A Simple Unbiased Hot-electron Polarization-sensitive Near-Infrared Photo-detector

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ABSTRACT: Plasmonic nanostructures can generate energetic “hot” electrons from light in a broadband fashion depending on their shape, size and arrangement. Such structures have a promising use in photodetectors, allowing high speed, broadband, and multicolor photodetection. Because they function without a bandgap absorption, photon detection at any energy would be possible through engineering of the plasmonic nanostructure. Herein, a compact hot electron-based photodetector that combines polarization sensitivity and circularly polarized light detection in the near infrared region was fabricated using an ITO-Au hybrid layer. Furthermore, the sensitivity of the device was significantly increased by adding a poled Azo molecular glass film in a capacitor configuration. The resulting device is capable of detecting light below the ITO bandgap at ambient temperature without any bias voltage. This photodetector, which is amenable to large-area fabrication, can be integrated with other nanophotonic and nanoplasmonic structures for operation at telecom wavelengths.

Keywords: Hot electron photodetector, NIR detection, Gold nanostructure, self-affine nanostructure, nonlinear-optics, tunnel effect.

Introduction

There currently exists a significant demand for IR broadband photoresponsive devices for applications ranging from photovoltaics and renewable energy to photodetection for military and civilian purposes.¹⁻⁵ When considering the effectiveness of those photosensitive devices, several factors must be considered including photoresponsivity, fabrication process, and cost.^{1,6} Moreover, the spatial resolution of IR photodetectors can be significantly improved by simultaneously sensing the intensity and polarization of the incident light.⁷ As polarization sensing is important for magnetooptical data storage⁸ and imaging, it is desirable to integrate polarization selectivity and detection in a single-device structure for applications such as surveillance, optical communications and quantum computing.⁹⁻¹¹

Photodetection through conventional procedures is based on light absorption by a material with a matching bandgap. However, this approach limits the range of wavelengths that can be detected, is not sensitive to polarization, and cannot be used accurately in the infrared range because of thermal noise.^{1,9,12} Recent approaches have attempted to circumvent these limitations.¹³ In particular, recent studies have shown that plasmonic structures are promising elements to convert light into electrical energy directly by generating energetic (“hot”) electrons.¹³⁻¹⁹ These hot electrons can be generated by nonradiative plasmon decay via electron-electron collisions through surface scattering processes in metallic surfaces and nanostructures,^{16,20} or at metal/semiconductor interfaces.²¹ This allows one to achieve broadband hot electron generation, even in the near infrared (NIR) range, simply by controlling the shape, size and arrangement of the nanostructures.²²

Metal–semiconductor Schottky junctions have been reported as the most efficient structures to collect hot electrons²³⁻²⁶

and generate a signal in photodetectors. However, previously reported photodetectors based on this methodology, including the ones using nanorods,²⁷⁻²⁸ nanowires,²⁹ metal gratings,³⁰ and waveguides³¹⁻³² are very costly to fabricate, and not suitable for large-scale fabrication. Furthermore, some reported instances of hot-electron-based photodetector devices are extremely sensitive towards the incident angle,^{28,33} or their responsivity depends on an external bias, which limits their efficiency.

Recent studies show evidence of hot electron injection into the ITO layer in an ITO-Au hybrid.³⁴ The highly conductive ITO-Au interface provides a very short Schottky barrier height, which causes no depletion region in the ITO, as electrons can tunnel across this barrier, leading to an Ohmic behavior. However, a local depletion at the interface can be formed under specific conditions,³⁴ which leads to a local rectifying Schottky barrier. These observations inspired us to strategically exploit this local depletion formation to design a device based on ITO-Au nanostructures for NIR photodetection. Herein, we demonstrate that ITO-Au nanostructures can indeed be used to fabricate a NIR photodetector.

The formation of a depletion region is known to be enhanced by applying an external electric field. It is therefore envisaged that in the current devices, generating a permanent local electric field with a thin layer of an organic material where the dipoles of the molecules are permanently aligned would provide a way to enhance device performance. Although organic small molecules are appealing materials for thin film applications, because they can easily be processed from solution, it is important for such purposes that the film morphology be controlled appropriately, and that the dipoles of the molecules be properly oriented and remain indefinitely in the desired orientation. Recently, a series of glass-forming azo

chromophores was reported, all of which showing the ability to form high-quality amorphous thin films from solution.³⁵⁻³⁶ While their dipoles can be conveniently oriented by a corona poling process, azo chromophores tend to reorient due to a series of light-triggered fast cis-trans isomerizations.³⁷⁻³⁸ Fortunately, one benzothiazole-based material, called Azoglass-530, showed a very small decay of its orientation over time, as it is known to undergo slow isomerization.³⁸

