Supporting Information

Single Nanoparticle Based Hetero-Nanojunction as a Plasmon Ruler for Measuring Dielectric Thin Films

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Materials and Methods

1. Fabrication of hetero-nanojunctions

The SiO_2@Si substrates (5 mm × 5 mm size, pre-cut from a Si wafer, <100> oriented, p-type, obtained from University Wafer with a thin native SiO_2 layer of ~2.3 nm,) were snow-jet cleaned to remove dust and contaminants. The substrates were treated with O_2 plasma (Femto, diener electronic, gas pressure 0.5~1 bar) for different time periods. The thickness of SiO_2 layer was determined by an alpha-SE ellipsometer. The bare Si substrate was obtained by etching the thin native SiO_2 layer in a HF buffer solution. The Si substrates with varying silica layers were then immersed in a 1 mM solution of 4,4′-dimercaptostilbene (dithiol; >96%, Aldrich) in tetrahydrofuran (THF) for 1 hr to allow the formation of a monolayer of dithiol molecules and subsequently rinsed with THF to remove the excess molecules from the surface. Then a drop of AuNPs with an average diameter of 100 nm (BBI life sciences; 5.60×10^9 particles/ml) was cast onto the dithiol functionalized SiO_2@Si substrates for approximately 1-30 min, followed by rinsing and air-drying to remove unattached AuNPs. It should be noted that the concentration of the AuNPs colloidal solution and the casting time were carefully adjusted to achieve a rather low NP surface coverage (shown in Figure 1g) in order to eliminate the inter-particle electromagnetic coupling. Typically, for adsorption on bare (HF and dithiol treated) Si surface 1 min were sufficient to obtain the kind of coverage shown Figure 1g and for SiO_2 surfaces a 10-30 min adsorption time was required. For the detection of adenine molecules, the pre-cut Si substrate was snow-jet cleaned and subsequently treated in O_2 plasma for approximately 1 min to activate the surface in order to improve the bonding between SiO_2 and adenine molecules. The functionalization of AuNPs with adenine was carried out by mixing 70 μL of 1 mM adenine

aqueous solution with 500 μL of 100 nm AuNPs. After stirring for 2 hr, the adenine-functionalized AuNPs were separated *via* centrifugation and re-suspended in DI water. Then a drop of functionalized AuNPs was cast onto fresh plasma-treated Si substrate. After drying, the substrate was rinsed in DI water and blow dried.

2. Simulations

A three-dimensional model using COMSOL Multiphysics v4.3 was constructed. The simulation was performed in two steps: the first step is for the substrate only, using Floquet boundary conditions combined with a port-boundary for the field excitation. The second step was solved with the AuNP on the substrate. Perfectly matched layers were used at the boundary to absorb the scattered radiation in all directions, particularly to prevent scattering artefacts from edges. The near-field was taken as the maximum value of the electric field in the middle of the gap normalized to the incident wave $|\boldsymbol{E}|/|\boldsymbol{E_0}|$. The AuNP was modeled separated from the Si substrate by a gap of 1.3 nm, corresponding to the length of the molecular spacer layer (in the current case dithiol molecules[1]) in addition to the thickness of the intervening silica layer. The *p*-polarized light at incident angles of 45° to the surface normal was used. The illumination angle of 45-deg was chosen for matching the 0.85 NA objective used for the Raman spectra collection. The complex refractive index of Au as a function of wavelength was taken from the literature.[2] The near-field was taken as maximum value of the electric field in the middle of the gap normalized to the incident wave $|\boldsymbol{E}|/|\boldsymbol{E_0}|$. The simulation was carried out at a wavelength of 633 only to understand Raman enhancements produced by the AuNP on substrate configuration.

3. Characterization

Raman spectra were acquired using a Renishaw inVia Raman system equipped with an integral microscope. An objective with the magnification of 100× (Leica, NA: 0.85) was used. Laser with wavelength of 633 nm was used as the excitation source. The dark-field scattering spectra were collected using an optical microscope (Olympus BX51) coupled to an Ocean Optics QE65000 spectrometer (spectral range: 200−1100 nm) with a 50 μm diameter optical fiber (Ocean Optics QP50-2-VIS-BX). An objective with a magnification of 100× (NA: 0.80) was used.

