Numerous efforts have been undertaken to develop rectifying antennas operating at high frequencies, especially dedicated to light harvesting and photodetection applications. However, the development of efficient high frequency rectifying antennas has been a major technological challenge both due to a lack of comprehension of the underlying physics and limitations in the fabrication techniques. Various rectification strategies have been implemented, including metal-insulator-metal traveling-wave diodes, plasmonic nanogap optical antennas, and whisker diodes, although all show limited high-frequency operation and modest conversion efficiencies. Here a new type of rectifying antenna based on plasmonic carrier generation is demonstrated. The proposed structure consists of a resonant metallic conical nano-antenna tip in contact with the oxide surface of an oxide/metal bilayer. The conical shape allows for an improved current generation based on plasmon-mediated electromagnetic-to-electron conversion, an effect exploiting the nanoscale-tip contact of the rectifying antenna, and proportional to the antenna resonance and to the surface-electron scattering. Importantly, this solution provides rectification operation at 280 THz (1064 nm) with a 100-fold increase in efficiency compared to previously reported results. Finally, the conical rectifying antenna is also demonstrated to operate at 384 THz (780 nm), hence paving a way toward efficient rectennas toward the visible range.

1. Introduction

Direct conversion of electromagnetic radiation into direct current (DC) through a rectification process has been recognized as one of the most appealing strategies for wireless power transmission and detection,[1] and at the same time, it is considered a viable solution to directly harvest solar energy[2] as an alternative technology to photovoltaics. By combining a rectifier (i.e., diode) and an antenna, rectenna devices can perform electromagnetic radiation-to-DC conversion.[3–6] While rectenna devices are known for efficient power conversion in the microwave range, high-frequency rectennas (i.e., at infra-red and visible frequencies) are still far from becoming a practical solution.[7–10] Even though, efficient rectennas at near-infrared and visible frequencies are very attractive as they could be employed in many scenarios beyond the applications of nowadays photovoltaic...
technology or semiconductor-based photodiodes. For example, high-frequency rectennas could be implemented for power generation at night time or during atmospheric/sand storms by exploiting black body radiation,

\[11,12\] a solution that could also find an important application in the space sector. Apart from these futuristic and fascinating scenarios, the rectenna concept has been demonstrated in the infrared range

\[13–20\] also by employing 2D materials,

\[20,21\] while in the visible range an interesting solution relying on carbon nanotubes (CNTs) was introduced, reaching conversion efficiency up to \( \approx 10^{-6}\% \).

\[22–24\]

The limited efficiency values obtained at high-frequencies are attributed to non-optimal geometry of CNTs and fabrication challenges inherent to the bottom-up fabrication process.

Here, aiming to boost the conversion efficiency above the state-of-the-art at near-infrared and toward visible frequencies, we take a different approach, circumventing the previous challenges by exploring nano-antennas engineered through top-down fabrication techniques capable of sustaining plasmonic modes with high-frequency resonances. This choice is motivated by the quest for strong and well localized electric field enhancement, resulting in facilitated electrons extraction when integrated within a rectenna architecture. Following this idea, we have numerically engineered, fabricated, and experimentally characterized a 3D plasmonic nanorectenna operating at 280 THz (1064 nm) and demonstrated the possibility of expanding its operation toward the visible range.

The envisioned architecture and the employed materials were chosen considering that the main aspect of the rectification process is the formation of a preferential current direction, which manifests itself upon the appearance of an asymmetric current-voltage (\( I-V \)) characteristic.

\[25,26\] To this end, the conceived nanorectenna consists of a fully integrated antenna-rectifier system. Following an asymmetric architecture, both from a geometrical \[27–29\] and material\[30\] point of view (see Figure 1a and b, respectively), the nanorectenna is defined by a point-contact Metal1-Insulator-Metal2 tunneling diode \[31\] (hereafter pc-M1IM2) where the pc-M1 component also plays the role of receiving plasmonic nano-antenna. In particular, we considered an Au-coated nanocone (pc-M1) and a flat 50 nm thick Ti substrate (M2) as the nanorectenna electrodes due to the significant difference in their work functions \( \phi \), with \( \phi_{M1} = 5.10 \text{ eV} \) and \( \phi_{M2} = 4.33 \text{ eV} \), respectively (see Figure 1b).