Herein, Azoglass-530 was used as an additional layer in the devices to generate a permanent local electric field to enhance hot electron collection. The resulting structure has been used in a lithography-free, large area fabricated, and visible-semi-transparent device that utilizes the hot electrons from plasmon decay and the nonlinearity of ITO to directly generate a photovoltage from light exposure. We demonstrate how self-affine Au thin films could be beneficial in generating hot electrons in the NIR region, and how a permanent oriented dipole such as poled Azoglass-530³⁸ could enhance the device performance as a photodetector.

This device structure allows the fabrication of hot electron-based photodetectors that are highly sensitive in the NIR range, that are sensitive to polarization, and that are easy and cost-effective to fabricate. The approach developed herein represents a significant milestone towards the development of energy conversion devices based on hot electrons, which could be beneficial in integrated optoelectronics.

Experimental Section

Sample Preparation

A transparent commercial ITO-coated glass substrate (Lumtec) with a 160 nm thick ITO layer with sheet resistivity of 15Ω/square was used as the bottom electrode. The ITO slide was cleaned with water, isopropanol, and acetone by sonication in an ultrasonic cleaner for 10 min in each solvent. The slide was dried with a stream of nitrogen. A 14 nm-thick gold thin film was deposited by Vacuum Thermal Evaporation at a chamber pressure of $\sim 10^{-6}$ Torr and a deposition rate of 0.2–0.4 Å/s. The ITO glass substrate was heated at 180 °C before and during the deposition process inside the vacuum chamber. The process and parameters were optimized to generate a gold thin film with an appreciable absorption at 1550nm. A 4.4 mM solution of Azoglass-530 which was prepared according to the literature³⁶ in dichloromethane was prepared and stirred for one hour. A thin film of Azoglass-530 was then deposited on top of the gold layer by spin-coating at 4000 rpm for about 40 seconds. Afterwards, the molecular orientation of the Azoglass-530 thin film was performed using a custom-built corona poling station.

The capacitor geometry utilized for the photovoltage measurements is as follows. The ITO-Au-Azoglass-530 bottom electrode and the top ITO electrode were assembled into a sandwich-type cell and sealed with a hot-melt spacer in between the electrodes (see Figure 1a). The 60 μm-thick spacer (Meltonix 1170-60PF, Solaronix, Switzerland) was placed around the Au-Azoglass-530 thin film. The gap between the electrodes was filled with air.

Photovoltage Measurement

The photovoltage measurements reported in this work were recorded with a Zurich UHF lock-in amplifier with an input impedance of 1 MΩ. The samples were illuminated with a

FemtoFiber Scientific (Toptica) laser source generating p-polarized light pulses centered at a wavelength of 1550 nm with 100 fs duration and 90MHz repetition rate. The beam was focused to a spot size of about 1000 μm² on the sample. The transmitted light was also collected and guided to the detection setup to measure simultaneously generated second and third harmonic signals. A half-wave plate (HWP) and a quarter-wave plate (QWP) were used to tune the polarization of the pump beam and generate linearly or elliptically polarized light, respectively.

Results and Discussion

Although Plasmon-induced carrier generation favors the excitation of electrons from near the Fermi energy, the population of the hot electrons generated by plasmon decay exhibits a plateau in the region between the low-energy Drude electrons and the highest possible energy, $E_f + \hbar\omega$, where ω is the photon frequency.⁵⁷ In TiO₂-Au and Si-Au junctions, which are the mostly studied hot electron collector junctions, a Schottky barrier of about 1 eV and 0.81 eV is formed at the interfaces, respectively. Therefore, these Schottky barriers prevent electrons with lower energies to pass through the junction, and only the high-energy electrons will have sufficient kinetic energy to overcome the barrier. It means that a portion of the generated hot electrons will not have any chance to be captured before thermalization in Au. However, for an Ohmic contact, where either no barrier or just a narrow barrier exists, low-energy electrons also have a non-zero probability to be collected by the junction. Theoretically, in an Ohmic junction with no barrier height, the detection window would be expected to cover the entire short-wave infrared spectral range, which is not limited by the Schottky barrier height. Moreover, the energetic hot electrons lose more energy through a Schottky barrier than an Ohmic junctions, so theoretically less voltage should be generated.

