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Exploring the Decay Channels of Plasmons

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Abstract

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When an incident electromagnetic wave at optical frequencies couples to a metallic nanostructure, it creates coherent resonances of free carriers in the metal known as plasmons. Plasmons can decay and generate carriers (hot electrons) that have higher energies than the Fermi level of the metal. Plasmon-induced hot electrons are important since they carry the energy signature of the absorbed incident photons. When a metallic nanostructure is patterned on a silicon substrate, hot electrons can be transported over the junction between the metal and the semiconductor, to be collected as a photocurrent. Plasmonic absorbers that generate hot electrons are tunable over much broader spectral regimes than semiconductor absorbers. However, the poor responsivity (~ 1mA/W) is the major drawback with these devices. Thus, increasing the photocurrent response is crucial for hot electron devices. In my research, we increase the current flow of hot electrons over a Schottky junction by modulating the Schottky barrier in reverse bias and we acquire a signal that is much greater than the original hot electron flow of the nanostructures. With this method we amplify the photocurrent signal using a CMOS compatible fabrication process on silicon substrates. Our approach to amplify the hot electron-based photocurrent opens up the possibility of making cheap plasmonic sensors with direct electrical readout, such as an on-chip plasmonic detector with tunable
wavelength sensitivity that can operate beyond the conventional semiconductor photodetectors.

Along with generating hot carriers in the absorptive decay channel, plasmons also lose some part of their energy to radiation. The plasmonic resonances of metallic nanoparticles concentrate electromagnetic fields into nanoscale regions. We used this property of plasmons to focus light on ultra-thin semiconductors (such as monolayers of MoS$_2$) to increase the light absorption in the material and therefore increase the photocurrent signal. In this work, by tuning the plasmon resonances of gold nanoshells to the direct band gap of monolayer MoS$_2$ and depositing them onto the surface of the material, we acquired a threefold increase in photocurrent and photoluminescence signal for the excitonic transitions of the monolayer. This finding provides a new mechanism toward increasing the quantum efficiency of ultra-thin semiconductors for opto-electronic applications, enables more than three times narrower spectral response than observed for nanoantenna-based devices. This approach opens up the possibility of plasmonic sensors with direct electrical readout, such as an on-chip surface plasmon resonance detector driven at a single wavelength.

When plasmon resonances decay, some part of their energy decays under the radiative channel and the metallic nanostructures scatter light. Aluminum nanostructures are highly promising plasmonic nanoantennas for their bright plasmonic light scattering. Even at the individual nanocystal level, however, the localized plasmons supported by Al nanostructures possess a surprisingly bright radiative response. Here, we show that when an Al nanocrystal is closely coupled to an underlying Al film, its dipolar plasmon peak linewidth narrows significantly, and reveals a remarkably enhanced scattering
efficiency. This behavior is far more dramatic in the aluminum nanoparticle-film system compared to such a system for other metals like gold, reducing the dipolar plasmon linewidth by more than half for aluminum. Our finding provides a new mechanism for narrowing plasmon resonances in aluminum-based systems, expanding the potential of aluminum plasmonics in real-world applications.
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Chapter 1: Introduction to Plasmonics

Plasmons, or collective oscillations of free electrons in metallic nanostructures, provide a mechanism for light concentration from free space into nanoscale volumes.\(^1\) Recently, plasmonics have been under a great interest for their properties that encompasses a broad range of technological applications from cancer therapy\(^2\textsuperscript{–}^4\) to solar cell energy harvesting\(^5\textsuperscript{–}^7\), metamaterials\(^8\textsuperscript{–}^{10}\), nonlinear optics\(^11\textsuperscript{–}^{13}\) and surface enhanced sensing and spectroscopy\(^14\textsuperscript{–}^{17}\). These technologies rely on the properties of plasmonic resonances: high localization of electromagnetic field, resonant scattering, and plasmonic absorption in nanoscale volumes. Much work has been done on making more efficient, wavelength and polarization sensitive plasmonic structures that are functional over a broad region of optical frequencies.

In this manuscript, chapter 2 will talk about how Schottky devices can be used to harvest hot electrons into a wavelength sensitive photocurrent. In addition, this chapter provides a detailed look at our technique to improve the external quantum efficiency and hot electron responsivity of Schottky photodetectors.

Chapter 3 demonstrates how plasmonic nanoshells can concentrate light on atomically thin materials and enhance the ultrathin material’s photoluminescence and photocurrent responsivity by more than a factor of two. This improves the potential of using 2D materials for ultrathin, transparent and flexible optoelectronics.
Finally, chapter 4 indicates our method to narrow the plasmonic resonance peaks of aluminum nanocrystals by coupling them to an underlying aluminum film. This chapter includes our experimental and theoretical approaches to explain this narrowing mechanism by plasmonic hybridization between the dipolar and quadrupole plasmons of the nanocrystal through the Al film. Our finding opens up new potentials for the applications of aluminum nanostructures where the wavelength sensitivity of the resonances is required.
Chapter 2: Enhancing Hot Electron Photocurrent with a Plasmonic Schottky Diode

2.1 Abstract

Plasmon-induced hot electrons have wide variety applications such as in photocatalysis and photodetection. When a metallic nanostructure is patterned on a silicon substrate, generated hot electrons can be transported over the junction between the metal and the semiconductor, to be collected as a photocurrent. Plasmonic absorbers that generate hot electrons are tunable over much broader spectral regimes than semiconductor absorbers. However, poor responsivity (~ 1mA/W) is a major drawback with these devices. Thus, increasing the photocurrent responsivity is crucial for hot electron devices. In this work, we increased the current flow of hot electrons over a Schottky junction by reducing the damping of hot electrons in the photoemission process under non-biased device conditions. Further, using a simple silicon fabrication process, we amplified the hot electron photoresponse by modulating the Schottky barrier height under bias and we acquire a signal that is much greater than the original hot electron flow of the nanostructures. Our approach to amplify the hot electron-based photocurrent opens up the possibility of making cheap plasmonic sensors with direct electrical readout, such as an on-chip plasmonic detector with tunable wavelength sensitivity that can operate beyond conventional semiconductor photodetectors.
2.1 Introduction

When an incident electromagnetic wave at optical frequencies couples to a metallic nanostructure, it creates coherent resonances of free carriers in the metal, known as plasmons, which creates a mechanism to concentrate free space electromagnetic waves into nanoscale volumes. Along with the high field localization, Plasmon resonances decay via light scattering and plasmonic absorption. Because of these decay channels surface plasmons are of great interest for a broad range of technological applications, such as metamaterials, solar cell energy harvesting, surface enhanced sensing and spectroscopy, and novel medical therapies.

