Controlled Surface Plasmon Resonance on Stable Substrates as an Optimized Sensing Platform

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Abstract: Precise control of localized plasmon resonance scattering spectra of gold nanoparticles on Al_2O_3 coated gold substrates were demonstrated. The scattering spectra remain stable after high power laser irradiation near the resonance wavelength.

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The localized surface plasmon resonance (LSP) of metal nanostructure is widely used in scientific studies and optical applications as a result of the high field enhancement it can provide, concentrated in a volume smaller than the classical diffraction limit. The associated strong light-matter interaction has enabled several applications including, photovoltaic response enhancement, enhanced nonlinear optical response, and various sensing modalities. Several studies have demonstrated that the extremely high field enhancements in the hotspots (locations with high electric field enhancement) of metal nanostructures enable detection of single molecules [1,2]. While many coupled plasmon resonance structures exist, the use of metal nanoparticles on polarizable substrates is attractive due to the simplicity of the system combined with a high degree of control of the local particle environment. Resonance spectra of metallic nanoparticles on substrates have been found to be reproducible, and tunable through variation of the particle-substrate interaction [3,4]. Recent studies on substrate-controlled localized plasmon resonance have used organic spacer layers to adjust the distance between metal nanoparticles and a substrate, resulting in control of the plasmon scattering spectra of the particles. While such organic layers present attractive features (solution processing, modifiable through organic chemistry), they may add background signal, and may degrade or change conformation upon irradiation.

In this study, we investigate plasmon enhanced light scattering of 60 nm diameter gold nanoparticles on an entirely inorganic platform consisting of Al_2O_3 coated Au films. In addition, the stability of the system upon high power laser irradiation is studied. The Al_2O_3 coated gold substrates were prepared by thermal evaporation of 50 nm gold films on a 2 nm Cr wetting layer on glass cover slides, followed by the deposition of thin Al films that fully oxidized upon exposure to ambient environment. Ethanol-diluted 60 nm diameter gold nanoparticle colloid solution (BBInternational, diluted to 2×10^8 particles/mL) was dropped on each substrate and left to dry. Figure 1(a) shows a darkfield microscopy image of gold nanoparticles distributed on a gold substrate.

Single particle scattering spectra of nanoparticles on the Al_2O_3 coated substrates were collected (~8×8 μm^2 collection area) using a 50× dark field objective and sent to an imaging spectrometer. Numerical simulations were carried out using the structural parameters as used in the experiment. The presence of a thin organic shell of a refractive index 1.5 was assumed to represent the likely presence of organic ligands in the colloid solution. Figure 1(b) presents the normalized scattering spectra of five nanoparticles on the five substrates (solid lines), and the calculated spectrum of a gold nanoparticle on a gold substrate with a 0.75 nm organic shell. The measured spectra show a blueshift of the LSP from 700 nm to 610 nm. The inset shows a snapshot of the simulated z-component electric field at 690 nm. The field is highly concentrated in the gap between the nanoparticle and the gold film. This field enhancement could be useful in sensing applications such as Surface Enhanced Raman Spectroscopy (SERS).

Electric field enhancements were probed by monitoring the simulated field inside a 1nm organic shell on the gold nanoparticle and compared with the z-component of the excitation field $E_{z,inc}$. The maximum observed z-polarized electric field $E_{z,max}$ corresponds to an enhancement factor $|E_z/E_{z,inc}|$ that ranges from ~290 to ~33 as the Al_2O_3 thickness increases from 0 to 4 nm. Figure 1(c) plots the maximum estimated Surface Enhanced Raman

Scattering (SERS) enhancement factor $|E_{z,max}/E_{z,inc}|^4$ in the organic shell versus wavelengths for different Al_2O_3 thicknesses. The peak SERS enhancement is higher than 10^6 for all plasmon resonance wavelengths and reaches a maximum of 7.4×10^9 in the absence of an Al_2O_3 coating. Please note that the simulations do not take into account non-local or quantum mechanical effects.

To investigate an ability to retain the spectrum shape and field enhancement factor, individual nanoparticles were exposed to 100 W/mm^2 laser irradiation at λ = 632.8 nm (He-Ne). The particles were excited using TM polarization in order to generate high field enhancement in the gap between the nanoparticle and the substrates. The laser was focused onto the substrates at a 15° angle using a 50× objective resulting in a measured spot diameter of 2.2 µm. Figure 1(d) presents spectra from gold nanoparticles on substrates without Al_2O_3 (black lines) and with a 1.3 nm Al_2O_3 coating (red lines). The solid and the dashed lines represent the spectra before and after one minute of high power irradiation, respectively. The scattering from nanoparticles on the substrate without an Al_2O_3 spacer layer show a large spectral change. Particle on the Al_2O_3 coated substrate show only a small redshift upon laser irradiation, and are therefore expected to provide stable field enhancement and Raman scattering signal under realistic measurement conditions.

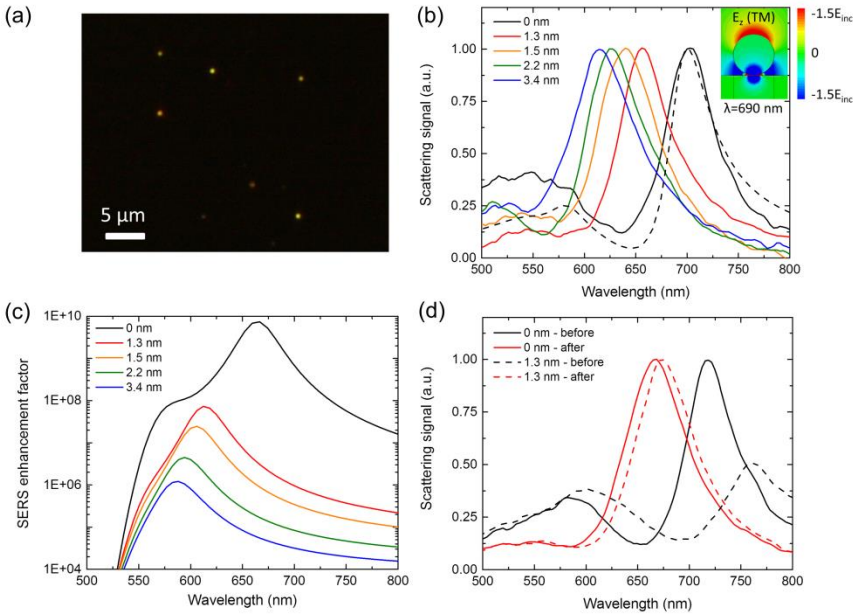

Fig. 1. (a) Darkfield microscopy image of gold nanoparticles distributed on a gold substrate. (b) Normalized scattering spectra of five gold nanoparticles on five different Al_2O_3-coated gold substrates and a simulated spectrum (dashed line). (c) Estimated SERS enhancement factor obtained from numerical simulations. (d) Measured scattering spectra of gold nanoparticles on a gold substrate (black lines) and on an Al_2O_3-coated gold substrate (red lines) before (solid lines) and after (dashed lines) one minute of 100 W/mm^2 irradiation at 632.8 nm.

This study of coupled resonances of gold nanoparticles on Al_2O_3 coated gold substrates shows a reliable plasmon resonance tuning method with a wide resonance tuning range of ~90 nm. The Al_2O_3 layer provides good stability upon laser irradiation. This stability, the known chemical and mechanical stability of Au and Al_2O_3, the achieved resonance wavelength range, and the anticipated low background signal from the substrate make the presented system a good candidate for a reliable plasmonic sensing platform.

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