Following by the discussion on Schottky and Ohmic junction, and inspired by experiments described in the literature on the plasmonic nanoantenna-ITO hybrid, we fabricated gold nanostructure arrays on top of ITO glass, which is the principal component in our NIR photodetector device design. Figure 1a, schematically depicts the device geometry based on a thin gold film in an air-gap capacitor configuration. A simple random gold nanostructure array was fabricated by depositing a 14 nm-thick gold film using Physical Vapor Deposition (PVD) on top of the preheated ITO-coated glass substrate. A Scanning electron microscopy (SEM) image of the deposited gold thin film is shown in Figure 1b. The resulting random gold-insulator (air) composite has a fractal morphology which could be characterized by a self-affine surface model.

As optical nonlinearities were observed in the photoreponse of the fabricated photodetector,³⁹ a custom photovoltage scanning apparatus was used for detailed data acquisition, in which the second and third harmonics generated are also detectable along with the generated photovoltage. The photovoltage response of the devices was measured under a local illumination in the near-infrared (NIR) at 1550 nm.

Figure 1. (a) Schematic representation of the Au-ITO based integrated NIR photodetector, (b) Photograph showing the transparency of the Au-ITO photodetector. The inset shows a Scanning electron microscopy (SEM) image of a 14 nm-thick Au thin film deposited on top of a heated ITO glass substrate revealing the self-affine structure.

In order to evaluate the effect of adding a permanent local electric field on device performance, devices were built with an additional thin layer of an organic compound into which the dipoles were permanently oriented (Figure 2a) by corona poling for 20 minutes. As shown in Figure 2b, the measured photovoltage shows a nearly linear dependence on the laser source irradiance below 60 mW average power. The photore-sponse as a function of time during illumination, for devices both with and without a layer of Azoglass-530, is illustrated in Figure 3a.

Figure 2. (a) Corona poling setup to induce a permanent dipole orientation of the Azoglass-530 layer on top of the gold nanostructure (with polarities shown appropriate for producing a negative corona discharge). (b) Photovoltage measurement showing dependency on the illuminated laser power, with the linear fit denoted as a red line.

As observed, the devices show a photoresponse upon irradiation that rapidly (0.5 s) reaches a steady state, and which is stable once saturation is reached, showing their potential as NIR photodetectors. A 4-fold enhancement in photovoltage is observed upon integration of the poled Azoglass thin film on top of the gold layer. This enhancement in photo-conversion efficiency indicates improved charge transfer efficiency in the presence of the local electric field generated by the permanently aligned dipoles from the Azoglass-530 molecules. To show the impact of permanent polarization direction on the generated photosignal, a series of devices was fabricated with either a positively poled layer (with positive charges oriented towards the Au layer), or a negatively poled layer (with negative charges oriented towards the Au layer) of Azoglass-530. A comparison between both sets of poled devices with unpoled devices (Figure S1) reveals that the signal enhancement is not triggered by Azoglass-530 itself, but rather by the presence and direction of the permanent polarization. Indeed, the photosignal is suppressed by a local permanent positive polarization generated by positively poled Azoglass-530 molecules, enhanced by an inverted local polarization direction, and unaffected by unpoled Azoglass-530. Although the devices incorporating the Azoglass-530 layer show enhanced photore-sponse, it is desirable that this photoresponse does not contin-

ue once illumination ceases, and that device's performance stays constant over extended periods of time. To confirm this, the photoresponse of the devices under repetitive On/Off illumination cycles with the NIR light source were performed (Figure 3b). A rapid increase or decrease in photovoltage is observed when the light source is turned on or off, respectively. The fitted curves confirm the exponential time dependence, yielding estimated rise and decay constants of 219 and 197 ms, respectively. The millisecond time scale photoresponse is attributed to the time constant of the low-pass filter of the lock-in amplifier used to characterize the device. More detailed discussion on other mechanisms contributing to the low speed of the photoresponse is given in the supporting information.

Figure 3. (a) Photoresponsivity at $\lambda=1550\text{nm}$ as a function of time of the ITO-Au detector, with and without a layer of poled Azoglass-530 (b) Repetitive on/off cycles of laser light. The green and yellow curves represent the rise and decay curve fits.