When plasmons decay via the absorptive channel, they generate carriers (hot electrons) that have higher energies than the Fermi level of the metal. Several groups have reported metal-semiconductor devices (such as Schottky diodes) that are extracting this hot electron photocurrent for photodetection. When electromagnetic waves couple to a metallic nanostructure patterned on a semiconductor substrate, the generated plasmons create hot electrons in the metal. Since the hot electrons have the same energy as their excitation photon, they are capable of transferring across the Schottky barrier at the metal-semiconductor interface and create a photocurrent signal even at zero bias. This type of device converts light captured by the nanoantenna into an electrical signal. Unlike semiconductor absorbers, the photoresponse of hot electron based photodetectors are tunable both in wavelength and in polarization of the incident light.

The biggest challenge for plasmonic hot electron photodetectors is their lower external quantum efficiency and photocurrent responsivity compared to conventional
semiconductor absorbers.\textsuperscript{29,30,34–36} Recently, multiple methods have been used to improve the responsivity of these detectors from few nA/mW at zero bias to few $\mu$A/mW. It has been shown that by using metallic metamaterials we can increase the plasmonic absorption close to 100\% which substantially improves the hot electron generation and consequently photocurrent responsivity up to 3.5 mA/W.\textsuperscript{34} Other researchers have demonstrated that by embedding the metallic nanostructures into the semiconductor to expand the contact area between them the extraction of hot electrons from the metal will be more efficient and the responsivity increases at zero bias by an order of magnitude.\textsuperscript{37,38} Moreover, several groups have reported amplification of the photocurrent responsivity under an applied voltage.\textsuperscript{39,40} In these devices the metallic nanostructure injects hot electrons into a semiconductor medium to increase its poor conductivity. Under an applied voltage the current that passes the semiconductor, when illuminated with light, increases substantially from the initial dark state, and this change in the electric current is a measure of responsivity. However, amplifying the responsivity limits the speed of these hot electron devices, due to the low speed of charge accumulation in the semiconductor inter-medium, making these devices very slow.\textsuperscript{39,40}

In this work, we show that by reducing the damping of the injected hot electrons into the semiconductor we increase the photocurrent responsivity of a gold/titanium-silicon Schottky nanodiode by an order of magnitude at zero bias. Further, employing two Schottky diodes in series, with one forward biased and the other reverse biased,\textsuperscript{41} we amplified the hot electron photoresponsivity and acquire a signal that is significantly larger than the original hot electron flow of one Schottky diode at zero bias. This is a
simple and compact method to increase the photocurrent responsivity of hot electron devices, while the unity gain bandwidth remains very high. Our approach opens up the possibility of making cheap plasmonic silicon-based sensors with responsivities comparable to InGaAs detectors.

2.3 Increasing the external quantum efficiency by reducing the hot electron damping

We used gold grating structures on n-type silicon substrates to harvest their hot electron photoresponse. Metallic gratings efficiently couple to light and have been previously used for their strong hot electron-induced photocurrent responses and their spectrally sharp resonance peaks. Figure 1a shows the cross sectional view of a periodic grating structure on an n-type silicon substrate and Figure 1b presents a scanning electron micrograph of the grating device with S=250 nm, P=1 \( \mu \)m and T=200 nm on an n-type silicon substrate.

Figure 2a demonstrates the band formation of the Schottky device. The gold gratings are deposited with a 3 nm titanium adhesion layer, which forms a Schottky barrier of 0.5 eV with the silicon substrate. Hot electrons generated in the gold that have higher energy than the barrier transfer across the titanium-silicon interface and relax to conduction band of silicon. In our devices, we put an indium ohmic contact to collect the injected electrons from the silicon. When the hot electrons reach the depletion region in the silicon opposite the Schottky barrier, because of the higher density of the holes in the
depletion region, some of the injected electrons recombine (Figure 2b). Thus, reducing the electron decay into hole traps at the depletion region significantly increases the hot electron flow from the Schottky diode.

To examine the hot electron damping in the depletion region, we fabricated identical gold grating structures on n-type silicon substrates with different dopant densities of $1 \times 10^{15}$, $1 \times 10^{17}$, and $5 \times 10^{19}$ cm$^{-3}$. These dopant densities correspond to resistivities of ~ 1, 0.01 and 0.001 ohm-cm, respectively. Appendix A demonstrates the I-V curves for the Schottky diodes. Figure 2c shows the photocurrent responsivity spectra of these three devices. Previously, silicon substrates with 1–10 ohm-cm resistivity have been used for hot electron photodetection in the NIR. However, in Figure 2c, we observe the substantial effect of the substrate dopant density on the quantum yield of the hot electron Schottky diodes. When the substrate resistivity is 0.01 and 0.001 instead of 1 ohm-cm, the hot electron photoresponse increases by a factor of two and a factor of ten, respectively (Figure 1c).

Figure 1: (a) Schematic of a gold nanoantenna-silicon Schottky diode. (b) Scanning electron micrograph of a gold grating structure on a silicon substrate with the grating...
thickness (T) of 200 nm, width (P) of 1 μm for the gold bars and 250 nm distance between them (S).

The significant increase in the hot electron photocurrent of the gratings is due to narrowing of the depletion region in silicon. Under no external electric field, the depletion width of the Schottky diodes decreases by increasing the career density (dopant density) of the bulk Si substrate according to the formula below:\[^{42}\]

\[
W = \sqrt{\frac{2\phi_B}{N_d}}
\]  

(1)

Where, \(W\) is the width of depletion region, \(\phi_B\) is the Schottky barrier and \(N_d\) is the doping density of silicon. For the Si substrates with resistivities of 1, 0.01 and 0.001 ohm-cm, \(W\) equals 260 nm, 12 nm and 2 nm, respectively. When the hot electrons reach the depletion region, some of them recombine into the holes (Figure 2b). Narrowing \(W\), as a result of increasing the dopant density in silicon, reduces the recombination probability and increases the photocurrent signal (Figure 2c). Appendix B shows the tunability of the photocurrent responsivities of the Schottky diodes on the substrates with different resistivities.
Figure 2: (a) Hot electron generation and injection in the band diagram of gold nanoantenna-silicon Schottky diode. (b) Schematic of electron decay into holes in the depletion region of the Schottky diode. (c) Photocurrent spectra at zero bias for similar
gold gratings with T=200 nm, P=1 μm and S=250 nm on silicon substrates with resistivities of 1, 0.01 and 0.001 ohm-cm.

