Nanoantenna Harmonic Sensor:

Theoretical Analysis of Contactless Detection of Molecules with Light

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Abstract

Nonlinear harmonic sensor is a popular wireless sensor and radiofrequency identification (RFID) technique, which allows high-performance sensing in a severe interference/clutter background by transmitting a radio-wave and detecting its modulated higher-order harmonics. Here we introduce the concept and design of optical harmonic tags based on nonlinear nanoantennas that can contactlessly detect electronic (e.g. electron affinity) and optical (e.g. relative permittivity) characteristics of molecules. By using a dual-resonance, gold-molecule-silver nanodipole antenna, within the *quantum mechanical* realm, the spectral form of the second-harmonic scattering can sensitively reveal the physical properties of molecules, paving a new route towards optical molecular sensors and optical identification (OPID) of biological, genetic, and medical events for the “internet of nano-things.”

Introduction

Nowadays, radiofrequency identification (RFID) has become one of the most commonly used technologies for automatic identification and data capture. It employs electromagnetic fields to transfer data for the purposes of automatically identifying and tracking tags attached to the monitored objects. RFID harmonic sensor is an emerging sensing device, which transmits a radio-wave and detects its high-/sub-harmonic responses (e.g. second-harmonic generation) from an electromagnetically nonlinear tag, i.e. transponder¹⁻⁴. Typically, a harmonic sensor tag receives a carrier wave at the fundamental frequency and converts the sensing parameters (e.g. movement, temperature, humidity, pressure, and material properties¹⁻⁴) into the modulated signal at the high-/sub-harmonic frequency (e.g. second-harmonic), later re-transmitted to the RFID reader (or interrogator), as illustrated in Fig. 1(a). The detection of up-/down-converted signal at the orthogonal frequency provides a unique sensing response against environments comprised of severe background clutter, jamming, and interference¹⁻⁴, thus being useful for subwavelength RFID tags and wireless sensors with small extinction/scattering cross-sections. While the harmonic sensor has emerged as a promising tool for the wireless sensing and identification in the radiofrequency (RF) domain, its infrared (IR) and optical counterparts are still under investigation. This is due to the fact that the electronic-circuit multiplier or mixer, employed for the frequency mixing or multiplication, are based on diodes and transistors that typically have cutoff frequencies below a few terahertz (THz), mainly caused by parasitic effects and finite transconductance gain.

Very recently, the pioneering idea of “internet of nano-things,” namely a nanoscale sensor network, has attracted wide interest in biological, medical, information processing and communication communities⁵⁻⁶. A nano-sensor, using nanoantennas for short wavelengths (e.g. THz and infrared) sensing and communication, is in the natural domain of molecules and therefore provides a perfect interface between biological phenomena and nano-devices⁵⁻⁶. Nevertheless, in most biological and medical applications, a

tiny nano-sensor could suffer from issues of low sensitivity and strong background interference, whereas the harmonic sensors, with a long history of successful RFID application, may offer the possibility of improving the sensitivity and background noise.

In this work, we will explore the background-free harmonic nano-sensors operating at near-infrared (NIR) wavelengths, aiming to contactlessly detect physical properties of nano-objects, such as DNAs, molecules, antigens, and proteins. The proposed NIR harmonic sensor is based on the molecule-shunt nanoantenna shown in Fig. 1(b). By downscaling the load region of the nanoantenna to the sub-microscopic size (a few nanometers or less), the multiphoton-assisted quantum tunneling⁷⁻¹² can occur, inducing thus second-order optical nonlinearity that produces second-harmonic generation (SHG), as necessary for wavelength conversion in the harmonic sensor system. Moreover, the SHG from a dipole nanoantenna formed by dissimilar plasmonic nanojunctions may exhibit the self-tuned amplitude modulation (AM) and/or frequency modulation (FM) that depend on electronic and optical properties of the loaded nanoparticle. This intriguing property offers the opportunity to contactlessly detect characteristics of loaded nanoparticles according to the second-harmonic scattering signal, which will be discussed in the following.

Results and discussion

Optical nanoantennas consisting of single or paired metallic nanostructures have been demonstrated to be effective in coupling the propagating light to and from a nano-dimensional volume¹³⁻¹⁶. When a nanoantenna is irradiated by light, coherent and collective oscillations of conduction-band free electrons (surface plasmons) can localize light to a subdiffraction-limited region, enabling the controllable local field enhancement in the proximity of the nanoantenna. Nanoantennas have been applied to enhance the excitation and emission of quantum emitters, e.g. single molecule or quantum dot¹³⁻¹⁶, to boost the nanoscale nonlinear optical responses¹⁷⁻²⁴, and to flexibly control the directionality and polarization²⁶⁻²⁷