Importantly, the photosignal exhibits strong polarization dependence, as shown in Figure 4, where the photovoltage is plotted as a function of the incident light polarization direction for both linearly and circularly polarized light. The laser was set with linear polarization, and a half-wave plate was used to rotate the polarization direction. Hereafter, *p*-polarization is referred to a wave polarized parallel to the plane of incidence, defined with the incident wave at an angle of θ with the sample surface, whereas *s*-polarization indicates a wave polarized

perpendicular to the plane of incidence. As seen in Figure 4, the maximum photoresponse is occurring for the polarization in the plane of the gold nanostructure (s-polarized incident light). Moreover, the photodetector can distinguish between linearly polarized light (LPL) and circularly polarized light (CPL). A quarter waveplate was used to convert linear polarization into elliptical or circular polarization. The photoresponse of the device when the polarization of the local illumination is changed from *p*-polarized light at 0° to CPL at 45° of the optical axis is also shown in Figure 4. The experiment concludes that, no matter the angle of incident LPL (α) relative to the incident plane, CPL always yields the largest photosignal from the photodetector.

Figure 4. Polarization-sensitive photoresponse of the photodetector upon irradiation with a linearly or circularly polarized laser with a power of 60 mW. The polarization dependence with linearly polarized light was measured at an incident angle $\theta \approx 30^\circ$ (polarization angles of 0° and 45° correspond to *p*-polarized and *s*-polarized incident light, respectively), while the polarization dependence of the photoresponse to circularly polarized light was measured at normal incidence. A schematic of the polarized illumination of a thin layer of gold nanostructure is shown in the inset.

Theory and Interpretation

Understanding the mechanism responsible for the generated DC voltage in the ITO-Au photodetector is critical in order to improve its sensitivity for integration into practical applications. As previously reported in the case of nanostructured metals and metal surfaces, which were illuminated with femtosecond laser pulses, detecting the second order nonlinear polarization in the forms of second harmonic generation (SHG)⁴⁰ and terahertz emission (THz)⁴¹ is highly expected. However, an in-depth analysis of our data reveals that the second-order nonlinearity of the gold thin film is not responsible for the generated signal in the ITO-Au detectors. Compared to previously reported gold thin film second order nonlinearities, the metal surface second order susceptibility tensor components ($\chi^{(2)}$) extracted from our data show significant differences. It has been shown both analytically and experimentally⁴² that at metal surfaces, the component $\chi_{zzz}^{(2)}$ is much larger than $\chi_{xxx}^{(2)} = \chi_{zyy}^{(2)}$.

Figure 5. (a) Optical absorption of the deposited 14 nm-thick gold thin film; (b) Hot electron generation and injection at the gold nanostructure/ITO interface.

However, our results in Figure 4 show that the detected DC voltage reaches a maximum for an in-plane optical excitation. Another remarkable difference is the effect of metal surface contamination on the nonlinear optical activity from the nanostructured metal surface.⁴¹ The effect of poling on the Azoglass-530 layer on top of the gold surface is shown in Figure S1, which clearly represents the significance of metal surface contamination on the generated photovoltage. Simply adding a layer of nonlinear optical Azoglass-530 has a negligible impact on the signal characteristics, hinting that the signal is not originating from the Au surface. Finally, the reported gold thin film THz electric field amplitude as a function of incident energy density⁴³ does not show any offset on the incident laser power which is in contradiction with the signal specifications observed in Figure 2b. Actually, the signal's laser power offset observed with the reported device cannot be explainable by the OR process at the gold layer. These observations show that the gold layer by itself is not the source of the generated signal, but rather the structure composed of the gold layer and its interface with the ITO layer is.

It is believed that the morphological development of vacuum-deposited gold films under nonequilibrium conditions will present a self-affine fractal form, i.e. a scale-dependent surface roughness.⁴⁴⁻⁴⁶ Basically, a self-affine surface is a feature of a

fractal structure whose pieces are scaled by different amounts in the x and y directions. Therefore, the optical properties of self-affine thin films are, in many respects, similar to those of fractal aggregates, such as possessing dipolar eigenmodes distributed over a wide spectral range, which differs from randomly (non-fractal) close-packed spheres, in which the absorption peak is always close to the individual plasmonic resonances of the individual particles.⁴⁷ The surface morphology of the gold thin film which is shown in Figure 1b is described in greater detail in the Supporting Information, using a height–height correlation function (HHCF) (Figures S5-S7).⁴⁸

The discrete dipole approximation (DDA), that was originally developed by Purcell and Pennypacker,⁴⁹ and developed later by Shalaev to calculate the optical responses of self-affine structures,⁵⁰ has been used to explain the absorption spectra of the deposited gold thin film (Inset in Figure 1b). Self-affine films can be modeled by point dipoles placed in the sites of a cubic lattice with period a (much smaller than the size of any spatial inhomogeneity). The film is thus simulated as a set of N virtually spherical particles. We assume that the characteristic size of the system is much lower than light wavelength $\lambda = 2\pi/k$, and that the incident electric field is equal at each particle, which are limitations corresponding to a quasi-static approximation. Therefore, the electric field can be denoted simply as $E_0 \exp(-i\omega t)$. The linear polarizability of any particular monomer i is given by the Lorentz-Lorentz formula:

$$\alpha_i^{(0)} = \alpha_0 = R_i^3 [(\epsilon_i - \epsilon_h)/(\epsilon_i + 2\epsilon_h)] \quad (1)$$