**2.3 Amplifying the hot electron-induced photoresponsivity**

Additionally, applying an external electric field to the hot electron path amplifies the photoresponsivity. We fabricated two Schottky diodes back to back and in series with each other (BBD) such that they are connected through the silicon substrate (Figure 3a). After laser excitation, hot electrons transfer from the gold nanostructure into the silicon conduction band in one of the diodes (Figure 3a-left diode). Under the external electric field, the injected electrons travel to the second Schottky diode and because of the existence of the barrier (Figure 3a-right diode) on their pathway, they accumulate behind the Schottky barrier. In this configuration, one diode is in forward and the other is in reverse bias. The accumulated electrons at the second Schottky barrier lower the barrier height and increase the photocurrent response significantly.\(^{41}\)

To create a BBD device we fabricated a grating nanostructure in which the interdigitated fingers are connected with each other through the silicon substrate (Figure 1a). The interdigitated rods of metal that create a grating is a good design for a BBD configuration since the nearby blocks are closely coupled to each other and generate strong plasmon resonances.\(^{30,43}\) In addition, the vicinity of the gold blocks to each other, in gratings, can create large external electric fields under small bias voltages. Further, the high surface coverage of metal in this case reduces the possibility of burning the metallic structures under high electric field applied.
Figure 3b represents the photocurrent responsivity of a BBD grating nanostructure with $S=250$ nm, $P=1$ $\mu$m and $T=200$ nm on an n-type silicon substrate (1-10 ohm-cm) under various external electric fields along with the photocurrent of a single diode grating at zero bias (Figure 2a and 2c). The responsivity of BBD amplifier increases with the eternal electric field and its spectral shape remains unchanged. Figure 3c demonstrates the I-V curves of a BBD with and without laser illumination. The illumination laser is 1500 nm in wavelength and 1.5 mW in power. At the large bias of 9 V we acquired the responsivity of 67 $\mu$A/mW.

We calculate the external quantum efficiency (EQE) of the BBD amplifier by analyzing the slope of the linear regions of the I-V curves for dark and illuminated conditions (inset of Figure 3c). The change in the conductance from dark to bright is linearly dependent on the external quantum efficiency:

$$
\Delta \sigma = q \left( \mu_n + \mu_p \right) \Phi \eta
$$

(2)

Where $\Delta \sigma$ is the change in the conductance, $q$ is the electron charge, $\mu_n$ and $\mu_p$ are the electron and hole mobilities, $\Phi$ is the photon flux, and $\eta$ is the EQE. With the laser power of 0.82 mW at 1500 nm, the photon flux is $1.81 \times 10^{15}$ s$^{-1}$ and $\Delta \sigma$ 2.2E-6 mho, thus the EQE is 0.41%. This is one order of magnitude higher than the EQE of 0.015% for a similar Schottky-ohmic device at zero bias (Figure 3b, black spectrum).
Figure 3: (a) Schematic of two nanoantenna Schottky diodes connected to each other via silicon substrate when the device is under an external electric field. The injected hot electrons from the left diode accumulate behind the depletion region of the right diode and reduce the barrier height. (b) Photocurrent spectra of a double Schottky device with $T=200$, $P=1 \, \mu m$ and $S=250 \, nm$ under various external fields. (c) I-V characteristic of the double Schottky device under dark (black) and laser illuminated (red) conditions. The inset shows a zoomed in view of the linear regime of the I-V curves.

To improve the photoresponse amplification, we encapsulated the injected electrons from metal in the silicon substrate. Figure 4a shows the schematic of a BBD amplifier on a silicon on insulator (SOI) wafer. The top silicon layer is a 1-10 ohm-cm n-type substrate with the thickness of 2 $\mu$m which is on top of a 1 $\mu$m thick SiO$_2$ layer. To trap the injected electrons in the silicon we etched the substrate and made silicon islands with 20 $\mu$m width, 100 $\mu$m length and 2 $\mu$m height. Figure 4a-bottom represents the schematic of the hot electron flow in the silicon island substrates and demonstrates larger flow of electrons between the nearby Schottky diodes compared to Figure 4a-top, where some electrons dissipate to places far from the diodes. Figure 4b shows an SEM image of a BBD amplifier on a silicon island.

To compare the hot electron photocurrent between the two configurations, we plotted their photoresponsivity peaks in respect to the applied external field (Figure 4c). For electric fields below 0.15 V/$\mu$m the photoresponses of the BBD grating device on a flat SOI wafer (red) is almost equal to the response of a similar device on a silicon island (black). The slight difference between the two is due to the slight variation in the
fabrication and geometrical factors. However, for larger external fields, the responsivity of the grating device on the Si island increases to substantially more than the responsivity of the gratings on a flat SOI wafer. When hot electrons pass the Schottky barrier into the Si substrate, under the applied electric field some electrons move toward the nearby Schottky diode, however, some electrons travel in the substrate to places that are far from the Schottky contact (Figure 4a, top). Because of the electron trapping in the silicon island, the density of the injected electrons accumulated behind the Schottky barrier of the secondary diode increases and results in more barrier lowering and a larger photocurrent signal.
2.4 Summary

In summary, we improved the external quantum efficiency of the Schottky nano-diods by an order of magnitude at zero bias through reducing the hot electron damping in the depletion region of the Schottky diodes. Moreover, employing a BBD grating
device we amplified the hot electron photocurrent responsivity under external electric fields. We further enhanced the photocurrent amplification by encapsulating the injected electrons in the silicon substrate to increase the conductivity of the Schottky barriers more effectively. Our approach opens up the possibility of making plasmonic silicon-based sensors that have wavelength and polarization sensitivity with high responsivity in the near infrared to be a good replacement to InGaAs photodiodes.
Chapter 3: Enhancing the Photocurrent and Photoluminescence of CVD-grown Single Crystal Monolayer MoS$_2$ with Resonant Plasmonic Nanoshells

3.1 Abstract

Monolayer molybdenum disulfide produced by controlled vapor-phase synthesis is a commercially promising new two-dimensional material for optoelectronics because of its direct bandgap and broad absorption in the visible and ultraviolet regimes. By tuning plasmonic core-shell nanoparticles to the direct bandgap of monolayer MoS$_2$ and depositing them sparsely (<1% coverage) onto the material’s surface, we observe a threefold increase in photocurrent and a doubling of photoluminescence signal for both excitonic transitions, amplifying but not altering the intrinsic spectral response.

3.2 Introduction

The realization of graphene growth by chemical synthesis has led to significant commercial interest in the employment of graphene’s unique optoelectronic properties arising from its two-dimensional nature.\textsuperscript{45-47} Advances in chemical synthesis have recently been made for several two-dimensional materials including hexagonal boron nitride,\textsuperscript{48} GeS,\textsuperscript{49} GaSe,\textsuperscript{50} and MoS$_2$\textsuperscript{51-54} enabling a scalable path toward commercial applications of their distinctive properties. MoS$_2$, a semiconducting transition metal
dichalcogenide, is of particular interest due to the emergence of a direct bandgap as it approaches monolayer thickness.\textsuperscript{55–57} Recently, several groups have demonstrated photodetection from mechanically exfoliated single layer \( \text{MoS}_2 \)\textsuperscript{58,59} and multilayer \( \text{MoS}_2 \) sheets.\textsuperscript{60,61} Single layer \( \text{MoS}_2 \) has been shown to possess a direct bandgap of 1.8 eV (in contrast to the 1.2 eV indirect bandgap of bulk \( \text{MoS}_2 \)).\textsuperscript{52,62} As a result of this direct bandgap, monolayer \( \text{MoS}_2 \) is a more efficient light-absorber (per layer) than its bulk phase,\textsuperscript{52} however, its subnanometer thickness results in a low absorption cross section.

