric field.

$$\nabla \times \left[\frac{1}{\mu_r}\left(\nabla \times \vec{E}_{sca}\right)\right] - {k_0}^2\left[\left(\varepsilon_r - \frac{i\sigma}{\omega\varepsilon_0}\right)\right]\vec{E}_{sca} = 0$$

3D models (Figure 1.b) of nanoparticles and core-shell nanoparticles with varying polymer shell thickness, which acts as a spacer layer, were built in the wave optics physics in COMSOL Multiphysics (version 5.3). A plane wave polarized in the Z-axis direction and propagating along the X-axis direction was solved for the scattered field in a wavelength domain study. The normalized electric field enhancement is estimated using the formula $|E|^2/|E0|^2$.

Results

The near-electric field simulation results shown in Figure 2 corroborate the experiments by providing crucial insight that near-field enhancements are vital for the photocatalytic reaction rate enhancement and have the highest benefit when the semiconductor photocatalyst and plasmon nanoparticle are in direct contact compared to interfacial contact. It is shown, through a combination of theoretical simulations, and photocatalytic activity tests, that for both insulating and conductive shells the near-field effect becomes insignificant for shell thicknesses exceeding 3 nm. observation hints at a dominant role of the near-field enhancement mechanism.

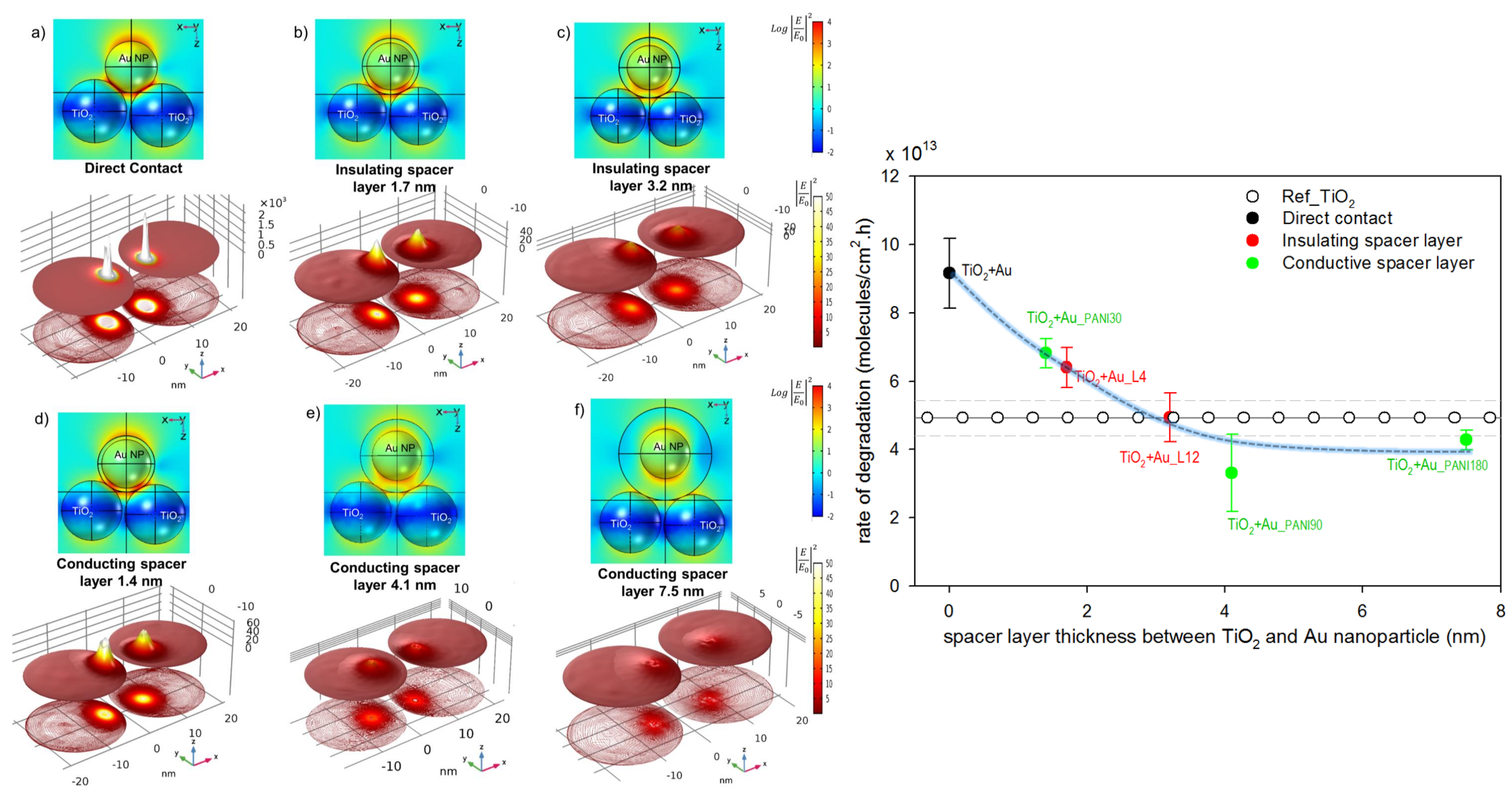

Figure 2. Left: Field enhancement distribution maps of Au-TiO_2 systems with the projection of TiO_2 surface contours with a height intensity scale at the bottom for different systems. Right: Experimental results of photocatalytic activity tests.

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