Plasmonic properties of metal-coated microsphere monolayers optimized for SERS applications

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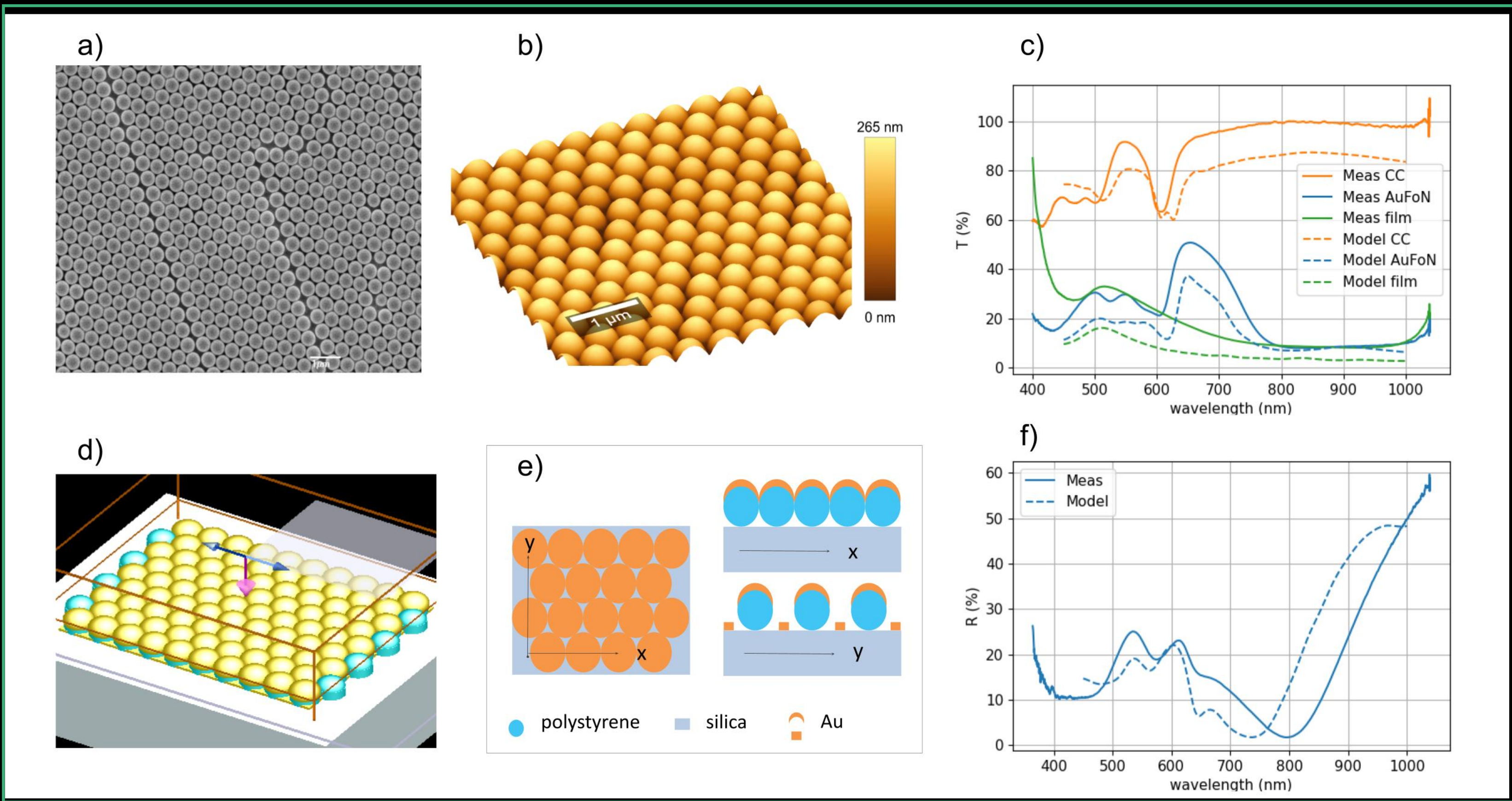
Metal-coated microsphere monolayers (MCMs) represent a class of plasmonic crystals with clearly proven capabilities as substrates for surface enhanced Raman spectroscopy (SERS). Their ability to amplify the intensities of Raman scattering of molecules by orders of magnitude relies on excitation of both localized and propagative surface plasmons. Using Finite-Difference Time-Domain (FDTD) simulations, we investigate the optical properties of gold-coated microsphere arrays, and their dependence on sphere size and thickness of the Au film, over a wide range of values. These optical properties can be linked to the existence of plasmonic effects.