Absorption enhancement can be achieved by utilizing the strong local field concentration of plasmons, coherent oscillations of free electrons in metallic nanostructures at optical frequencies, at the resonant wavelength of the nanostructure. Consequently, several groups have demonstrated the role of plasmonics in enhancing the measured photocurrent from both prototypical semiconducting materials\textsuperscript{63} and two-dimensional materials.\textsuperscript{64,65} In this manuscript we resolve the theoretically predicted excitonic transitions from the absorption peaks in the wavelength-sensitive photovoltaic signal of monolayer \( \text{MoS}_2 \) and we demonstrate the enhancement of these peaks in both photocurrent and photoluminescence spectra by tuning the plasmonic resonance of silica-gold nanoshells (AuNS) to the energy region of the excitonic transitions in monolayer \( \text{MoS}_2 \).

3.3 Photocurrent and Photoluminescence enhancement with plasmonic nanoshells
CVD-grown MoS$_2$ monolayers were synthesized following the recipe as previously reported in which we expose MoO$_3$ to sulfur at high temperature and allow for the growth of MoS$_2$ single crystals.$^{51}$ Large single-crystal monolayers of MoS$_2$ (SCM MoS$_2$) were initially identified using optical microscopy, then characterized by Raman spectroscopy to confirm their monolayer nature. The mobility of the SCM MoS$_2$ is in the range of 2-10 cm$^2/(V\cdot s)$, measured with Hall effect probes. The uniform continuous growth of SCM MoS$_2$ results in the macroscopic triangular shapes crystals as shown in Figure 1a. Electrodes were patterned on top of triangular individual crystals using photolithography and then backgated to form a photosensitive Field Effect Transistor (photoFET) device. The scanning electron microscopy (SEM) image and schematic of a typical photoFET are shown in Figures 1a, and b, respectively.
Figure 5: (a) SEM image of MoS$_2$ device coated with nanoshells. Monolayer MoS$_2$ is the blue triangle underneath the yellow gold electrodes. The scale bar is 5µm. The inset is a higher magnification image of nanoshells on the surface. (b) Schematic of the MoS$_2$ photoFET. The inset represents a magnified view of nanoshells on MoS$_2$.

To enhance the intrinsically low absorption cross section of monolayer MoS$_2$ we exploit the tunable plasmon resonance of gold nanoshells (AuNS). Resonant light is absorbed efficiently by the AuNS, generating a local field at the surface of the MoS$_2$. This results in enhanced electron-hole pair generation in the monolayer and an increased photocurrent.$^{66,67}$ We have deposited AuNS on the device surface with an average interparticle distance of less than 1 µm to avoid plasmon coupling between adjacent nanoparticles, typically at a surface concentration of $< 1\%$ (varying from $0.2\%$ to $0.6\%$). The scattering cross-section of AuNS on the MoS$_2$ monolayer is measured with darkfield
spectroscopy under unpolarized white light illumination, showing a strong scattering maximum in the spectral region of 600 - 700 nm (Figure 2a). The AuNS were designed to have a SiO₂ core with a 60 nm radius and an outer Au shell thickness of 30 nm.

The plasmonic enhancement of both the photocurrent spectrum and the photoluminescence spectrum were observed. We clearly observe an enhancement (Figure 2b, green spectra) of more than a factor of three in the photocurrent responsivity, while the spectral shape remains consistent with that of the pristine device (Figure 2b, red spectra). Enhancement factors ranged between 1.5 and 3.5 across multiple tested devices due to experimental variations in the dispersion of AuNS atop the MoS₂, implying that enhancement could be more dramatically increased with optimization of the AuNS surface coverage.

For photoluminescence (PL) spectroscopy, the device is excited with a 514 nm laser before and after coverage with the dispersed AuNS (Fig. 2c) Placing AuNS on the MoS₂ surface and again measuring the PL with the same laser at equal laser power we detect a PL signal which is approximately twice that of the pristine sample. The higher PL signal is likely the direct result of increased photoabsorption in the MoS₂ due to the AuNS (Figure 2c, green curve). PL spectroscopy confirms the improvement seen in the photocurrent signal (Figure 2b) after placing AuNS on the surface.

The photocurrent responsivity of pristine SCM MoS₂ photoFET (Figure 2b, red curve) displays two peaks, one at 630 nm (1.97 eV) and the other at 680 nm (1.82 eV). These peaks are in good agreement with the calculated direct-gap excitonic transitions for a single layer MoS₂.⁵⁵,⁶⁸ The two peaks in the spectral signature arise from spin-orbit
coupling of the valance band electrons at the K symmetry point of the direct bandgap. The energy difference of the band separation is 150 meV, in agreement with literature values. The sharp decay in the photocurrent spectra at wavelengths longer than 680 nm indicates the absence of the indirect bandgap in the monolayer. This is qualitatively distinct from the absorption spectra of bulk MoS$_2$, where the indirect bandgap of 1.3 eV causes an additional shoulder in the spectrum at nominally 960 nm in wavelength. Similarly, PL of pristine MoS$_2$ (Figure 2c, red curve) shows two peaks, one at $\sim 630$ nm (1.97 eV) and the other at $\sim 682$ nm (1.81 eV). The locations of these peaks are very close to the peak positions measured with photocurrent spectroscopy. The
The relative strength of these two peaks is also in good agreement with the expectations for single-layer MoS$_2$ where the PL signal of the higher energy transition (~2 eV) is seen to decay to nearly zero as the number of layers decreases. For both photocurrent and photoluminescence the addition of AuNS serves only to increase the overall signal level and has very little effect on the position of the detected peaks.

