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Gap controlled plasmon-dielectric coupling effects investigated with single nanoparticle-terminated atomic force microscope probes

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Precise positioning of a plasmonic nanoparticle (NP) near a small dielectric surface is not only necessary for understanding gap-dependent interactions between a metal and dielectric but it is also a critical component in building ultrasensitive molecular rulers and force sensing devices. In this study we investigate the gap-dependent scattering of gold and silver NPs by controllably depositing them on an atomic force microscope (AFM) tip and monitoring their scattering within the evanescent field of a tin dioxide nanofiber waveguide. The enhanced distance-dependent scattering profiles due to plasmon-dielectric coupling effects show similar decays for both gold and silver given the strong dependence of the coupling on the decaying power in the near-field. Experiments and simulations also demonstrate that the NPs attached to the AFM tips act as free NPs, eliminating optical interference typically observed from secondary dielectric substrates. With the ability to reproducibly place individual plasmonic NPs on an AFM tip, and optically monitor near-field plasmon-dielectric coupling effects, this approach allows a wide-variety of light-matter interactions studies to be carried out on other low-dimensional nanomaterials.

Quantifying near-field optical interactions at a dielectric or metal surface is extremely useful in the design of tip enhanced near-field microscopes,^{1,2} surface plasmon resonances,³⁻⁵ nonlinearly optics,^{6,7} and other ultrasensitive detection schemes.⁸⁻¹⁰ However, to properly evaluate local light-matter interactions, the gap between two surfaces has to be controlled with high precision (< 1 nm) and reproducibility without interfering with the optical signal. In the case of a plasmonic nanoparticle (NP) and a dielectric surface, one surface has to be moved relative to the other and either held fixed while an optical measurement is taken or the system has to allow real-time optical feedback while separation distances are modulated. Of the many methods to control gap separation between a metal nanoparticle and dielectric surface which include

polyelectrolytes multilayers,¹¹⁻¹⁴ self-assembled monolayers,^{15, 16} and thin oxide layers grown on the NP,⁷ the direct manipulation of a single NP using scanning probe methods is preferred as it provides the most straightforward and clean method to reproducibly probe interactions close to a surface. In fact, atomic force microscope (AFM) tips modified with metal NPs have been used for force indentation and tapping-mode imaging as well as to discover the unique optical phenomena such as single molecule fluorescence and second-harmonic generation of dyes.^{6, 17} Unfortunately, the methods to link an individual NP to a cantilever tip generally require either complicated chemistries to attach or grow, or high-resolution microscopy techniques (e.g., confocal microscope) to monitor the tip.¹⁷⁻²³ Here, we describe a simple and robust strategy to pick up a single metal NP on the end of AFM tips and use the tips to routinely investigate the gap-dependent optical coupling between the NP and a dielectric nanofiber waveguide (WG).

Previously we demonstrated that the movement of plasmonic NPs embedded in the near-field of a tin dioxide (SnO₂) nanofiber WG can be tracked with angstrom-level spatial sensitivity.¹³ The NP-WG separation distance in this system is monitored by simply measuring the far-field scattering intensity. The large enhancement in the distance-dependent scattering is due to a combination of effects including the strong plasmon-dielectric coupling between the NP and WG surfaces as well as the exponentially decaying evanescent field of the WG. This WG system not only provides an ideal platform to study gap-dependent plasmon-dielectric coupling effects, but understanding near-field light interactions in these materials also paves the way for a new breed of ultrasensitive molecular rulers and force transducers.²⁴

To routinely link a single plasmonic NP to the end of AFM tips, we modified the method developed by Kalkbrenner *et al.* of using PEI coated probes to pick up gold NPs under confocal microscopy¹⁹ and combined it with a force mapping strategy that utilizes ideal electrostatic