The optical response of MCMs was simulated using Ansys Lumerical FDTD:

- A finite array of 9x10 polystyrene spheres;
- Closed-packed hexagonal structure;
- Sphere sizes: 200-1000 nm, Au film thickness: 40-200 nm;
- The Au film represented as ellipsoidal caps on top of the spheres, and an array of particles in between spheres, on the substrate.

Figure 1. (a) SEM and (b) AFM images of MCMs; (c) measured and modelled transmittance spectra for 50nm Au on 500 nm spheres, for bare colloidal crystals, MCM and a flat Au film; (d) snapshot of the simulation setup in Lumerical; (e) schematic representation of the simulation setup in x-y, x-z and y-z transects; (f) measured and modelled reflectance spectra for 60 nm Au on 500 nm spheres.

The inferred absorbance (1-T-R) of MCMs shows a well-defined band, owing to the existence of localized surface plasmons. Electric fields are strongly amplified near the junctions between two adjacent spherical caps.

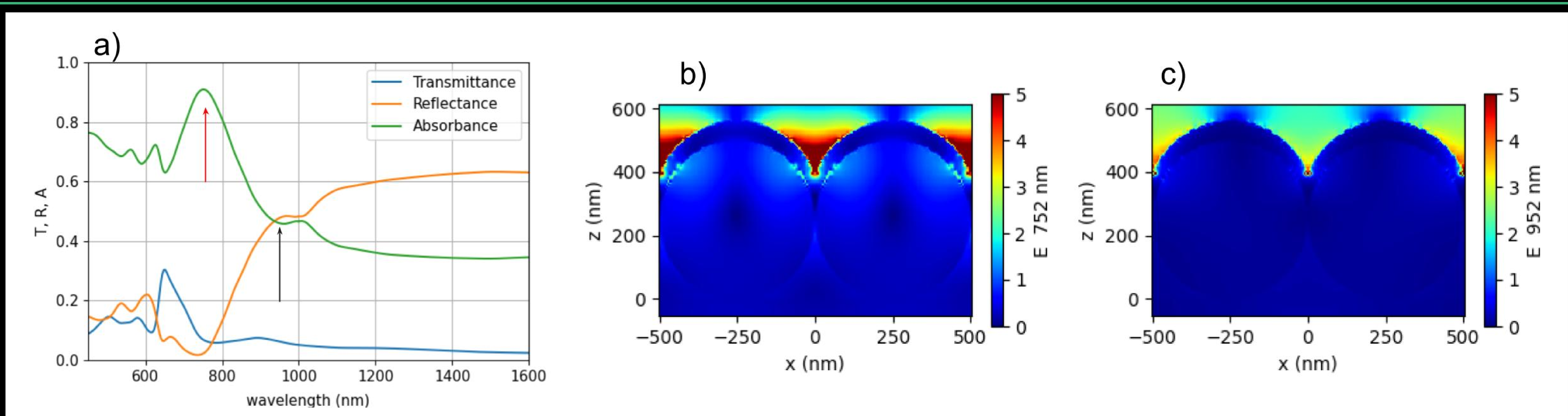


Figure 2. (a) Transmittance, reflectance and absorbance of 60 nm Au on 500 nm spheres in air; electric field magnitudes (b) at the maximum absorbance wavelength (indicated by red arrow in a) and (c) 200 nm away from the maximum absorbance wavelength (indicated by black arrow in a)