To demonstrate that the measured photocurrent is being produced solely within the MoS$_2$, we spatially mapped the responsivity of the device (Figure 3). Laser illumination
of 645 nm, 680 nm and 750 nm was used to map the photocurrent. The laser spot was focused to ~ 2µm in diameter and the beam spot was rastered over the device area with no significant change in the laser beam intensity. The left-most image in Figure 3 shows the SEM image of the laser-scanned area; the current was measured between the two middle electrodes as indicated by the illustration of the circuit. A reduction in the photocurrent signal as the laser wavelength was varied from 645 nm to 680 nm to 750 nm is consistent with the spectral shape of the photocurrent in Figure 2b. Figure 3 establishes that all the photocurrent measured between the electrodes comes from the excited carriers in MoS₂ and no additional signal appears to be obtained from either gold electrodes or the substrate. As a further validation of the photocurrent properties, we have observed that the photocurrent signal remains stable with repeated laser on/off cycles and that its response time is less than 6 ms for both on and off laser switching.
3.4 Conclusion

In summary, we have investigated CVD-grown MoS$_2$ single crystals using photocurrent spectroscopy. The measured photocurrent reveals two distinct absorption peaks, confirmed with our photoluminescence spectra, at 1.82 eV and 1.97 eV which are in good agreement with theoretical predictions for the direct excitonic transitions in MoS$_2$. We show that the absorption can be enhanced by more than a factor of three with less than 1% surface concentration of plasmonic silica-gold nanoshells tuned to the region of excitonic transition. This plasmonic enhancement is observed in both photocurrent and photoluminescence signals without altering the intrinsic spectral features. The observation that single-crystal MoS$_2$ properties are strongly enhanced by bandgap-resonant plasmonic nanoparticles, even at very low concentrations, paves the way toward the coupling of plasmonic nanoparticles and nanostructures to this unique 2D layered direct-gap semiconductor for further modification of its electronic and optical properties.

3.5 Methodes

Photocurrent spectroscopy was performed by illumination with an ultrabroadband-supercontinuum laser (Fianium SC400) with wavelength selection from an Acousto-Optical Tuning Filter (AOTF). The laser beam was focused to ~ 2 µm in diameter; small enough to place the laser spot in the center of a 4 µm gap between the electrodes to avoid
contact effects. Photocurrent responsivities were acquired using a lock-in amplifier (Signal Recovery 780) referenced to the 1.3 kHz modulated laser beam. Phase-sensitive measurement is important to avoid the convolution of thermal effects in our measurements of MoS$_2$ caused by the laser beam. All photocurrent measurements performed here were done under 80 V gate voltage ($V_G$) and 1 V source-drain voltage ($V_{DS}$).

**PhotoFET fabrication** is done by growing SCM MoS$_2$ on a SiO$_2$ (300 nm on Si wafer) substrate and employing a single step UV lithography for patterning the electrodes on top of MoS$_2$. For UV lithography, we spun-coated LOR8A as a lift-off resist for 40 sec and 3500 RPM, then the sample was soft baked for 4 minutes at 160°C. We did the same spin coating process on S1813 photoresist and baked it for 1 minute at 110°C. After mask alignment and UV exposure, we developed our sample in MF-319 for 45 sec. 4/100 nm of Ti/Au was evaporated on the sample and it was soaked in PG remover (to dissolve LOR8A) and Acetone (to dissolve S1813) repeated. LOR8A is used to improve the lift off and to avoid sonication (which alters contacts destructively). After fabrication the samples were annealed at 200°C for 90 minutes in a furnace purged with hydrogen and nitrogen to improve the electrode contact resistance and to improve the material’s visible absorbance. Prior to the measurements, to further reduce surface contamination, we put the samples in 4E-8 Torr vacuum for more than 6 hours to remove contamination from the MoS$_2$ and the contacts.

**Dispersing the AuNS on the photodetector surface:** the device was treated with a 1% solution of poly4-vinylpyridine (PVP) to create a homogenous adhesion on the device.
surface. After functionalizing the device surface with PVP, we put a droplet of AuNS suspended in water solution on the MoS$_2$ devices and waited for ten minutes before rinsing with de-ionized water and blowing with dry nitrogen. This method has been shown to provide a clean and uniform particle dispersion on the substrate.$^{72}$ The existence of PVP on the sample is crucial; without a homogenous adhesion layer the particles will tend to aggregate unpredictably.
Chapter 4: Pronounced Linewidth Narrowing of an Aluminum Nanoparticle Plasmon Resonance by Interaction with an Aluminum Metallic Film

4.1 Abstract

Aluminum nanocrystals and fabricated nanostructures are emerging as highly promising building blocks for plasmonics in the visible region of the spectrum. Even at the individual nanocrystal level, however, the localized plasmons supported by Al nanostructures possess a surprisingly broad spectral response. We have observed that when an Al nanocrystal is coupled to an underlying Al film, its dipolar plasmon resonance linewidth narrows remarkably, and shows an enhanced scattering efficiency. This behavior is observable in other plasmonic metals, such as gold; however it is far more dramatic in the Aluminum nanoparticle-film system, reducing the dipolar plasmon linewidth by more than half. A substrate-mediated hybridization of the dipolar and quadrupolar plasmons of the nanoparticle reduces the radiative losses of the dipolar plasmon. While this is a general effect that applies to all metallic nanoparticle-film systems, this finding specifically provides a new mechanism for narrowing plasmon resonances in Aluminum-based systems, quite possibly expanding the potential of Al-based plasmonics in real-world applications.

4.2 Introduction
Metallic nanostructures support coherent oscillation of electrons.\textsuperscript{73} These excitations, known as surface plasmons, couple strongly to light, concentrating it to subwavelength volumes\textsuperscript{1} and producing large optical field enhancements.\textsuperscript{74,75} The extraordinary properties of surface plasmons have triggered the development of numerous applications in areas as diverse as nonlinear optics,\textsuperscript{76–78} ultrasensitive biosensing,\textsuperscript{79–81} photocatalysis,\textsuperscript{27,82} and solar energy harvesting.\textsuperscript{21,83} However, the majority of these have involved the use of nanostructures made of gold or silver, whose scarcity and resultant high cost clearly limits their large-scale use. Additionally, the intrinsic properties of gold and silver add further constraints: for example, interband transitions in gold (silver) increase the plasmon damping for wavelengths shorter than 550 nm (400 nm), precluding access to much of the visible and UV spectral regions. In addition, the oxidation of silver nanostructures severely degrades the plasmonic response over time, limiting long-term device applications.

Aluminum has recently emerged as a highly viable potential alternative to noble metals for large-scale or large-area plasmonic applications.\textsuperscript{84–87} Aluminum nanostructures can support plasmons with wavelengths ranging from the near-IR to the UV, thanks to the high plasma frequency of the bulk material,\textsuperscript{88–90} and the self-terminating oxide layer provides long-term stability.\textsuperscript{87} Unlike gold and silver, aluminum is compatible with complementary metal-oxide semiconductor (CMOS) technology, opening up new possibilities for integration with electronics in on-chip device applications. Some of these properties have already been used in applications such as nonlinear plasmonics,\textsuperscript{91} color filtering\textsuperscript{92–94} or color printing.\textsuperscript{95–97} However, to fully exploit the advantages of aluminum for plasmonics, we also need to acknowledge its inherent limitations. One limitation is
the broad linewidth of aluminum plasmons at visible frequencies. This broadening is due to an unoccupied band above the Fermi energy that results in interband transitions in the red region of the visible spectrum. So despite improvements in nanofabrication,98,99 including the recent synthesis of high purity aluminum nanocrystals,100 the bright plasmon modes of aluminum are inherently broader than the plasmons supported by noble metal structures due to their larger radiative losses.101