Where R_i is its sphere radius $R_i = (3/4\pi)^{1/3} a$ (chosen in order to satisfy the equality between the total volume of all spheres and the total volume of the object under study), ϵ_i and ϵ_h are the bulk dielectric permittivity of the film material and host medium, respectively. In the case of fractal clusters, there may be aggregated spheres monomers that form a cluster, so the sphere radius should be smaller than the assumed R_i here. However, theoretical⁵¹ and experimental results show that in the case of very close monomers the dipole field generated by one monomer is not homogeneous inside the adjacent particle and reaches a maximum near the point of contact between the monomers. Therefore, in fractal structures, either utilizing a higher-order multipole expansion (more than just dipole moments), or using a model in which neighboring spheres are allowed to intersect geometrically⁵² was suggested. This allows us to treat the film as a cluster of polarizable monomers that interact with each other via light-induced dipoles. We denote the dipole moment of the i^{th} monomer located at position r_i , as d_i , which can be written in terms of the incident field and all scattered fields by the other dipoles. Therefore, a coupled-dipole equation (CDE) can be used to express the dipole moments d_i as a function of the coupling of monomers with the incident field and between each other:

$$d_{i,\alpha} = \alpha_0(\omega) [E_{inc,\alpha} + \sum_{j \neq i}^N \hat{W}_{\alpha\beta}(r_i - r_j) d_{j,\beta}] \quad (2)$$

$$\hat{W}_{\alpha\beta}(r_{ij}) = \langle i\alpha | W | j\beta \rangle = \frac{3(r_{ij})_\alpha (r_{ij})_\beta}{|r_{ij}|^5} - \frac{\delta_{\alpha\beta}}{|r_{ij}|^3} \quad (3)$$

where $W_{\alpha\beta}(r_{ij})$ is the quasistatic dipole-dipole interaction operator between particles, the Greek subscripts denote the Cartesian components, $\delta_{\alpha\beta}$ is a delta function, and $r_{ij} = r_i - r_j$. The solution of equation 2 gives the local electric field, $E_{i,\alpha}$ and polarizability tensor $\alpha_{i,\alpha\beta}$ of the i^{th} dipole as follows:

$$E_{i,\alpha} = \alpha_0^{-1} d_{i,\alpha} = \alpha_0^{-1} d_{i,\alpha\beta} E_{inc,\beta} \quad (4)$$

$$\alpha_{i,\alpha\beta} = \sum_{j,n} \frac{\langle i\alpha | n \rangle \langle n | j\beta \rangle}{\alpha_0^{-1}(\omega) - \omega_n} \quad (5)$$

Where $|n\rangle$ and ω_n are $3N$ eigenvectors and eigenfrequencies of the interaction matrix W . The absorption cross-section of the cluster is proportional to the imaginary part of the average cluster polarizability:

$$\sigma_{\text{abs}} \propto \text{Im}[\langle \alpha(\omega) \rangle] = \text{Im} \left[(1/3N) \sum_i \text{Tr} [\alpha_{i,\alpha\beta}] \right] \quad (6)$$

Where N is the number of particles in a cluster. Note that considering the definition of fractal structure including a power law dependence of N on the cluster's gyration radius (which implies a spatial scale-invariance), and the density-density pair correlation function (which depends on fractal dimension) limits the available system eigenmodes for fractal clusters. These restrictions mean that there are always close neighbors for any particle in a fractal cluster that cause strong interactions between the neighboring particles, resulting in the formation of wide spectral range modes which can be excited by a homogeneous field. For example, the eigenmodes of gold fractal cluster aggregates span the visible and infrared parts of the spectrum, which is in agreement with the observed broad absorption spectrum of our deposited thin film in Figure 5a. In contrast, for a non-fractal random medium such as closed-packed spherical particles, where the correlation function is constant, modes are confined to a narrow range close to the resonance of an individual particle, happening for a spherical particle at $\epsilon_i = -2\epsilon_h$. Note that as we considered the roughness feature of the gold thin film as an array of metallic nanoparticles, where the resonance (polarizability) is associated with collective electron oscillations called surface plasmons, it is meaningful to name the eigenmodes of the gold fractal surface the "plasmon's wavefunction".