of nanofocused radiations, to name a few nanophotonic applications. Recently, it has been theoretically and experimentally demonstrated that when an intense pulsed laser illuminates a dipole nanoantenna, the quantum conductance may exist in the nanojunction between two metallic nanodimers, as a result of photon-assisted tunneling (PAT)⁷⁻¹². The quantum conductance has relevant nonlinear components, which can be enhanced by the surface plasmon coupled between two metallic nanostructures, displaying various nonlinear optical responses, such as rectification²⁸⁻²⁹, high-harmonic generation³⁰, and self-scattering modulation via the nonlinear two-photon absorption (TPA)^{8,12}. The overarching goal of this work is to understand the sensitivity of detuned (*amplitude modulation*, AM³¹) and spectral shift (*frequency modulation*, FM³¹) of SHG signals from specific molecule-shunt dual-resonance nanoantenna, when the electronic property (e.g. electron affinity) and/or the optical property (e.g. relative permittivity or refractive index) of its nanoload are varied. Such nonlinear optical signal modulation may be used to realize the harmonic nanosensor in the internet-of-nanothings paradigm.

Figure 1(b) shows the geometry of a conical-dipole nanoantenna that also makes a metal-insulator-metal (MIM) nanojunction³². Such 3D nanostructures can be fabricated using the focus-ion-beam milling and patterning³³ and holographic fabrication³⁴. The charge transport mechanism in this MIM junction depends on the physical separation and difference in Fermi levels of two metallic dipole arms, as well as the electron affinity χ [eV] and the static relative permittivity K of the insulator. When the separation between two metals is very small, currents can flow between two terminals by means of the quantum tunneling effect [see the inset of Fig. 1(b)]. The (dark) current-voltage behavior of a dissimilar MIM junction can be described by the well-known Simmons formula³⁵ [see Appendix A]. Figure 2(a) reports the current-voltage behavior for a silver (Ag)-insulator-gold (Au) nanodisk, varying the electronic affinity of the insulator. The work function of Ag (metal 1) and Au (metal 2) are $\Phi_1 = 4.26$ eV and $\Phi_2 = 5.1$ eV, and, for simplicity, $K = 4$ is assumed throughout this study. The thickness of the insulator

is $a=5$ nm, and the radius of the nanodisk is $d=1$ nm. As can be seen in Fig. 2(a), the asymmetric current-voltage behaviors are obtained as a direct consequence of quantum tunneling through a dissimilar MIM nanojunction ($\Phi_1 \neq \Phi_2$). Figure 2(a) also compares current-voltage behaviors at different temperatures. It is noted that for a relatively high barrier height at the metal-insulator interface, the thermally-assisted tunneling effect is fairly weak. Unless otherwise specified, here we assume $T = 300$ K. Figure 2(b) reports the corresponding Fowler-Nordheim (FN) plot of Fig. 2(a). It is seen that when the applied bias is increased from zero to a very high voltage³², the electron transport mechanism would transit from the direct tunneling (logarithmic growth) to the FN tunneling or field emission (linear decay).

In the generalized scenario, the applied voltage across the nanojunction has both static (dc) and optical (ac) components: $V(t) = V_{dc} + \frac{1}{2}(V_{\omega}e^{-i\omega t} + c.c.)$, where ω is the angular frequency. The presence of optical fields across the MIM nanojunction may adiabatically modulate the electron potential energy³⁶⁻³⁷. According to the Tien-Grodon's theory³⁶⁻³⁷, a monochromatic electromagnetic wave will introduce new quantum-well virtual states separated from the unperturbed ground state by $\pm n\hbar\omega$, with a state density proportional to $J_n(qV_{\omega}/\hbar\omega)$, where $J_n(\cdot)$ is the n -th order Bessel function and $\hbar\omega$ is the photon energy. Here positive and negative n respectively represent photon absorption and emission processes, which can be viewed as the creation of effective electron densities at energies $qV_{\omega} \pm n\hbar\omega$. Under an optical excitation, the time-dependent current is in the form of Fourier series:

$I(t) = \sum_{m=0}^{m=+\infty} \frac{1}{2} (I_{m\omega} e^{-im\omega t} + c.c.)$,³⁶⁻³⁷ and the strengths of current components are given by³⁶⁻³⁷:

$$I_{\text{illum}} = \sum_{n=-\infty}^{\infty} J_0^2(\alpha) I_{\text{dark}}(qV_{dc} + n\hbar\omega) \quad (1)$$

$$I_{m\omega} = \sum_{n=-\infty}^{\infty} J_n(\alpha) [J_{n+m}(\alpha) + J_{n-m}(\alpha)] e^{-im\alpha} I_{\text{dark}}(qV_{\text{dc}} + n\hbar\omega), \quad (2)$$

where $\alpha = qV_{\omega} / \hbar\omega$, I_{illum} and $I_{m\omega}$ represent the dc ($m=0$) and m -th frequency-dependent currents under illumination: At near-infrared and visible frequencies, the photon voltage is usually greater than the ac electric voltage, i.e. $V_{\omega} \ll \hbar\omega / q$. Applying the small argument approximation of $\alpha \ll 1$, the summations in (1)-(2) can be simplified to³⁶⁻³⁷:

$$I_{\text{illum}} = I_{\text{dark}}(V_{\text{dc}}) + G_0^{(2)} |V_{\omega}|^2 \quad (3)$$

$$I_{\omega} = G_{\omega}^{(1)} V_{\omega} + G_{\omega}^{(3)} |V_{\omega}|^2 V_{\omega} \quad (4)$$

$$I_{2\omega} = G_{2\omega}^{(2)} V_{\omega}^2, \quad (5)$$

where the first and second terms in (3) are the dark current and rectified current. The in-phase, ac-driven current at the fundamental ($m=1$) and second-harmonic ($m=2$) frequencies are given by (4) and (5), respectively. The quantum conductances $G_{\omega}^{(1)}$, $G_0^{(2)}$, $G_{2\omega}^{(2)}$, and $G_{\omega}^{(3)}$ are respectively responsible for the optical power dissipation, optical rectification producing dc current, SHG, and TPA [see Appendix B for their expressions]. The optical rectification and SHG, as second-order effects, can exist only in the dissimilar MIM junction or in the similar MIM junction with dc bias. There are also other higher-order harmonics in (2), such as the third-order nonlinear current producing the third-harmonic generation (THG). They are, however, shorted by the nanoantenna's capacitance. Also, the third-order TPA process^{8,12,30} is relatively weak compared to second-order responses, under a moderate illumination intensity. Figures 2(c) and 2(d) show the spectrum of normalized $G_{\omega}^{(1)}$ and $G_{2\omega}^{(2)}$ for the MIM nanojunction shown in Fig. 2(a). There is no dc offset ($V_{\text{dc}} = 0$ V) and the electron affinity of the insulator is swept. Here the dashed lines represent the classical small-signal approximation results:

$G_{\omega, \text{classic}}^{(1)} = (\partial I_{\text{Dark}} / \partial V_{\text{dc}}) \big|_{V_{\text{dc}}=0}$ and $G_{2\omega, \text{classic}}^{(2)} = \frac{1}{4} (\partial^2 I_{\text{dc}} / \partial V_{\text{dc}}^2) \big|_{V_{\text{dc}}=0}$. In the absence of dc load line, there is no rectified dc power. Here we must emphasize that $G_{2\omega}^{(2)}$, directly related to the SHG efficiency, may sensitively depend on χ of the insulator. In addition, it is seen that in the IR and visible regimes, $G_{2\omega}^{(2)}$ is at least two orders of magnitude larger than classical predictions, while at low photon energy (long wavelength), the linear and nonlinear quantum conductance approaches the classical limits (dashed lines). The inset of Fig. 2(d) reports the ratio of SHG responsivity (nonlinear current $I_{2\omega}$ generated per power absorbed) between classical and quantum treatments: $\gamma_Q / \gamma_{\text{classic}} = (G_{2\omega}^{(2)} / G_{\omega}^{(1)}) / (G_{2\omega, \text{classic}}^{(2)} / G_{\omega, \text{classic}}^{(1)})$. It is evident that the PAT effect may enhance the SHG responsivity, although $G_{\omega}^{(1)}$ related to the power dissipation increases with frequency as well. Such enhancement may benefit NIR harmonic sensors which require frequency upconversion of the sensed signal. We note that when the photon energy reaches the photoionization threshold value: $2\hbar\omega > \varphi_2 - (\text{image potential})$, $G_{2\omega}^{(2)}$ saturates and abruptly decreases. In this scenario, the asymmetric tunneling between dissimilar electrodes (i.e. $I_{\text{Ag} \rightarrow \text{Au}} - I_{\text{Au} \rightarrow \text{Ag}} \neq 0$), which gives rise to the rectification effect, may disappear, as illustrated in the inset of Fig. 2(d).

In the realm of classical electromagnetism, an optical nanoantenna is responsible for the flow of displacement current, and its interaction with the optical fields (e.g. scattering, tuning, loading, and matching) can be interpreted by the optical circuit (or meta-tronics) theorem proposed by Engheta³⁸⁻³⁹. Figure 3(a) shows the equivalent optical circuit model of a nanoantenna in the receiving mode³⁸⁻⁴⁰. The intrinsic dipole impedance of the nanoantenna is given by $Z_{\text{dip}} = R_{\text{dip}} - iX_{\text{dip}}$, where $R_{\text{dip}} = R_{\text{rad}} + R_{\text{loss}}$, R_{rad} is the radiation resistance, responsible for the scattering in the receiving mode, R_{loss} is the resistance associated with the plasmon damping, and X_{dip} is the reactance associated with the