Here we report the surprising observation that when aluminum nanocrystals are deposited onto an aluminum film, their dipolar plasmon linewidth is substantially narrowed, which in the case of our experiments, is by nominally a factor of two. It is well known that, in general, the interaction between a nanoparticle and a substrate can alter the optical response of a nanoparticle.102,103 Substrate-induced modifications are particularly strong for metallic substrates supporting surface plasmon polaritons.22,104–108 Here, by carefully monitoring the scattering spectra of individual nanocrystals, we observe that nanoparticles positioned on an aluminum film display a dipolar resonance with a significantly reduced linewidth and enhanced intensity compared with corresponding nanoparticles deposited on a dielectric (silica) substrate. Through a simple theoretical model, we show that the narrowing originates from a substrate-mediated hybridization of the dipolar and quadrupolar nanoparticle plasmons. This interaction reduces the radiative losses of the nanoparticle.

4.3 Narrowing of the dipolar plasmon resonance of an aluminum nanoparticle placed on an aluminum film
The system we studied is depicted schematically in Figure 1(a). It consists of a chemically synthesized aluminum nanocrystal on an aluminum film of known thickness deposited onto a silica substrate (see methods for details of the fabrication process). Both the nanocrystal and the film are coated with a self-terminating aluminum oxide layer of a thickness of \( \sim 3 \) nm that protects each structure from further oxidation. The thickness of the oxide layer is included in the dimensions of both the nanocrystal and the film. We examined the optical response of this coupled system by measuring single-particle scattering spectra in a dark-field microscope using unpolarized illumination (see methods for more details on the experimental setup). The corresponding spectra are shown in Figure 1(b) for Al nanocrystals with diameters of 100 nm (top) and 100 nm (bottom). The spectra shown in gray correspond to a nanocrystal atop an aluminum film of 35 nm thickness, while the blue spectra correspond to a nanocrystal of the same dimension placed directly on the silica substrate. Scanning electron microscope (SEM) images of the analyzed nanocrystals are shown in insets on the right of the Figure. For nanocrystals on a silica substrate, both spectra display a single broad peak in this energy range, corresponding to the dipolar plasmon of the nanocrystal. For a nanocrystal on an aluminum film, however, two distinct peaks appear in each scattering spectrum. These can be classified as the hybridized dipolar (lower energy) and quadrupolar (higher energy) modes of the coupled nanocrystal-film system. In all cases, the nature of the modes is identified by analyzing the corresponding induced charge density maps and by analyzing the contribution of the different multipolar orders to the scattering spectrum (see appendices C and D for more details). Here we clearly see that the presence of the aluminum film results in a drastic reduction of the resonance linewidth of the dipolar
plasmon mode. For the case of a 180 nm particle diameter, the linewidth (FWHM) is reduced from 1.27 to 0.66 eV, a 40% reduction in linewidth, and for the 100 nm diameter case, the linewidth is reduced from 1.38 to 0.48 eV, a 65% reduction in linewidth. This linewidth narrowing is accompanied by a large increase in scattering intensity. This effect appears to be general to plasmonic nanoparticle-film systems, but has not been the focus of analysis until now: in Reference 44, for example, the linewidth narrowing for a 60 nm diameter gold nanoparticle atop a 30 nm thick gold film is 33%.
Figure 8 Narrowing of the dipolar plasmon resonance of an aluminum nanoparticle placed on an aluminum film. (a) Schematic of the geometry. (b) Experimental single-particle dark-field scattering spectra of aluminum nanoparticles with diameters $D=180$ nm (top) and $D=100$ nm (bottom) on an aluminum film of thickness $T=35$ nm (gray curves), and directly on the silica substrate (blue curves). Unpolarized illumination and a collection numerical aperture of 0.28 was used in all cases. Right: scanning electron microscope (SEM) images of the nanoparticles used to obtain these spectra, with the scale bar corresponding to 100 nm.
4.4 Reducing the radiative losses of the plasmon resonance of aluminum particle

To understand the origin of this resonance narrowing, we performed calculations of the scattering efficiency under the same conditions as in the experiment (i.e., unpolarized illumination with the same incident and collection angles). We assume the nanocrystalline particles to be perfectly spherical. The presence of the oxide layer in both the nanocrystal and the film imposes a minimum distance of 6 nm between their metal surfaces, ensuring that nonlocal and quantum effects can be safely neglected. This allows us to rely on a classical description based on the solution of Maxwell's equations. We use a semi-analytical model that is based on an expansion of the fields into spherical waves centered around the nanoparticle, combined with Mie theory and Fresnel coefficients to describe the response of the nanoparticle and the substrate, respectively. With this approach, we obtain a set of self-consistent equations for the fields that account for the infinite sequence of scattering events between the nanoparticle and the substrate. Upon solving these equations, we obtain the near and far fields, and from them the scattering efficiency (further details on this approach can be found in the SI).
Figure 9 Interaction between an aluminum nanoparticle and an aluminum film. The scheme at the top depicts the geometry used in the calculation. The lower plot shows the scattering efficiency spectrum for a spherical aluminum nanoparticle of diameter $D = 80$ nm located at a distance $H$ from an aluminum film of thickness $T = 35$ nm, calculated with the semi-analytical model described in the text. We consider unpolarized illumination with the same incident and collection angles as in the experiment.

Using this semi-analytical model, we calculate the scattering efficiency for a nanoparticle of diameter $D = 80$ nm placed at varying distances $H$ from an aluminum
film of thickness $T = 35$ nm (Fig. 2). When the nanoparticle is far from the film, corresponding to when the coupling is weak, the spectrum shows a single broad dipolar resonance. However, when $H$ is reduced and the coupling becomes stronger, the dipolar mode redshifts slightly and becomes narrower. At the same time a second resonance, corresponding to the quadrupolar plasmon of the nanoparticle, appears at higher energies. This behavior originates in the hybridization of the dipolar and quadrupolar plasmons of the nanoparticle caused by the symmetry-breaking introduced by the presence of the aluminum substrate. As a result, the quadrupolar resonance acquires part of the “bright” character of the dipolar mode$^{111,112}$ becoming easily visible on the scattering spectrum. Correspondingly, the dipolar resonance becomes darker, with a reduction in linewidth. Interestingly, mode hybridization has been also exploited in other systems, such as metal-insulator-metal structures, to obtain narrow resonances by reducing the penetration of the electric field into the metallic parts of the structures.$^{113}$