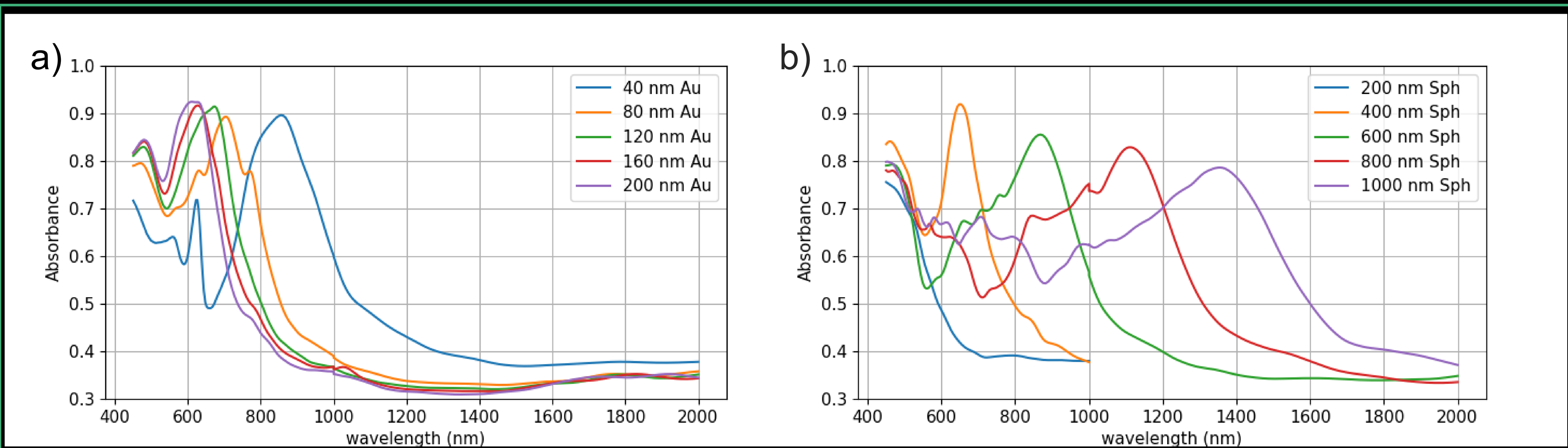
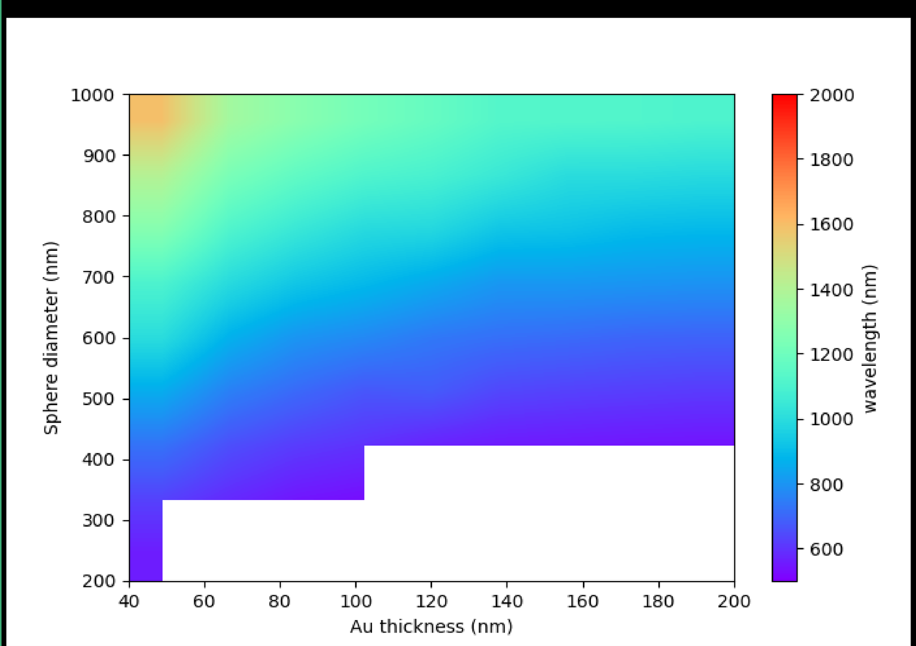


Figure 3. (a) MCM absorbance spectrum for 500 nm spheres and different Au film thicknesses; (b) MCM absorbance spectrum for 60 nm Au film on different sphere sizes.



MCM absorbance maximum shifts depending on the Au film thickness and the sphere diameter.

Figure 4. Maximum absorbance wavelength for a range of sphere sizes and Au film thicknesses.

A secondary absorbance was identified for large sphere diameters (>600 nm) and Au film thicknesses (>160 nm). This secondary maximum has a distinct distribution of the electric field, suggesting it is due to multipolar surface plasmons.