near-field stored energy. Applying the Thevenin's theorem for the equivalent circuit, when light impinges on the nanoantenna, it induces an open-circuit voltage $V_{oc} = E_{inc} L_{eff}$, where E_{inc} is the electric field strength of incident light and L_{eff} is the effective length of the nanoantenna³⁹⁻⁴⁰. Due to the small gap dimension and the continuity of the displacement current flowing along the nanodipole, the electric fields inside the nanogap (load region of the nanoantenna) are reasonably uniform and polarized along the dipole axis. Hence, the load impedance of the nanoantenna can be expressed as $Z_{load} = -1/i\omega C_{gap}$,³⁹⁻
⁴⁰ where $C_{gap} = \epsilon_r \epsilon_0 \pi a^2 / d$ is the geometry-yielded capacitance, a is the radius at the top of the nanoconical-frustum, ϵ_r and d are the relative permittivity and the thickness of the nanoload, and ϵ_0 is the free space permittivity. As known from Figs. 2(c) and 2(d), when the plasmonic nanojunction is only a few nanometers, quantum conductances become measurably crucial, and the optical circuit model for the nanoantenna^{8,12} must be modified. The quantum-corrected load impedance now becomes $Z_{load} = [G_{\omega}^{(1)} - i\omega C_{gap}]^{-1}$, which includes the first-order quantum conductance $G_{\omega}^{(1)}$ in parallel to the classic capacitance C_{gap} . The voltage across the nanogap can be readily obtained as $V_{gap} = V_{oc} Z_{load} / (Z_{load} + Z_{dip})$, and the local electric field is given by $E_{gap} = V_{gap} / d$. It is well known that a nanoantenna achieves its resonance and high field enhancement under the condition of $\text{Im}[Z_{load}] = -iX_{dip}$. Typically, $|E_g|$ can be orders of magnitude greater than $|E_{inc}|$ of the impinging light, due to the plasmonic resonance of the nanoantenna.

Under the undeleted-pump approximation, valid for low harmonic loss^{24,41}, the second-harmonic scattering power can be calculated with the Norton equivalent circuit shown in Fig. 3(b). Once the electric field at the gap E_{gap} is known, according to (5), the nonlinear currents induced by the PAT effect at the nanogap can be calculated as $I_{2\omega} = G_{2\omega}^{(2)} V_g^2$, feeding the nanoantenna to reradiate second-

harmonic waves. We should note that a dual-band nanoantenna resonating at the desired fundamental and second-harmonic frequencies are needed to efficiently couple the pumping wave into the nanogap and to reradiate the SHG signal. In this work, we conducted full-wave simulations [CST Microwave Studio] to study the dual-band conical nanodipole structure in Fig. 1(b), which is formed by equally-sized Ag and Au dipole arms with top radius $a=5$ nm and base radius $b=20$ nm. The total length of the nanoantenna is $L=161$ nm and the gap size is $d=1$ nm. Here we ignore the quantum size effect in metallic nanostructures without loss of generality. However, we note that the quantum confinement effect could exist in an ultrathin metallic nanostructures (typically < 10 nm)⁴²⁻⁴³, which may affect behaviors of localized surface plasmon resonance. Below the onset of interband transition⁴⁴, the relative permittivity of Ag and Au follow the Drude-type dispersion model: $\epsilon_m = \epsilon_\infty - \omega_p^2 / [\omega(\omega + i\gamma)]$, where empirical parameters for Ag are $\omega_p/2\pi = 2175$ THz, $\gamma/2\pi = 4.35$ THz and $\epsilon_\infty = 5$, and for Au are $\omega_p/2\pi = 2164$ THz, $\gamma/2\pi = 16.68$ THz and $\epsilon_\infty = 9.5$ ⁴⁴. We assume that the refractive indices of the dielectric nanodisk $n' = \sqrt{\epsilon_r}$ and the background medium n_b are both equal to 1.5. The nanoantenna is illuminated by a plane wave propagating in the z -axis, with its electric field polarized parallel to the dipole arms (x -axis) [Fig. 1(b)]. Figure 3(c) reports its input impedance against frequency, showing two resonances at 225 THz (fundamental frequency) and 450 THz (second-harmonic). Figure 4(a) reports the corresponding local field enhancement $|E_g/E_{inc}|$ against frequency for different values of n' . It can be seen that in all cases, the field enhancement can be as high as 1100 at the fundamental frequency and around 180 at the second-harmonic. These values are obtained after the power dissipation due to metal loss and effect of quantum conductance ($G_\omega^{(1)}$) are considered, and results agree quantitatively with those obtained from the optical circuit theory^{12,39-40} (not shown here). The strongly localized electric fields may greatly enhance the PAT-induced optical nonlinearities at the nanogap^{12,19-24}, enabling the