Eq. 4 can then be used to express the local electric field in terms of the eigenfunctions and eigenfrequencies of the interaction operator. Note that in fractals, the interaction between the resonance dipoles (light-induced plasmon oscillation) induced in particles is short-ranged in nature. This results in spatial localization of the optical excitations at various random locations in a fractal cluster and its surface. Those areas are known as "hot" spots where the electromagnetic energy is accumulated, because the dilatation symmetry operator that characterizes self-affine surfaces does not support plane running waves.

An optically driven plasmonic nanostructure has two relaxation channels: nonradiative decay and radiative decay. Radiative decay is the release of plasmon energy via a photon, also called scattering. Nonradiative decay refers to all other processes unrelated with photon emission and can take place in metal nanostructures through interband (5d and 6sp for gold) or intra-band transitions (in 6sp for gold). The nonradiative decay rate of a plasmon in a nanostructure shows contributions from both bulk (γ_b) and surface (γ_s) decay rates. The bulk term that is naturally appearing from the expression of the bulk dielectric constant of a metal can be split in two terms as follows:

$$\gamma_b = \gamma_{\text{Drude}} + \gamma_{\text{interband}} \quad (7)$$

Where γ_{Drude} is the Drude relaxation constant contributing to the metal dielectric constants and which is responsible for friction-like dissipation. $\gamma_{\text{interband}}$ is the interband transition that is active in silver and gold, mostly in the UV-Vis part of the spectrum which is not part of the current discussion. On the other hand, as the plasmon-induced perturbing potential is near field, it is localized to the surface of the nanostructures, and thus surface contributions to the decay process will be important. The collisions of a nanostructure's free electrons

with its boundary (electron-surface contribution) can be formalized within the phenomenological theory of Kreibig⁵³ as:

$$\gamma_s = \frac{v_F}{L_{\text{smfp}}} \quad (8)$$

where L_{smfp} and v_F are the surface mean free path and the Fermi velocity of the metal, respectively. The quantum mechanical origin of the surface collision damping (Landau Damping) and the related spectrum broadening (γ_s) can be explained by direct transitions between two free electrons with different k vectors. It is well-established that the vertical intra-band transition in metals is forbidden due to momentum conservation.⁵⁴ However, collisions with metal surfaces where the transitional symmetry normal to the surface is broken provide recoil, thereby invalidating momentum conservation, and a surface plasmon polariton with energy ($\hbar\omega$) equal to the energy difference between two electrons can then be absorbed to drive a direct intra-band transition. Note that since in the quantum mechanical picture, only electrons at the Fermi surface contribute to conductivity (free electrons), the surface relaxation time of plasmons can be defined as a function of Fermi velocity and mean free path between memory-canceling collisions as Eq.8. We should note that in nanostructures with hot spots (dimers, fractal structures, etc.), this process may occur not only near the surface, but also in hot-spot regions in the bulk (where again the momentum is not conserved). The L_{smfp} for fractal nanostructures also depends on the size of the nanostructures and on the geometry of the hot spots.

In summary, plasmon-induced carrier generation at the surface and within hot spots favors the excitation of electrons from the Fermi energy, resulting in substantially higher-energy electrons than the Fermi energy, referred to as "hot electrons" (their formation is illustrated in Figure 5b). In such generation of hot carriers, an electron can pick up the photon with energy $\hbar\omega$ localized through the plasmon waves at the surface, and reach the higher free conduction band of the metal, up to $E_f + \hbar\omega$. This allows substituting the surface-scattering process by a more general hot-electron mechanism as:

$$\gamma_s = \frac{\text{Rate}_{\text{hotelectron}} \cdot \hbar\omega}{E_{\text{plasmon}}} \quad (9)$$

Where $\text{Rate}_{\text{hotelectron}}$ and E_{plasmon} are the rate of generation of hot electrons and the energy stored in the coherent motion of the electrons in a localized plasmonic wave. We have to mention that, in the excitation spectrum of our study at 0.8 eV, the bulk inter-band transition of gold is not a possible channel for plasmon decay. Therefore, hot electron generation through the surface and hot spots, which are distributed all over the bulk of fractal media, have a high probability to constitute the main channel for plasmon decay in our thin film. Combining equations 8 and 9, we get:

$$\text{Rate}_{\text{hotelectron}} = \frac{v_F \cdot E_{\text{plasmon}}}{L_{\text{smfp}} \cdot \hbar\omega} \quad (10)$$

E_{plasmon} in the classical limit is related to the local dielectric function and the electric field is derived from Eq.4. The spatial distribution of high local fields also defines L_{smfp} . The hot electron generation mechanism was described in a more detailed manner in several studies.⁵⁵⁻⁵⁷

At this point, we should note that as the thickness of the plasmonic nanostructure is 14 nm, which is smaller than the hot electron diffusion length,⁵⁸ there is a high probability of hot electrons diffusing through the gold-ITO interface.