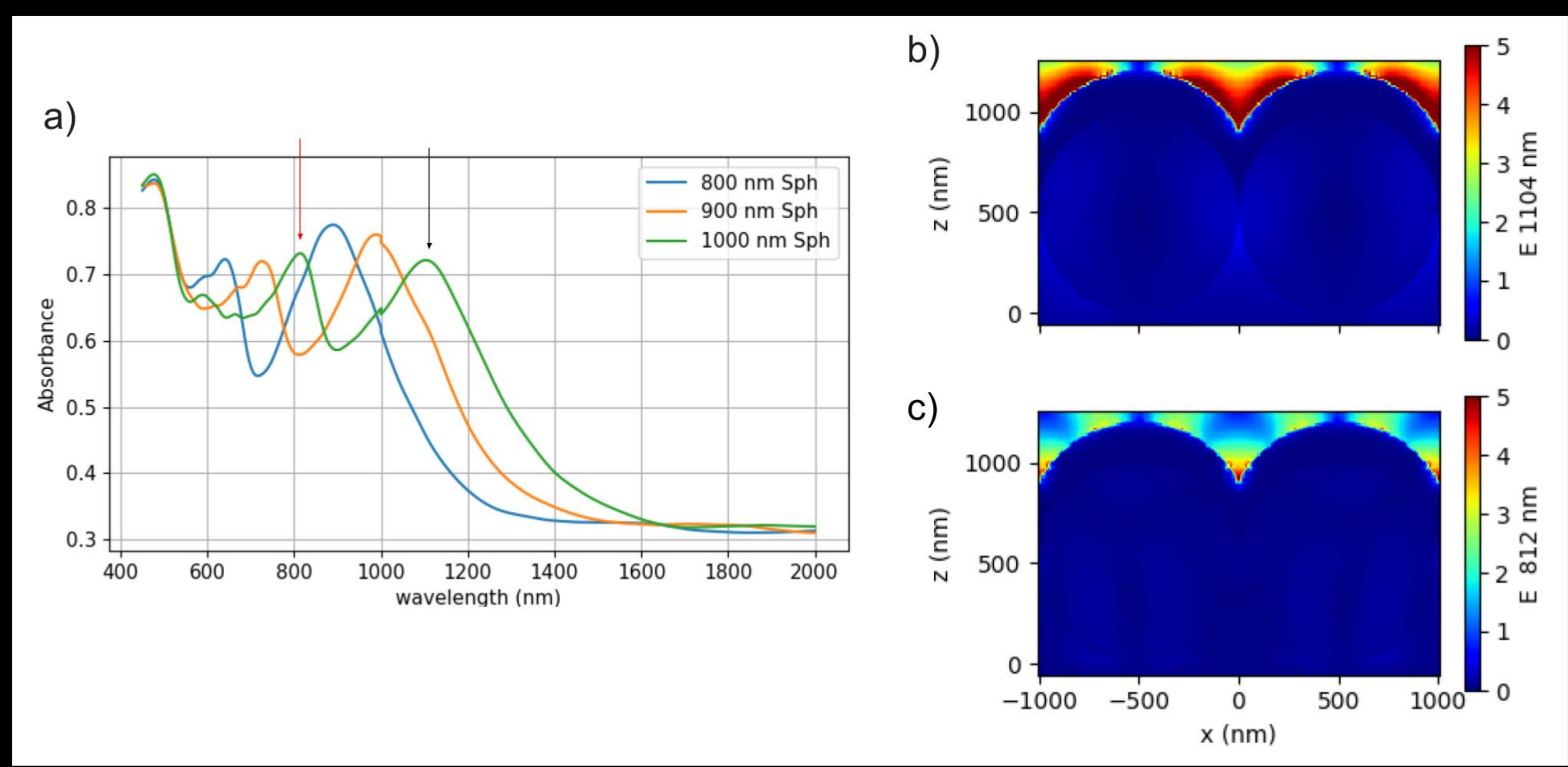


Figure 5. (a) Absorbance spectra for 200 nm Au on spheres between 800 and 1000 nm in air. The arrows indicate the wavelengths at which electric fields are shown in (b) and © for 200 nm Au on 1000 nm spheres.

Conclusions

- A model which reproduces well experimental results was implemented;
- The plasmon-induced absorbance of MCMs can be tuned by adjusting the sphere diameter and Au film thickness from the visible to the near-IR spectral range;
- A secondary absorbance band was identified and attributed to multipolar plasmon excitations;
- These results can be exploited for optimizing the SERS efficiency of MCM for sensing applications.

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