observation of nanoscale nonlinear optical responses with reasonable intensity of the pumping light. As an example, the SHG power is proportional to the fourth power of electric field $P_{\text{SHG}}^{(2)} \propto |E_\omega|^4$. At resonances of this dual-band nanoantenna, the reactance of nanoload substantially cancels the intrinsic reactance of the nanoantenna. For instance, $X_{\text{dip}}|_{225 \text{ THz}} = 457 \, \Omega$, $-\text{Im}[Z_{\text{load}}]|_{225 \text{ THz}} = 452.3 \, \Omega$, $X_{\text{dip}}|_{450 \text{ THz}} = 127 \, \Omega$, and $-\text{Im}[Z_{\text{load}}]|_{450 \text{ THz}} = 226 \, \Omega$ are obtained for a nanoload with $n' = 1.5$. The inset of Fig. 4(a) shows the far-field scattering patterns of this nanoantenna. A dipolar scattering pattern is seen at the fundamental frequency, typical for the long-wavelength resonance of subwavelength radiators. We note that the plasmonic property of metallic nanorods also shortens the effective guided wavelength along it, rendering a subwavelength size of the nanoantenna. The scattering pattern at the second-harmonic is slightly different, due to the elongated effective length. In Fig. 4(a), we note that when the value of n' increases (which effectively increases the capacitance of nanoload), the nanoantenna's resonant frequencies show a trend of redshift³⁹, as predicted from the circuit model in Fig. 3(a). Figures 4(b) and 4(c) show the contours of magnitude and vectors of electric fields for the same nanoantenna at 225 THz and 450 THz; here $n'=1.5$ is assumed for the nanoload. It is clearly seen that the local electric fields can be considerably enhanced in the proximity of metals, particularly inside the nanogap where the PAT-induced optical nonlinearity and SHG are expected to be enhanced.

In the following, we discuss how the nanoantenna-enhanced $G_{2\omega}^{(2)}$ in a dissimilar plasmonic nanojunction can potentially realize a NIR harmonic nano-sensor for characterizing and identifying nanoscale molecular features, as shown in Fig. 1(b). Here we focus on detecting two physical properties: electron affinity and relative permittivity. As expected, a nanoload with higher electron affinity exhibits a lower potential barrier at the metal-insulator interface, which facilitates quantum tunneling and results in a

larger $G_{2\omega}^{(2)}$ or correspondingly higher SHG efficiency. Hence, the electron affinity of the nanoload determines the peak intensity of SHG signal. On the other hand, the refractive index of nanoload determines the shunt capacitance in the circuits of Figs. 3(a) and (b), which essentially controls the nanoantenna's resonant frequencies and therefore the frequency of maximum SHG power. As a result, the interplay between the nanoload's electron affinity and the relative permittivity may regulate the spectral peak and intensity of SHG from the nonlinear nanoantenna, offering a useful tool for labeling molecules, nanoparticles, DNA, proteins, and organelles. From the optical circuit model in Fig. 3(b), the SHG power can be derived as:

$$\begin{aligned}
 P_{2\omega}^{\text{sca}} &= \frac{1}{2} \left| \frac{I_{2\omega} Z_{\text{load}}(2\omega)}{Z_{\text{load}}(2\omega) + Z_{\text{dip}}(2\omega)} \right|^2 \text{Re}[Z_{\text{dip}}(2\omega)] \eta_{\text{rad}}(2\omega) \\
 &= \frac{(G_{2\omega}^{(2)})^2}{2} \left| \frac{V_{\text{oc}}(\omega) Z_{\text{load}}(\omega)}{Z_{\text{dip}}(\omega) + Z_{\text{load}}(\omega)} \right|^4 \left| \frac{Z_{\text{load}}(2\omega)}{Z_{\text{load}}(2\omega) + Z_{\text{dip}}(2\omega)} \right|^2 \text{Re}[Z_{\text{dip}}(2\omega)] \eta_{\text{rad}}(2\omega),
 \end{aligned} \tag{6}$$

where $I_{2\omega} = G_{2\omega}^{(2)} V_{\text{gap}}^2(\omega)$ and η_{rad} is the radiation efficiency of the nanoantenna. According to the full-wave simulation result, $\eta_{\text{rad}} \approx 35\%$ is obtained around the fundamental frequency and the second-harmonic. The second-harmonic scattering cross-section, which offers a quantitative measurement of nonlinear scattering, can be defined as the ratio of SHG power $P_{2\omega}^{\text{sca}}$ to the incident irradiance I_{inc} :