Peak assignments of adenine[3]

Raman shift (cm^{-1})	**Assignments**
735	ring breath whole molecule
1181	bend C8H, N10-H11, str C4-N9, N3-C4, C6-N10
1253	bend C8-H, N9-H, str N7-C8
1322	str C2-N3, N1-C2, C5-C6, C5-N7
1380	bend C2-H, N9-H, str C8-N9, C4-N9
1466	str C2-N3, N1-C6, bend C2-H, sciss NH_2
1532	str N7-C8, bend C8-H, sciss NH_2
1586	sciss NH_2

Bend: bending; str: stretching; sciss: scissoring

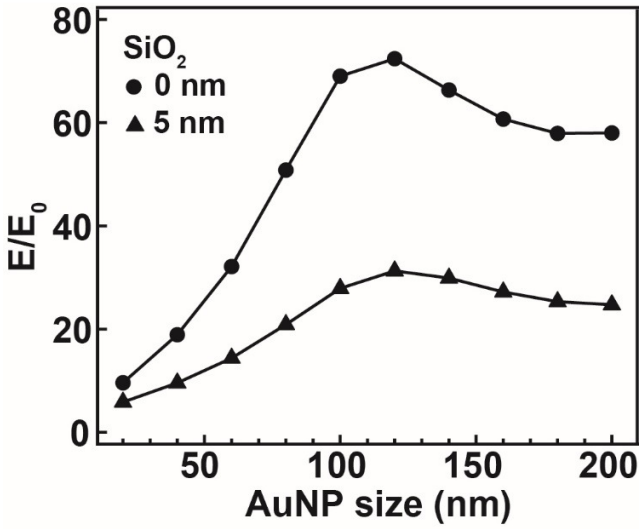


Figure S1. The simulation of the effect of Au NP size on the near-field property for the Si substrate and for the 5 nm SiO_2@Si substrate.

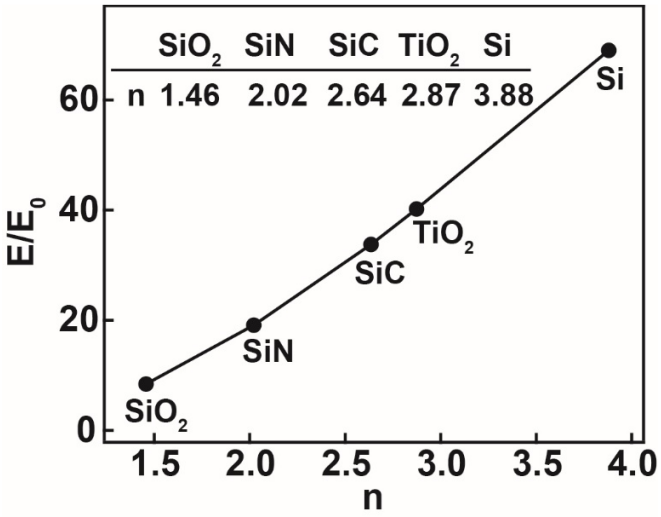


Figure S2. Simulation of the effect of refractive index of dielectric substrates on the electromagnetic field enhancement. The 100 nm Au NP is placed 1.3 nm above different dielectric substrates. The electromagnetic field is calculated at the gap at a wavelength of 633 nm.