There at the interface, an Ohmic semiconductor-metal junction is formed between the gold and the ITO which is a heavily n-doped semiconductor (n+) with a lower workfunction than gold. Although there are some chemical changes at the

interface which may affect interfacial work-functions, still we can estimate the junction barrier height using values from literature. Gold work-function is in the range of 5.1 to 5.5 eV⁵⁹ and the work function of a highly conductive ITO substrate is about 4.7 eV.⁶⁰ This yields a potential barrier height range of about 0.4 to 0.8 eV. Moreover, hot electron population exhibits a plateau in the region between the low-energy Drude electrons and the highest possible energy as discussed before.⁵⁶ As shown in Figure 6a, gold hot electrons can then tunnel through the junction barrier known as field emission or flow over the potential-energy barrier known as thermionic emission depending on their energy.

Figure 6. Illustration of the tunneling effect at the junction between highly doped n-type ITO and Au. E_{fITO} : ITO fermi level energy, E_{fAu} : gold fermi level energy, Φ_{Au} : gold workfunction, Φ_{ITO} : ITO workfunction, Φ_b : barrier against electron flow between metal and N-type semiconductor, and Φ_{local} : local potential caused by poled molecules. (a) Au-ITO (b) Negatively poled Azoglass-530/Au-ITO.

The effect of the polarization generated by the poled Azoglass-530 layer is pictured in Figure 6b. One method for tuning the metal work-function is by using an array of dipole moments in direct contact with the metallic layer.⁶¹ Owing to the consequent interfacial electric field, the vacuum level outside the metal will be shifted higher or lower depending on the orientation of the dipoles relative to the metal surface, that implies a new effective work function.⁶¹ A dipolar thin layer with a net polarization directed away from the gold (Inset of Figure 2a) is required to reduce the gold effective workfunction and consequently shorten the barrier at the ITO-Au junction. The Fowler–Nordheim (FN) tunneling theory⁶² for Ohmic contacts predicts an increase in the tunneling flow due to the barrier height reduction in conjunction with the more likely thermionic emission of hot electrons through the junction with a shorter

barrier. The signal enhancement shown in Figure 3a is the consequence of the permanent polarization at the Au surface.

Thereafter, there are two different possible processes which can contribute to the detected DC voltage. The first mechanism is composed of the hot electron tunneling current through the barrier, which generates a detectable surface charge on the cell's electrodes. The detected offset in Figure 2b can be explained by this tunneling effect. The photovoltage in Figure 2b is simply $V = \sigma \cdot e \cdot t / \epsilon$, in which σ is the surface density of hot photoelectrons and t is the average distance through which the hot electrons travel through the junction (e is the electron charge and ϵ is the dielectric permittivity of ITO).

The second possible process is the electric-field induced optical rectification (OR), a $\chi^{(3)}$ process where one of the electric fields is provided by the static depletion field at the interface. Due to the depletion region at the ITO/Au interface, a DC electric field $E_z^{(DC)}$ is generated into the ITO. The large third order nonlinear optical susceptibility of ITO at the selected wavelength (1500nm)⁶³ can be related to the surface depletion field-induced optical rectification as:

$$P_z^{(0)} = \chi_{zjkz}^{(3)}(0, \omega, \omega, DC) E_j^{(\omega)} E_k^{(\omega)} E_z^{(DC)} \quad (11)$$

Where P is the nonlinear polarization, $\chi^{(3)}$ is the third order susceptibility tensor and the $E^{(\omega)}$ is the incident light electric field at frequency of ω . As a result, a static polarization $P^{(0)}$ is formed inside the ITO at high illumination intensity. The slight deviation from linearity at high pump power (Figure 2b), may be attributed to the optical rectification at the depletion region.

Experimentally, we do not detect any photoresponse for areas of the ITO substrate devoid of gold, which shows that the effect is entirely induced by the symmetry-breaking surface depletion field at the interface between the ITO and gold nanostructure layers.