The scattering efficiency of the dipolar resonance of a nanoparticle is proportional to the square of the amplitude of its polarizability. We can describe the various contributions to this quantity using a straightforward harmonic oscillator model. Within this simple approach, the plasmon is modeled as an oscillator with a total charge $q$ and mass $m$, whose amplitude satisfies the following equation of motion:$^{114–116}$

$$m \ddot{x} = qE - ma_0^2x - m\gamma_{nr} x + \frac{1}{2m} q^2 \dot{x}^2 \quad (1)$$

The terms on the right-hand side of this expression correspond, respectively, to the driving force associated with the external field $E = E_0 e^{-i\omega t}$, the restoring force with resonant frequency $\omega_0$, the friction caused by the intrinsic damping $\gamma_{nr}$, and the
Abraham-Lorentz force accounting for the radiation reaction.\textsuperscript{117} By solving this equation, we obtain the plasmon dipole moment \( d = qx \), and the corresponding well-known expression for the polarizability\textsuperscript{118} \( \alpha = \frac{d}{E} \):

\[
\alpha = \frac{(\omega_p^2/2\omega_0^2)\gamma_r}{\omega_0^2 - \omega^2 - i\gamma_m \omega - i(\omega^2/\omega_0^2)\gamma_r}
\]  

(2)

Here, we have defined \( \gamma_r \equiv (2\omega_p^2/3c^2)(\epsilon^2/m) \) as the effective radiative decay rate of the plasmon resonance. The linewidth of the resonance expressed by this polarizability has two contributions, associated with nonradiative losses at a rate \( \gamma_{nr} \) and radiative losses at a rate \( \gamma_r \). The magnitude of the nonradiative loss is determined by the value of \( \gamma_{nr} \), which in the absence of finite size effects, depends solely on the material properties. The radiative losses, however, are proportional to \( \gamma_r \). This parameter determines the coupling between the plasmon and the external field and is thus related to the brightness of the resonance (e.g., a completely dark plasmon would have \( \gamma_r = 0 \)). By the dipolar and the quadrupolar modes of the nanoparticle coupling to the aluminum film, the value of \( \gamma_r \) is decreased, which reduces the radiative losses, narrowing the dipolar resonance linewidth. Incidentally, in our experiments, the aluminum oxide layer separating the nanocrystal and the film helps prevent an increase in nonradiative losses.
Figure 10 Effect of nanoparticle size on the narrowing of the plasmon resonance linewidth. (a) Calculated scattering efficiency spectra for aluminum nanoparticles of different diameters $D$ placed on a $T=35$ nm aluminum film (left), and on a silica substrate (right). The spectra in the right panel are multiplied by a factor of 8 to improve visibility. The dashed lines serve as a guide for the eye to indicate the trend of the dipolar resonance. The upper insets show the schematics of the simulated geometries. All calculations are performed using the same method and conditions as in Figure 2. (b)
Calculated linewidth of the dipolar resonance for the nanoparticles on the aluminum film (gray) and on the silica substrate (blue), as obtained from the spectra of panel (a).

This narrowing mechanism is only efficient for systems in which the radiative losses dominate the linewidth. Because these types of losses occur at a rate $\gamma_r$, we expect the narrowing of the linewidth to be more pronounced for nanoparticles with large sizes relative to the wavelength or for those made of materials with a higher plasma frequency. This explains why linewidth narrowing is a smaller effect for gold. To corroborate this hypothesis, we use the semi-analytical model to calculate the scattering spectrum of spherical aluminum nanoparticles with different diameters. Figure 3(a) shows the spectra obtained for aluminum nanoparticles of increasing diameter on an aluminum film with $T = 35$ nm (left panel), as well as for the same nanoparticles sitting directly on a silica substrate (right panel). Comparing these spectra we observe that, for all values of $D$ under consideration, the dipolar resonance is narrower when the nanoparticles are on the aluminum film. However, the difference in linewidth between dielectric and metallic film substrates varies with particle diameter. This is shown in Figure 3(b), where we plot the linewidth as a function of particle diameter obtained by fitting the dipolar resonances of Figure 3(a) to Lorentzian functions, both for the nanoparticles on the aluminum film (gray) and on the silica substrate (blue). Interestingly, the linewidth for the nanoparticles placed on the aluminum film remains almost constant, suggesting that radiative losses are already substantially reduced by the presence of the film. For the nanoparticles on a dielectric substrate (silica), the linewidth seems to reach a saturation value, likely due to both the nonlinear dependence between $\gamma_r$ and $D$, and the redshift of the resonance. Similar calculations using nanoparticles and films made of gold instead of aluminum are
shown in appendix E, showing that, as expected, the narrowing of the resonance is less efficient than in the aluminum structures due to the lower frequencies of the gold dipolar plasmon. Although the narrowing is associated with the darkening of the dipolar plasmon, the scattering efficiency for the nanoparticles on the aluminum film is almost one order of magnitude larger than for nanoparticles of the same dimension on a silica substrate, as shown both experimentally in Figure 1(b) and theoretically in Figure 3(a). This is because the field exciting the nanoparticle contains a component coming from the reflection on the substrate, which is obviously larger when the aluminum film is present. The same effect causes an enhancement of the scattered intensity by redirecting the light emitted towards the substrate. Therefore, the coupling with the aluminum film produces not only narrower but also brighter resonances.

To further characterize the plasmon narrowing mechanism, we measure the single-particle scattering spectra of aluminum nanocrystals of $D = 130$ nm deposited on aluminum films with varying thicknesses $T$. The experimental spectra are shown in the left panel of Figure 4. For values of $T$ larger than 35 nm, the linewidth of the dipolar resonance (signaled by a shadowed area) remains almost constant. However when the thickness of the aluminum film decreases, becoming comparable to the skin depth of the material ($\sim 15$ nm for aluminum at 2.3 eV), the dipolar plasmon peak height is reduced and broadens, approaching the case of no aluminum film (i.e., $T = 0$). These experimental results are well supported by the numerical calculations shown in the right panel, which are obtained by solving Maxwell's equations using the finite-difference time-domain (FDTD) method (see methods for more details). We use this approach
instead of the semi-analytical model because it allows us to introduce the nonspherical shape of the nanoparticles. This is necessary since the Al nanocrystals used in the experiment are not completely spherical (Fig. 1(b)), so we model them as ellipsoids (see sketch in the upper part of Figure 4) with a surface-parallel long axis of 130 nm and a perpendicular short axis of 111 nm. We use the same unpolarized illumination, incident direction, and collection angles as in the experiment. The very close agreement between experiment and simulation further supports our interpretation of the narrowing mechanism.
Figure 11 Effect of film thickness on the plasmon linewidth. The left panel shows a series of experimental single-particle scattering spectra for aluminum nanoparticles of diameter D=130 nm placed on top of aluminum films of different thicknesses T, as depicted in the upper inset. The right panel shows numerical simulations of the scattering efficiency performed by using a finite-difference time-domain approach for the same film thicknesses shown in the left panel. In both panels the case with T=0 refers to the particle positioned directly on the silica substrate.
4.5 Conclusion