Achieving high-frequency rectification requires nano-scale components. In this respect, Figure 1c depicts the state-of-the-art efficiency of rectennas working at high frequency, from 200 to 600 THz (the red dots represent the results from this work). The plot clearly shows an efficiency decrease upon frequency increase, which strongly highlights the need for nano-scale solutions to improve rectennas efficiency. To this end, we adopted an integrated design to merge the rectifier and antenna functionalities. The fast rectifying component is achieved with a tunneling diode composed of a thin insulator (I) layer coupled to a plasmonic nanocone tip (M1). Indeed, electron tunneling through thin barriers is widely considered to occur at the femto-second scale.

\[33,34\] Electron tunneling-based devices can thus, in principle, respond to high-frequency radiation (PHz) without lagging. In this perspective, our nanorectenna device employs a few nm-thick TiO\(_x\) (I) layer on top of a Ti (M2) electrode, finally resulting in a remarkable efficiency improvement with respect to the state-of-the-art.

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**Figure 1.** a) Illustration of point contact MIM (pc-M1IM2) nanorectenna illuminated by an externally propagating collimated beam. b) 1D energy diagram of an asymmetric M1IM2 structure. M1 and M2 have work functions \( \phi_{M1} \) and \( \phi_{M2} \), respectively. Under zero-bias condition, all Fermi levels are aligned. Applying a positive bias to M2 leads to a forward bias situation where electrons near the Fermi level flow from M1 to M2. Applying a negative bias to M2 leads to a reverse bias situation where electrons flow from M2 to M1. The dashed red curve highlighted for the forward bias situation manifests the energy diagram change occurring in point contact configuration. c) Summary of experimental rectennas efficiency at high frequencies. The asterisk (*) refers to an efficiency estimation when only the tip-apex is considered (see Section 2.6).
From a classical point of view, the maximum achievable rectification frequency $\omega_{\text{rect}}$ is proportional to the inverse of the of resistance and capacitance associated with the tip/substrate system, which in turn is found to increase upon reduction of the tip-apex dimension.\[13\] This result, even though deriving from the classical approximation of the metal-insulator-metal (MIM) described in terms of lumped circuit elements, highlights the importance of a nanometric-sized metallic tip for high-frequency operation. This requirement is further stressed by the reduction of the electron mean free path ($e\text{MFP}$) upon frequency increase ($=1/\omega$).\[10\] Moreover, a reduced apex size determines an enhancement of surface electron scattering, allowing to expel electrons more efficiently than a planar metallic surface. This physical characteristics represents an added element of asymmetry to the already mentioned geometrical and material asymmetries, all supporting the flow of a DC current from the nanocone tip toward the Ti layer passing through the TiO$_x$ barrier. Additionally, no strong coupling effects between the plasmonic mode and the TiO$_x$ are expected\[37–39\] due to the very different frequency positioning of the TiO$_x$ absorption peak ($\approx 300$ nm) and the plasmonic mode resonance ($1064$ nm).

Via the scheme of the pc-M1IM2 nanorectenna shown in Figure 1a, electromagnetic radiation is harnessed and converted into surface plasmon resonances (SPRs), with energy $h\omega_p$ where $\omega_p = 2\pi/\lambda_{\text{PC}}$ by the plasmonic nanocone (pc-M1). The conical shape of the antenna supports asymmetric plasmonic modes that favour electromagnetic energy concentration at the apex of the structure.\[40\] Moreover, the damping rate of plasmons, which causes the excitation of electron-hole pairs, shows a conversion rate which scales inversely proportional to the square of the curvature radius\[41-43\] namely related to geometrical constrictions that fosters surface scattering events.\[43-44\] This process produces a relatively large concentration of hot-electrons (HEs), with energies up to $h\omega_p$ above the Fermi level, available for tunneling through the insulator layer. Importantly, surface scattering relaxes the linear momentum conservation constraint facilitating the plasmon-exciton coupling and the emission of electrons along the plasmon propagation direction.\[45\] These considerations suggest that HEs can be efficiently generated mainly at the tip-apex, which is coincidently at the right position for getting collected, being the tip-apex in contact with the TiO$_x$ insulator layer. In this respect, the cone-to-substrate contact radius $C = 1.3$ nm, see Supporting Information) with a dimension much smaller than the electron mean free path in Au ($\approx 40$ nm), facilitates the collection through the TiO$_x$ barrier by tunneling mechanism of most of the HEs generated in the gold nanocone.\[46,47\]

2. Results and Discussion

2.1. Optical Design and Simulations

To identify a good performing geometrical configuration, we employed both analytical and 3D Finite Element Method (FEM) numerical simulations (see Experimental Section