The linear polarization sensitivity of the NIR photodetector can be explained by the strong dichroism between s - and p -polarized light at the Au nanostructure. As mentioned earlier, the proper solution of Eq.5 would result in $\text{Im}(\alpha_{\parallel} \equiv \frac{1}{2} \langle \alpha_{i,xx} + \alpha_{i,yy} \rangle)$ which describes the absorption of s -polarized light (in the x - y plane) and $\text{Im}(\alpha_{\perp} \equiv \langle \alpha_{i,zz} \rangle)$ which is proportional to the absorption of p -polarized light (in the normal z direction). Analyzing the two spectra of $\alpha_{\parallel}$ and $\alpha_{\perp}$ for a self-affine film shows a clear dichroism.⁶⁴ $\alpha_{\parallel}$, which corresponds to longitudinal modes, shows larger values at longer wavelengths, whereas transverse modes with $\alpha_{\perp}$ are located in the short-wavelength part of the spectrum. This can be explained by the mean polarizability per particle which is mostly related to the dipole coupling between islands, and is different for in-plane and out-of-plane excitations. If we consider dipole-dipole interactions in the film, such as short-distance asymmetrical dimer interactions, longitudinal and transverse modes will correspond to excitation along (bonding type) and perpendicular (anti-bonding type) to the interparticle axis, respectively. Therefore, as it has been shown for gold dimers,⁶⁵ a red and blue shift of plasmon resonances, corresponding respectively to bonding and anti-bonding interactions, is expected.

Furthermore, to explore the circular polarization sensitivity of the detector, a series of z -scan measurements has been carried on ITO glass slides. The comparison of open-aperture Z -scan measurements between linearly and circularly polarized light (see Supporting Information, Figure S2) shows an enhancement in light transmittance. Transmittance increases from 23% (10.5 mW) to 54% (26.5 mW) at the focal point.

Transmittance enhancement is due to a decrease in the ITO multiphoton absorption when the incident light on the ITO glass is circularly polarized. Therefore, photo-signal generation reaches a maximum with circularly polarized light due to the increase of incident light onto the Au layer after passing through the ITO glass. This last result gives additional evidence that hot electron generation occurs within the Au layer as opposed to the ITO layer.

Concerning the photodetection sensitivity, while the maximum responsivity value looks smaller than those previously reported for NIR carbon nanotube photodetectors and hot-electron based ones, we expect that significantly larger responses will be achieved by (1) optimizing the absorption spectrum of the plasmonic nanostructure using arrays of nano-antenna²² and deep-trench/thin metal arrays³³ fabricated by lithography. However, the deposition of a random plasmonic nanostructure on top of ITO glass via simple and reproducible self-assembling deposition methods to obtain the desired absorption spectrum would be preferable. (2) improving the permanent local electric field via the optimization of the molecular structure of the poled material, and (3) using a custom-designed ITO glass with careful control over the ITO deposition process and using an optimal glass substrate for NIR transmission. Additionally, the detected photovoltage is inversely proportional to the photodetector capacitance, therefore the photodetection sensitivity can be further improved by lowering the detector's capacitance (area).

Conclusions

In conclusion, we have developed a technique to fabricate a large-area, polarization-sensitive and semi-transparent near infrared (NIR) hot electron photodetector. Our investigation shows how engineering of the plasmonic nanostructure-ITO interface at the atomic level can improve the hot electron injection efficiency. The introduction of an additional layer of poled Azoglass-530 in the device provides a permanent polarization, which results in a four-fold increase in device photovoltage emphasizing the modifications to the interface energetics.

To the best of our knowledge, this is the first polarization-sensitive photodetector without any bandgap absorption and nanofabrication process that works in the NIR region. In this device, the plasmonic nanostructure is used as both a direct light-harvesting and carrier generation element, where variations of light polarization, even circularly polarized light, can be detected without any additional optical component. This may be beneficial for miniaturized and integrated devices. There are still many open challenges in the field, such as the enhancement of the carrier injection process, exploring a wider range of plasmonic materials, and other structures of random objects. Ultimately, we believe that advances in this new mechanism of photodetection may give rise to additional unforeseen applications in energy harvesting, encoded fibre optics and free-space communications, polarimetric imaging, emission and sensing applications, light detection technologies, and rectifying antenna photovoltaics.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website: www.pubs.acs.org

Additional photoresponse graphs, SEM images of the Au nanostructures, height-height correlation function (HHCF) for the Au nanostructures.

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ABBREVIATIONS

NIR, Near-Infrared; ITO, Indium Tin Oxide; LPL, Linearly Polarized Light; CPL, Circularly Polarized Light; TPA, Two-Photon Absorption; HWP, Half-Wave Plate; QWP, Quarter-Wave Plate.

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