$\xi_{2\omega} = \oint_{\text{s}} \bar{S} \cdot \hat{r} \, \text{d}\mathbf{s} \Big|_{2\omega} / I_{\text{inc}} = P_{2\omega}^{\text{sca}} / I_{\text{inc}}$, where $\bar{S}$ is the scattered power density. Figures 5(a)-(c) show contours of $\xi_{2\omega}$ for the nanoantenna in Fig. 4 with $\chi = (2.35, 2.45, 2.55) [\text{eV}]$, varying the projected second-harmonic frequency and n' of the nanoload. It is seen that the SHG peaks redshift with respect to the increase in n' , as can be understood from Fig. 4(a). Furthermore, $\xi_{2\omega}$ increases with the increase in χ , which reduces the tunneling barrier to facilitate the PAT process and enhance its induced nonlinear current. As a consequence, by detecting the spectral forms of SHG, a background-free and

multifunctional-sensing OPID tag can be realized with the capability of characterizing molecules with various electron affinity and relative permittivity. Figure 6(a) shows $\xi_{2\omega}$ versus the frequency for the same nano-sensor loaded with six different nanoparticles: A: $(n', \chi[\text{eV}]) = (1.3, 2.35)$, B: $(n', \chi) = (1.3, 2.45)$, C: $(n', \chi) = (1.3, 2.55)$, D: $(n', \chi) = (1.5, 2.35)$, E: $(n', \chi) = (1.5, 2.45)$, F: $(n', \chi) = (1.5, 2.55)$. Figure 6(b) records the value and the corresponding frequency of the maximum of $\xi_{2\omega}$ for nanoloads with various values of χ and n' ; each step represents $\Delta\chi = 0.05 \text{ eV}$ and $\Delta n' = 0.05$. By recording the center frequency and the corresponding maximum $\xi_{2\omega}$ from the measured SHG data, and mapping them to the corresponding set of (χ, n') in Fig. 6(b), the molecular features of the nanoparticle can be readily identified. Similar to those RFID harmonic sensors, the proposed NIR harmonic sensor could be implemented in a frequency-hopping scheme, through the optical parametric oscillator (OPO) frequency tuning of laser. Finally, we note that the strength of SHG signal depends on the intensity of illumination. The SHG conversion efficiency can be defined as the ratio between the SHG power and the maximum power collected by the nanoantenna at the fundamental frequency: $\eta_{\text{SHG}} = P_{2\omega}^{\text{sca}} / I_{\text{inc}} \xi_{\text{eff}} = \xi_{2\omega} / \xi_{\text{eff}}$, where ξ_{eff} is the maximum effective aperture size of the nanoantenna related to its directivity.⁴⁵ In general, the physical upper bound of ξ_{max} for a subwavelength radiator is $3\lambda_0^2 / 8\pi$ ⁴⁵. For a loaded nanoparticle with $\chi = 2.6 \text{ eV}$ and $n' = 1.5$, the SHG efficiency at 550 THz is $0.95 \times 10^{-5} \%$ for the irradiation of 5 MW/cm^2 . The SHG power is expected to be significantly increased by raising the irradiation. Nonetheless, such efficiency is comparable to, or even higher than, that of the nanoantenna loaded with nanoparticles of strong nonlinear optical property^{24,41}. We believe that the SHG conversion efficiency can be further enhanced by engineering electronic structures of MIM tunneling barrier, as well as optimizing the radiation efficiency and impedance matching of nanoantenna.

The plasmon-enhanced, PAT -induced nonlinearity in the nanoantenna may offer tremendous advantages in the nonlinear nano-optics, as the high-harmonic generation and wavelength mixing are enhanced in the nanoscale optical regime.

Methods

Dark current from a dissimilar MIM junction. According to the Simmon's model³⁵, when a dc bias V_{dc} is applied to the MIM junction, as shown in Fig. 1(b), the tunneling current density can be expressed as:

$$I_{\text{Dark}}(V_{dc}) = A_{\text{MIM}} \frac{4\pi m_0 q}{h^3} \int_0^\infty D(\mathbf{E}_x) d\mathbf{E}_x \int_{\mathbf{E}_x}^\infty [F(\mathbf{E}) - F(\mathbf{E} + qV_{dc})] d\mathbf{E}, \quad (7)$$

where A_{MIM} is the cross-section area of MIM junction, q is the electron charge, m_0 is the electron mass, h is the Plank constant, F is the Fermi-Dirac distribution function, $\mathbf{E}$ and $\mathbf{E}_x$ are respectively the total and longitudinal energy of electrons, D is the electron transmission probability. The charge transport mechanism in the MIM junction depends on the difference between Fermi levels of two metals. When a dc bias is applied, currents can flow between two metals by means of the tunneling effect. At equilibrium, the well-known Simmons formula can describe the current-voltage behavior of this MIM junction:

$$I_{\text{Dark}}(V_{dc}) = I_{1 \rightarrow 2} - I_{2 \rightarrow 1} = I_{\text{Dark},0} \left[\bar{\varphi} \exp(-A\sqrt{\bar{\varphi}}) - (\bar{\varphi} + qV_{dc}) \exp(-A\sqrt{\bar{\varphi} + qV_{dc}}) \right] \quad (8)$$

where $I_{\text{Dark},0} = A_{\text{MIM}} q / 2\pi h (\beta \Delta s)^2$, $I_{1 \rightarrow 2} = I_{\text{Dark},0} \left[\bar{\varphi} \exp(-A\sqrt{\bar{\varphi}}) \right]$ is the current density flowing from metal 1 to metal 2, and $I_{2 \rightarrow 1} = I_{\text{Dark},0} (\bar{\varphi} + qV_{\text{dc}}) \exp(-A\sqrt{\bar{\varphi} + qV_{\text{dc}}})$ is the current density flowing from metal 2 to metal 1, $A = 4\sqrt{2m_0\pi\beta\Delta s}/h$, β is the correction factor defined in Ref. 35 as