**Figure 2.** a) Extinction spectrum from an isolated Au nanocone and its electric near-field enhancement factor calculated at the cone apex. Resonance at $\lambda = 1064$ nm (280 THz) is found for an Au nanocone with height 300 nm and base diameter 200 nm. The simulated linearly polarized incident radiation is tilted by 12° with respect to the normal of the cone axis ($X$-axis in Figure 1a), as shown in Figure 1a, mimicking the experimental conditions. b) Absorbed electromagnetic power $Q$ versus wavelength calculated in the apex-end of the Au tip, for three Au coating thicknesses (i.e., 10, 20, and 30 nm, always within the eMFP). The cone is formed by a Pt-C core with base 200 nm, height 300 nm, Pt-C tip radius $R = 20$ nm, and covered with a top-deposited Au layer with thickness $t_{\text{Au}} = 20$ nm (all these values represent the experimental parameters). In the simulations, the experimental evaluation of the contact radius $C$ and substrate thickness have been employed as well, with $C = 1.3$ nm, $\text{TiO}_x = 2$ nm, and $T_0 = 50$ nm (see Supporting Information). In the right, the figure also shows the absorption maps calculated at 780 and 1064 nm for input intensities of 7.10 and 12.95 MW m$^{-2}$, respectively. From the scale bar, the strongest absorption is obtained at $\lambda = 1064$ nm. c) $|E|^2$ in logarithmic scale calculated along a line passing through the center of the cone. $Z = 0$ corresponds to the contact point between the Au tip and the TiO$_x$ substrate, $Z > 0$ corresponds to the Au coating of the tip. The dashed line represents the position in the substrate where the electric field has decayed down to $1/e$ of its maximum value. d) SEM image of the nanocone fabricated on the AFM milled probe before (core formed by Pt-C) and after Au coating. The red dots represent the tip radius (different coating thicknesses have been considered returning an overall tip radius in the range 20–40 nm).
and Supporting Information). In particular, the analytical approach\(^{[36]}\) was chosen to gain a quick grasp on the dimensions of an isolated Au nanocone with a resonance around 280 THz (1064 nm) and still be operative at 384 THz (780 nm). The resulting cone dimensions, base diameter 200 nm and height 300 nm, were fed into our FEM numerical model to confirm the resonance frequency both in terms of electric field and power density \(Q = \frac{1}{4} \varepsilon_0 \varepsilon \omega E^2\) absorbed by the conical tip (the corresponding power, integrated within the apex volume, is shown Figure 2b, left), which is a good estimator of the HES capable of crossing the MIM barrier.\(^{[37]}\) Indeed, three Au coating thicknesses were considered (i.e., 10, 20, 30 nm), all below the eMFP of Au in the visible range. Furthermore, with \(\approx 2\) nm-thick TiO\(_x\) layer on top of 50 nm of Ti (see Supporting Information), the simulation results show a resonance shift with respect to Figure 2a. This result highlights the importance of considering the actual materials involved in the cone fabrication (Au & Pt-C versus Au) together with the substrate when estimating the frequency of the cone resonances. The absorption maps (Figure 2b, right) at 280 THz (1064 nm) and 384 THz (780 nm) show an absorption mostly localized at the apex region, reinforcing the consideration that the HESs involved in the photocurrent generation mainly originate from the zone of the cone localized in proximity (i.e., within the eMFP) of the TiO\(_x\) substrate. In terms of power absorption at 280 and 384 THz, our numerical results show a better performance for the 280 THz case (later confirmed by a higher 280 THz experimental photocurrent). This result can be qualitatively explained by recalling that i) the nanocone dimensions were chosen to specifically sustain the 280 THz mode, and ii) the eMFP goes with \(\omega^{-2}\)\(^{[16]}\) thus determining a reduced photocurrent upon frequency increase.

Figure 2c shows the electric field intensity calculated along the cone axis into the substrate materials. A quick field intensity decay into the Ti layer (1/e is reached after just 2.3 nm from the TiO\(_x\)/Au interface) suggests limited HESs generation into the substrate due to the tip radiated field. It should also be noted that the absolute value of the \(k\)-vector associated with photons is generally much smaller than the wave vector associated with free electrons in a metal, thereby strengthening the picture of a negligible photocurrent contribution due to photons directly impinging on the Ti substrate.