In summary, we have shown that the coupling of an aluminum nanoparticle to an underlying aluminum film results in dipolar plasmon resonances with significantly reduced linewidths and enhanced intensity compared with an aluminum nanoparticle placed on a dielectric substrate. We show that this effect is due to a reduction in the radiative losses of the dipolar plasmon, which is caused by the substrate-mediated hybridization of this mode with the quadrupolar mode of the nanoparticle. The narrowing mechanism described in this work is expected to happen for any metal, although is larger for systems whose dissipation is dominated by radiative losses, as is the case with aluminum, due to its higher plasma frequency relative to silver or gold. We also address the dependence of this linewidth narrowing effect on particle diameter, and on film thickness. While general, the results presented here describe a new and specific mechanism for reducing the scattering linewidth of aluminum nanostructures. Indeed, these observations may substantially influence future aluminum plasmonic nanostructure design to exploit film-coupling effects in lineshape-engineered devices, from which applications requiring narrow resonances could benefit.

4.6 Methods

Sample fabrication: The silica substrates were first cleaned by sonicating them in acetone for 5 min and rinsed with isopropyl alcohol. After that, the substrates were masked with alignment grids used for transmission electron microscopy, and then
99.999% pure aluminum was evaporated over them with the desired thickness. The base pressure of the chamber and the evaporation rate were $5 \times 10^{-7}$ Torr and 1 Å/s, respectively. The aluminum nanocrystals were deposited on the substrate by diluting them in isopropanol alcohol (concentration) and then spin coating the solution on the substrate (1500 rpm, 1 min).

**Experimental setup:** The samples were illuminated using a continuum light source (Energetiq LDLS) filtered with a monochromator. The illumination was focused on the substrate with an incidence angle of 50°, using reflective optics to minimize the optical losses along the beam path. The dark-field scattering signal of the particles was collected at normal angle using a 15x, 0.28 NA finite conjugate objective (Edmund Optics, UV ReflX).

**Theoretical methods:** Semianalytical model: The semianalytical model used in this work was developed in Ref. 1. In brief, the method starts with an expansion of all fields in terms of spherical waves centered on the nanoparticle. Then Mie theory is used to relate the fields scattered by the nanoparticle with the corresponding incident fields. Similarly, Fresnel coefficients are used to calculate the fields reflected and transmitted by the substrate. Conversion matrices between spherical and plane waves in the particle-substrate gap are introduced to switch between the two representations in that region, thus allowing us to plug Mie coefficients to describe scattering by the former and Fresnel coefficients for the latter. Imposing the adequate continuity conditions to the 2 fields, a self-consistent set of equations is obtained, which accounts for the series of infinite scattering and reflection events happening at the nanoparticle and the substrate,
respectively. Solving these equations, the electric field, and therefore, the scattering intensity are obtained. We used similar conditions as in the experimental setup, corresponding to incident and collection angles of 50° and 16°, respectively. We also assumed a 3 nm thick aluminum oxide layer covering both the nanoparticles and the film. The dielectric functions of aluminum, aluminum oxide, and silica were taken from Ref. 2.

**Numerical simulations:** We performed numerical simulations for Figure 4 of the main paper using a commercial finite-difference time-domain (FDTD) software package (Lumerical 8.9.163). The shape and size of the nanoparticles were chosen based on the experimental scanning electron microscope (SEM) images. In all cases the nanoparticles and the aluminum films were covered with a 3 nm thick aluminum oxide layer. Unless otherwise stated, we used unpolarized illumination, with an incidence angle of 50° and a collection angle of 16° with respect to the substrate normal, in accordance with the experimental conditions. As in the semianalytical model, the dielectric functions of aluminum, aluminum oxide, and silica were taken from Ref. 2. Perfect-matched layers were used as boundary conditions to simulate the infinite substrate and absorb scattered light. All calculations were converged to ensure the reliability and accuracy of the simulation results.
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Appendix A: I-V curves of Schottky Ohmic Devices

Figure 12: I-V curves of Schottky ohmic devices in Figure 1 of the manuscript. The grating devices are almost identical to each other and the substrate with different doping densities of \(1 \times 10^{15}\), \(1 \times 10^{17}\), and \(5 \times 10^{19}\) cm\(^{-3}\) that correspond to substrate resistivities of 1, 0.01 and 0.001 ohm-cm, respectively.

Appendix B: Photocurrent Spectra at Zero Bias for Gold Gratings on Silicon Substrates with Different Resistivities
Figure 13: Photocurrent spectra at zero bias for gold gratings on silicon substrates with resistivities of 1 ohm-cm (a), 0.01 ohm-cm (b) and 0.001 ohm-cm (c). In each plot, the geometrical parameter of gratings changes from 800 nm to 900 nm, 1000 nm and 1100 nm while the T=200 nm and S=250 nm.

Appendix C: Charge Distribution and Mode Identification for a Particl-film System
Figure 14: Analysis of the character of the different modes appearing on the scattering spectra. We compare the experimental spectra with numerical simulations performed using a FDTD solver (see previous section). The corresponding results are shown in the middle panel, for the nanoparticle sitting either on the aluminum film (left) or the silica substrate (right). The agreement between experiment and theory is remarkable. The different geometrical parameters used in the simulations are shown in the upper panels. For simplicity, we consider s-polarized illumination in both the experimental and the
simulated spectra. Furthermore, to improve visibility, the experimental spectra are vertically offset, and all curves in the right plot are multiplied by a factor of 8. Analyzing the induced charge densities of the different resonances, we confirm that the first peak of these spectra (i) corresponds to a dipolar mode, while the second one (ii) is associated with a quadrupolar mode.

Appendix D: Analysis of the Contribution of the Different Multipolar Orders to the Nanoparticle Scattering
Figure 15: Analysis of the contribution of the different multipolar orders to the nanoparticle scattering. (a) Scattering efficiency calculated for different cutoffs on the multipolar expansion, $l_{\text{max}}$. We consider a spherical aluminum nanoparticle of diameter $D = 80\text{nm}$ located on an aluminum film of thickness $T = 35\text{nm}$ (see inset on panel (b),}
notice that the particle and the film are separated by two 3 nm-thick oxide layers). (b) Calculated linewidth of the dipolar resonance as a function of $l_{\text{max}}$.

**Appendix E: Linewidth of the Dipolar Resonance of Gold Nanoparticles on Gold Films and Silica Substrates**

![Graph](image)

Figure 16: Comparison of the linewidth of the dipolar resonance of gold nanoparticles deposited on gold films and silica substrates. The geometry under consideration is the same as in Figure 10 of the main paper. Namely, nanoparticles with different diameters $D$ are placed 6nm away from a $T = 35\text{nm}$ thick gold film (orange curve) or from the silica substrate (blue curve).