$\beta = 1 - [1/(8\bar{\varphi}^2\Delta s)] \int_{s_1}^{s_2} [\varphi(x) - \bar{\Phi}]^2 dx$ (s_1 and s_2 are limits of barrier at Fermi level), $\bar{\varphi}$ and $\Delta s = s_2 - s_1$ are the mean potential barrier height relative to the Fermi level and the barrier width for tunneling electrons.

In the reverse bias mode, of which the metal 1 with lower work function is negatively biased, the height of tunneling barrier, which takes into account the potential barrier lowering due to the image force, is given by

$$\begin{aligned} \varphi(x) &= \varphi_1 + (\Delta\varphi - qV) \frac{x}{s} - \frac{q^2}{4\pi K \epsilon_0 s} \left[\frac{x}{2} + \sum_{n=1}^{\infty} \frac{ns}{[(ns)^2 - x^2]} - \frac{1}{ns} \right] \\ &\approx \varphi_1 + (\Delta\varphi - qV) \frac{x}{s} - 1.15 \ln[2] \frac{q^2}{8\pi K \epsilon_0} \frac{s}{x(s-x)}, \end{aligned} \quad (9)$$

where s is the thickness of tunnel barrier, $\Delta\varphi = \varphi_2 - \varphi_1$, $\varphi_i = \Phi_i - \chi$ is the barrier heights at the interface between metal i and oxide, Φ_i is the work function of metal i , and χ is the electron affinity of oxide.

From (9), the mean barrier height $\bar{\varphi}$ is given by:

$$\bar{\varphi} = \frac{1}{\Delta s} \int_{s_1}^{s_2} \varphi(x) dx \approx \varphi_1 + \frac{s_2 + s_1}{2s} (\Delta\varphi - qV) - 1.15 \ln[2] \frac{q^2}{8\pi K \epsilon_0 \Delta s} \ln \left[\frac{s_2(s-s_1)}{s_1(s-s_2)} \right], \quad (10)$$

where the limits of the barrier at the Fermi level s_1 and s_2 are given by the real roots of the cubic equation:

$$\varphi_1 + (\Delta\varphi - qV) \frac{x}{s} - 1.15 \ln[2] \frac{q^2}{8\pi K \epsilon_0} \frac{s}{x(s-x)}. \quad (11)$$

From (8), (10), and (11), the reverse-bias dark current density can be calculated.

In the forward bias mode, of which the metal 1 with lower work function is positively biased, the mean barrier height $\bar{\varphi}$ is given by:

$$\bar{\varphi} \approx \varphi_2 - \frac{s_2 + s_1}{2s} (\Delta\varphi + qV) - 1.15 \ln[2] \frac{q^2}{8\pi K \epsilon_0 \Delta s} \ln \left[\frac{s_2(s-s_1)}{s_1(s-s_2)} \right], \quad (12)$$

where s_1 and s_2 are given by the real roots of the cubic equation:

$$\varphi_2 + (\Delta\varphi + qV) \frac{x}{s} - 1.15 \ln[2] \frac{q^2}{8\pi K \epsilon_0} \frac{s}{x(s-x)}. \quad (13)$$

From (8), (12) and (13), the forward-bias dark current density can be calculated. In a MIM structure, a transition to hopping or diffusive transport is difficult, since the field-induced breakdown occurs prior to reaching the bias necessary to bring about the change in mechanism, typical for quantum tunneling devices. When the applied bias is increased from zero to a high voltage, the carrier transport mechanism would transit from direct tunneling to field emission (Fowler Nordheim tunneling).

Quantum conductances. At infrared and visible wavelengths, the PAT-induced quantum conductance has nonlinear components. The fundamental and second-harmonic components can be derived as^{30,36-37}:

$$G_{\omega}^{(1)} \approx \frac{q}{\hbar\omega} \frac{I_{\text{Dark}}(V_{\text{dc}} + \hbar\omega/q) - I_{\text{Dark}}(V_{\text{dc}} - \hbar\omega/q)}{2} \quad (14)$$

$$G_{\omega}^{(3)} \approx \left(\frac{q}{2\hbar\omega} \right)^3 \left[I_{\text{Dark}}(V_{\text{dc}} + 2\hbar\omega/q) - I_{\text{Dark}}(V_{\text{dc}} - 2\hbar\omega/q) - \right. \\ \left. - I_{\text{Dark}}(V_{\text{dc}} + \hbar\omega/q) + I_{\text{Dark}}(V_{\text{dc}} - \hbar\omega/q) \right] \quad (15)$$