conditions between the AFM tip and substrate to pick up an individual NP.^{25, 26} The AFM tips were first scanned in contact mode on a silicon surface to slightly flatten the tip end. Both AFM tips and silicon chips were cleaned in a piranha solution for 10 min and then rinsed with de-ionized (DI) water. The dull AFM tips were immersed in 5% polyethylenimine (PEI) for 1 hour, and then rinsed with DI water to remove any residual polymer. Citrate-stabilized NPs (80 nm diameter) were centrifuged and spin-coating onto the silicon chip to form a partial monolayer of NPs. To reduce the capillary adhesion of water during AFM force indentation, the NP chips were immersed in hydrofluoric acid (5% in water) to remove the silicon oxide layer of the chip and hydrogenate the surface. Once the AFM tips and NP silicon chips were prepared the tips could be indented on the chip in force mapping mode in air to locate a single NP. After centering the tip on a NP, the NP was picked up by increasing the applied force. As shown in Fig. 1a, the attachment of the NP causes an abrupt change in the force mapping image (i.e., NP disappears) and a decrease in the adhesion force during the force curves helps confirm that the NP has been transferred to the tip. Direct evidence for the attachment of single gold and silver NPs was confirmed with scanning electron microscopy (SEM) which also allowed us to verify a success rate of ~ 75% for attaching either silver or gold NPs (Fig. 1b). The NP-terminated AFM tips are mechanically stable in air and fluids. This was not the case for metal-sputtered tips which showed rapid scratching and metal delamination from the tip when repeatedly contacted with a surface (Fig. S1†).²⁰ We tested a variety of AFM tips and found that cantilevers with spring constants ranging from 0.03 N/m to 0.6 N/m had similar results. If the spring constant was too small, the AFM tip remained adhered to the thin capillary layer on the substrate not allowing movement in the z-range during piezoelectric translation. If the spring constant was too large, the NPs were moved away by the AFM tip due to large shear forces during indentation.

Fig. 1 Attaching NPs on AFM tips and their optical responses. (a) (Left) A typical force mapping image along with force curves using a PEI coated AFM tip centered around a single NP. (Right) A force mapping image with force curves after increasing the force to pick up the NP. The black and red lines are the extension and retraction traces during force mapping around a single NP on the silicon chip, respectively. The solid and dotted lines correspond to force curves before and after pickup, respectively. (b) SEM images of the AFM tip after picking up a single gold (upper image) and silver (lower image) NP. (c) Scattering spectra taken from the end facet of the WG and from individual gold and silver NPs in water. (Black) Spectra taken at the end facet of a clean waveguide after exciting it with a UV laser (325 nm) on the opposite end. (Red) Scattering spectra of a single NP sitting on the SnO_2 WG while being excited with the near-field. (Blue) Scattering spectra of a single NP sitting on an ITO surface excited under dark-field epi-illumination.

To obtain scattering spectra and produce scattering intensity references for the distant-dependent studies, NPs were directly fixed to the surface of the SnO₂ WGs. This was achieved by transferring WGs (cross-sectional dimensions of 200-400 nm) to a quartz chip (Fig. S2†) and aminizing the surface by immersing the chip in a 5% aminepropyltrimethoxysilane solution in ethanol for 1 minute. Then the WGs were placed in a colloidal solution of citrate stabilized gold or silver NPs which electrostatically attached to the positively charged WG surface. There is a blue shift (~ 40 nm) in the scattering peak for both gold and silver NPs when they are excited by the evanescent field of the WG (Fig. 1c) compared to the scattering profile of individual NPs dispersed on an indium tin oxide (ITO) substrate (excited with a dark-field epi-illumination). The shift in the scattering peak is likely caused by the excitation with the guided modes compared to the white light source used in the dark-field epi-illumination, rather than a difference in the refractive index between the two surfaces. Because waveguiding is stronger for the shorter wavelengths, the resulting scattering spectrum is a deconvolution of the plasmon resonance and the guided wavelengths.

Fig. 2 Integrated AFM/optical setup. (a) Photograph showing the experimental setup of the integrated AFM/UV laser excitation mounted on an inverted optical microscope. (b) Schematic of the experimental setup showing the WG, AFM cantilever, laser excitation, shortpass filter and collection objective. The

laser excites the WG at an $\sim 45^\circ$ angle relative to the sample plane. NP1 and NP2 correspond to the distance-controlled scatterer and the reference scatterer, respectively.