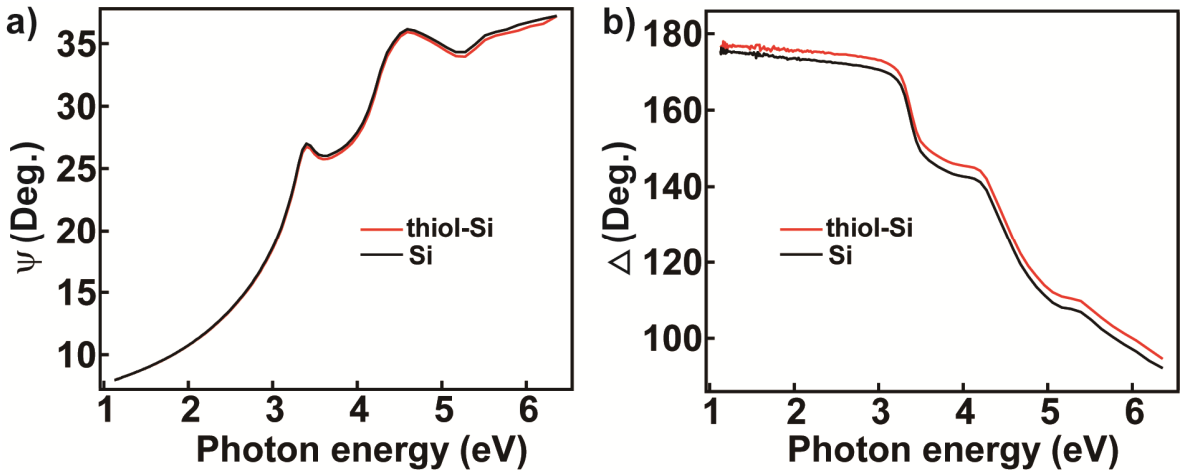
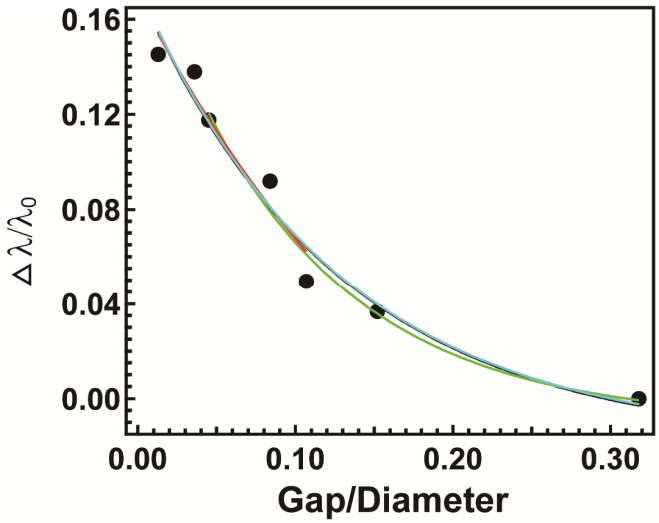


Figure S3. Experimental ellipsometric spectra of ψ and Δ for 4-aminothiophenol functionalized Si and Si substrates. The thickness of the thiol monolayer was determined as 0.64±0.80 nm (MSE = 0.002699) with the aid of Lorentz oscillator model, which confirms the immobilization of thiol molecules on the Si substrates. Moreover, the thickness of this thiol is expected to be half of the 4,4′-dimercaptostilbene used in the paper, thus justifying the use of 1.3 nm as the thickness of the dithiol layer.



Gap/Diameter fitting range	Exponential fitting function	τ
0.013 ~ 0.318 (—)	$y = -0.0186 + 0.192e^{-x/0.127}$	0.127
0.013 ~ 0.107 (—)	$y = -0.101 + 0.271e^{-x/0.211}$	0.211
0.045 ~ 0.318 (—)	$y = -0.00940 + 0.202e^{-x/0.101}$	0.101
0.013 ~ 0.318 (—)	$y = -0.0182 + 0.0941e^{-x/0.133} + 0.0976e^{-x/0.121}$	0.133, 0.121

Figure S4. Experimental fractional plasmon shift *vs* ratio of gap to AuNP diameter, which were fit to single-exponential decays over different ranges (black, red and green curves) and double exponential (blue curve) decays. The final fitting results and the decay constants from the fittings are listed in the table. Note that the plasmon maximum for 30.5 nm SiO_2 spacer layer has been used as the reference ($\lambda_0 = 544$ nm) for calculation of the shift. The gap is set as the SiO_2 thickness and the length of the dithiol molecules (1.3 nm).

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