$$G_0^{(2)} \approx \left(\frac{q}{2\hbar\omega} \right)^2 \left[I_{\text{dc}}(V_{\text{dc}} + \hbar\omega/q) - 2I_{\text{dc}}(V_{\text{dc}}) + I_{\text{dc}}(V_{\text{dc}} - \hbar\omega/q) \right] \quad (16)$$

$$G_{2\omega}^{(2)} \approx \left(\frac{q}{2\hbar\omega} \right)^2 \left\{ \frac{1}{2} I_{\text{dc}}(V_{\text{dc}}) - [I_{\text{Dark}}(V_{\text{dc}} + \hbar\omega/q) - I_{\text{Dark}}(V_{\text{dc}} - \hbar\omega/q)] + \right. \\ \left. + \frac{1}{2} [I_{\text{Dark}}(V_{\text{dc}} + 2\hbar\omega/q) - I_{\text{Dark}}(V_{\text{dc}} - 2\hbar\omega/q)] \right\} \quad (17)$$

For moderate intensity of incident light, higher-order conductance components can be ignored.

Conclusions

We have presented a nonlinear quantum-nanoantenna that extends the concept of RFID harmonic sensor to the NIR and visible domains, aiming to detect and identify molecules, DNAs, antigens, and proteins in a nano-dimensional load region. We have shown that the nonlinear conductance, stemming from the multiphoton-assisted plasmon tunneling, can generate the second-harmonic scattering with its amplitude and frequency self-modulated by the physical properties of the loaded nanoparticle. We envisage here that this nanoantenna-based harmonic sensor may enable a variety of intriguing nanophotonic, biological, and imaging applications.

Acknowledgements

The Authors would like to thank Dr. Andrea Alù at the University of Texas at Austin for fruitful discussions on optical nanoantennas.

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FIG 2 (a) Current-voltage characteristic and (b) corresponding Fowler-Nordheim plot for a silver-insulator (molecule)-gold nanojunction with different electron affinities of the insulating layer. Frequency dependencies of (c) first-order (linear) and (d) second-order (nonlinear) normalized quantum conductance (quantum conductivity) of the insulating layer, with different electron affinities. Dashed lines represent the classical limit (small-signal approximation). The inset of (d) shows the ratio of second-harmonic responsivity between the quantum mechanical and classical treatments, as well as the energy band diagram at the threshold frequency, which breaks the asymmetric tunneling and saturates the rectification effect.

FIG 3 (a) Equivalent optical circuit model for the nanoantenna in Fig. 1(b), where C_{gap} is the geometry-yielded nanocapacitor, $G_Q^{(1)}$ is the quantum conductance related to the PAT process, and the intrinsic dipole impedance $Z_{dip} = R_{rad} + R_{loss} - iX_{dip}$. (b) Equivalent optical circuit model for the nanoantenna fed by the induced nonlinear current at the second-harmonic, under the weakly depletion condition. (c) Input impedance (blue lines) and the intrinsic impedance (red lines) for the nanodipole antenna with total length $L = 160$ nm, top radius $a = 5$ nm, base radius $b = 20$ nm, and nanogap $d = 1$ nm; ω_0 and $2\omega_0$ represent the nanoantenna's fundamental and second-order resonances.

FIG 4 (a) Frequency dependencies of the electric field enhancement inside the nanogap, varying the refractive index of the nanoload. The inset of (1) shows the far-field scattering patterns at the fundamental frequency and the second-harmonic for nanoload with $n' = 1.5$; ω_0 and $2\omega_0$ represent the nanoantenna's fundamental and second-order resonances. (b) Contours of electric field strength in the near-field of nanoantenna; red arrows show the snapshot vectors of electric fields.

FIG 5 Contours of second-harmonic scattering cross-section $\xi_{2\omega}$, varying the second-harmonic frequency and refractive index n' of the nanoload. The electron affinities of the nanoloads are: (a) $\chi = 2.35$ eV, (b) $\chi = 2.45$ eV, and (c) $\chi = 2.55$ eV.

FIG 6 (a) $\xi_{2\omega}$ versus frequency for molecules with different physical properties: A: $(n', \chi[\text{eV}]) = (1.3, 2.35)$, B: $(n', \chi) = (1.3, 2.45)$, C: $(n', \chi) = (1.3, 2.55)$, D: $(n', \chi) = (1.5, 2.35)$, E: $(n', \chi) = (1.5, 2.45)$, F: $(n', \chi) = (1.5, 2.55)$. (b) Chart of the maximum $\xi_{2\omega}$ and corresponding peak frequency, which is obtained from Fig. 5 and can be used to map physical signatures to specific molecules.