In order to carry out the controlled distance-dependent scattering experiments, a UV excitation laser was integrated with an AFM scanner mounted on an inverted optical microscope (see Fig. 2). To help guide the position of NP1 (i.e., the nanoparticle on the AFM tip), and provide a reference for the scattering intensity when the NP1 is in contact with WG, a second NP (NP2) was attached directly on the SnO₂ surface prior to carrying out the AFM experiments using techniques similar to those described above. To couple light into the WG, a helium-cadmium continuous wave laser ($\lambda = 325$ nm) was focused onto one end of the WG to generate white defect emission in the SnO₂. Because the excitation energy is larger than the band gap of SnO₂ ($E_g = 3.6$ eV), and the band edge is dipole forbidden, sub-band levels can be populated (e.g., due to oxygen vacancies in the crystal) which generates a broad emission spectrum across the visible range. Some of the defect emission is trapped in the nanofiber due to the high index of refraction of SnO₂ and launched down the WG.^{27, 28} To eliminate light collection from the AFM's feedback laser ($\lambda_{\text{peak}} = 650$ nm), and boost the signal-to-noise ratio from the scattering NPs, a 600 nm shortpass filter was used in the collection optics prior to the quantitative charge coupled device (CCD) camera. After aligning the NP1-terminated AFM tip with the center of the waveguide, it was moved into the near-field at a slow speed of 8 nm/s. Fig. 3a shows the scattering intensity of a gold NP as a function of tip-WG separation as well as the scattering intensity from a reference particle attached to the WG surface. As anticipated the maximum scattering intensity achieved with the NP1-terminated tip is similar to that of NP2. We observed small dips in some of the scattering intensity profiles at max force when using the NP1-terminated AFM tips which can be explained by the sliding of the NP1 toward the edge of the WG during larger loads. When we

intentionally applied a large shear force to transfer NP1 from the AFM tip to the WG, we found that the intensity of NP1 after transferring is comparable to NP2 (Fig. 3b). Thus there appears to be negligible interference from the AFM tip that might influence the optical interaction of the NP with the WG surface. We also ran the same experiment using silver NP-terminated AFM tips, and a larger peak scattering intensity is observed (Fig. 3c). Experimental details and movie are included in the ESI.[†] As discussed in more detail later, plasmonic materials can have different light-matter interactions depending on their composition, size, or shape, and in the case for silver it is expected to have a stronger scattering intensity than gold due to a larger scattering cross-section. Importantly, these scattering experiments can be reproducibly generated using the described protocol for functionalizing AFM tips with individual NPs.

Fig. 3 Optical response of NPs in the near-field of a WG. (a) Indentation trace (black) using a gold NP1-terminated AFM tip. The bright spot (point 2) is a reference gold NP2 that is attached to the SnO_2 surface which gives a nearly flat continuous signal (red). The slight decrease in signal at max force is caused by a decrease in guided power as NP1 on the AFM tip extracts a larger amount of light out of the WG at small separations. The optical image (inset) shows the reference NP2 and the outline of the AFM cantilever (red dashed line) when it is far away from the WG (white dashed line, light is guiding from top to bottom). The tip position is highlighted with a red cross and moves perpendicular (i.e., in and out of the image plane) to the surface. The top x-axis represents distance between the tip and the waveguide. (b) Comparison between the scattering intensity of a gold NP1 (point 1 – black trace), after being detached

from the AFM tip via an applied shear force, and a gold reference NP2 (point 2 – red trace). (c) Indentation trace (blue) of a silver NP-terminated AFM tip compared to the same gold nanoparticles in (b).

Because the AFM cantilever is controllably moved in the z direction, an accurate near-field map of the scattering intensity vs distance can be compiled from different NPs and directly compared to simulations. Fig. 4 shows finite-difference time-domain (FDTD) simulations carried out on the WG system and overlaid with experimental data. Although the polarization of the guided light is difficult to control in the experiments, given that the light is generated from defect states in the SnO_2 crystal, the exact polarization state of the excitation source can be defined in the simulations (See Fig. S3†). From the localized power (time-averaged Poynting vector) distribution images it can be seen that the light-matter interaction with p-polarized light [or transverse magnetic (TM), where the electric field is orthogonal to the WG surface and in the plane of the shown inset image] is much stronger than that of s-polarized light [or transverse electric (TE), where the electric field is parallel to the WG surface and coming out of the page when looking at the inset image]. In addition, p-polarized light has a slightly smaller decay constant compared to s-polarized light. The steeper decay and larger E-field enhancement of the TM mode is due to the creation of a stronger dipole and induced dipole (i.e., charges are in closer proximity) in the metal NP and WG, respectively. This enhancement can be best described by an effective polarizability of the NP defined as $\alpha_{eff} = \alpha(1 + \beta)/(1 - \alpha\beta/16\pi(r + d)^3)$,^{3,4} where α is the polarizability of the plasmonic NP, β is the magnitude of the substrate image [i.e., $\beta = (\epsilon_s - 1)/(\epsilon_s + 1)$, where ϵ_s is the permittivity of the substrate], r is the radius of the NP (~ 40 nm) and d is the separation distance between the NP and WG. Furthermore, the scattering intensity and scattering cross-section of the NP are directly related to the effective polarizability through the following expression:

$$I \propto C_{sca} e^{-\frac{d}{\gamma}} = \frac{8\pi^3}{3\lambda^4} |\alpha_{eff}|^2 e^{-\frac{d}{\gamma}} \quad (1)$$

where I is the scattering intensity, C_{sca} is the scattering cross-section of the nanoparticle near a dielectric surface, γ is the evanescent decay constant of the WG in water, λ is the wavelength of the guided light (centered at ~ 500 nm), and d is the distance between the NP and the WG surface. Therefore, the TM mode generates a larger effective polarizability in the metal NP due to a stronger coupling between the dipole (metal) and induced-dipole (SnO_2), and it is evident that the experimental decay has better agreement with the TM excitation, suggesting that this polarization produces the dominant scattering signal on the WG. Likewise, silver and gold can have different scattering cross-section (see Fig. 3c) and suggests that silver could have a steeper (smaller) decay constant compared to gold. However, in the experiments we observed very similar decays for the gold and silver NPs (Fig. 4b). The scattering-distance data with fittings using eq. 1, where γ is the only fitting parameter, gave the same decay constant of 34 nm.

Fig. 4 Comparison of experimental and simulated NP scattering intensity decays vs distance. (a) Experimental (black squares) and FDTD simulation data (solid lines) of the scattering-intensity vs distance for the gold NP system. Both p-polarized and s-polarized light are shown for the simulation data. The inset shows cross-sectional images of the simulation showing the electromagnetic power distribution around a gold NP for the two excitation polarizations. (b) Experimental (black and red squares) and

analytical solution (black and red solid lines) data showing the normalized scattering intensity vs distance for a gold and silver NP scattering in the near-field of a SnO_2 WG.

The scattering decay constants can be strongly dependent on many factors including excitation wavelength, AFM tip/sample optical interference, nanoparticle size/shape, waveguide size, and metal composition. These experiments resulted in slightly different scattering decays compared to those our group measured using polymer spacers to incrementally separate the NPs from the WG surface.^{13, 14} The simulations and experimental data in this work suggest that the AFM tip and NP position does not interfere with the scattering experiments, so this is an unlikely cause for the different decay constants. Besides the strategy for controllably separating the NP from the waveguide, the collection geometry for this work is also different. With the AFM/optical microscope we are collecting on the opposite side from where the NP is being moved through the evanescent field. This could change the collection efficiency (e.g., photons can scatter off the WG prior to reaching the collection objective) and ultimately the near-field mapping. However, we have carried out various controls with nanoparticles positioned (confirmed with SEM image) on different sides of the WG and observe similar scattering intensities from the individual NPs (Fig. S4†). The discrepancies are most likely coming from variations in the size/shape of the nanofiber which can alter the power and wavelength that the plasmonic NP interacts with.

In conclusion, we have developed a simple method for efficiently (~75% success rate) linking individual plasmonic NPs to the end of an AFM tip and have used these probes to controllably move the NP within the near-field of a nanofiber WG to map out the scattering intensity as a function of distance with nanometer resolution. We demonstrated through experiments and FDTD simulations that the decays are independent of whether the NP is on the AFM tip or free-standing. The decay constants for the distance-dependent scattering for gold and

silver NPs have similar values mainly due to the intimate relationship with the exponentially decaying optical power in the evanescent field. Simulations also confirm that the strongest plasmon-dielectric coupling effects are observed when the dipole in the plasmonic NP and induced-dipole in the dielectric are aligned end-to-end along the axis that runs through the NP and WG. These probes not only find immediate application in studying near-field light-matter interactions on 1D and 2D materials, but can also be leveraged for controlled tip-enhanced Raman spectroscopy and imaging.

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