### 2.2. Nanorectenna Fabrication and Characterization

Upon identifying a set of geometrical parameters for an adequate optical performance through numerical calculations, the next step was to fabricate the system formed by the Pt-C/Au nanocone in contact with a TiO\(_x\)/Ti substrate. In particular, the nanocone shown in Figure 2d was realized on top of an atomic force microscope (AFM) cantilever through focus ion beam (FIB) lithography (see Experimental Section). The AFM was used to characterize the pc-MIIM2 nanorectenna through precise control over the landing position of the Au nanocone and by tuning its contact force on the TiO\(_x\). This set-up features the AFM scanning contact mode of the nanocone over the substrate surface while detecting, with nanometric resolution, structural defects in the MIM junction (see Experimental Section). Furthermore, the characterization set-up consisted of laser sources, optical components, pico-current amplifier, and electronics to simultaneously perform modulated optical excitation and synchronous electrical detection measurements (see Experimental Section and Supporting Information).

In this regard, with the final objective of determining the performance of the proposed nanorectenna architecture, we measured the \(I–V\) characteristic of the junction composed of a single Au nanocone brought in contact with TiO\(_x\) natively grown on a Ti film (for TiO\(_x\) deposited via atomic layer deposition see Supporting Information), which was characterized via XPS and ellipsometry (see Supporting Information). Figure 3a shows the experimental \(I–V\) nanorectenna characteristics obtained in dark and illuminated conditions, the latter resulting from illuminating the nanocone with a 100% amplitude modulated square wave profile beam with \(\approx 4\) \(\mu\)m wide focal spot. It is evident from the figure that the current measured in the forward bias under dark conditions is quantitatively higher than the reverse bias counterpart, confirming the diode-like (asymmetric) behavior of the nanorectenna. Furthermore, upon illumination, additional current is generated in the pc-M1IM2, as confirmed in Figure 3b, where the synchronism between the measured current and the laser modulation is demonstrated. We shall stress that this extra current generation also occurs at 0 voltage, that is, the ideal light-detection condition, as it rules out any possible effect due to the applied bias.

In our nanorectenna device, different physical mechanisms concur in the final result. In this regard, the energy diagram of the pc-MIIM2 nanorectenna shown in Figure 1b is a useful tool, although its construction is complex as it depends on both material properties and interfaces geometrical configuration. Specifically, the 3D nature of the point contact geometry\(^{[28]}\) challenges the applicability of the simple 1D energy diagram shown in Figure 1b. The actual energy diagram shows pronounced convexity/concavity (see red dashed line under forward bias) due to i) conical geometry of the point contact and ii) image force/electrostatic effects depending on the applied bias condition.\(^{[49]}\) In particular, when pc-M1 and IM2 are brought together to form a junction, the bands will tilt due to the adjustment of the Fermi levels. Under forward bias conditions, the Fermi level of M2 is lowered with a consequent tilting and bending of the band (red dashed line in Figure 1b), resulting in a narrowing of the oxide barrier. Especially in our case, where a strong asymmetry characterizes the pc-M1IM2, a small bias can significantly tilt the barrier, thus allowing for an enhanced tunneling current in the top part of the energy diagram (similar considerations apply for reverse bias).

Overall, due to the nanorectenna shape and choice of materials, two main mechanisms can contribute to the current flowing from M1 to M2 in the pc-M1IM2 structure: i) direct tunneling, namely HESs tunneling through the barrier with a width equal to the thickness of the insulator, and ii) Fowler-Nordheim...
(FN) tunneling, where HEs tunnel through the triangular-shaped tilted barrier with a width smaller than the insulator thickness. In particular, we highlight that both the direct and Fowler-Nordheim mechanisms benefit from forming a plasmonic resonance on the nanocone. Indeed, this allows for the excitation of HEs physically located near the interface M1-I, capable of transitioning from the Au nanocone tip into the TiO\textsubscript{x}/Ti substrate. A contending physical mechanism to excitation and transfer of electrons across the nanorectenna is the internal photoemission (IPE). This phenomenon describes the

Figure 3. a) $I$–$V$ characteristic of a single Au nanocone (20 nm Au coating)/TiO\textsubscript{x}/Ti-50 nm nanorectenna. The black and red curves denote dark and illuminated current, respectively. The employed wavelength is $\lambda = 1064$ nm with an input intensity equal to 12.95 MW m$^{-2}$. The short circuit current $I_{SC}$ and the open circuit voltage $V_{OC}$ are highlighted. b) Temporal profiles of the laser beam (black color) and simultaneously measured current (blue color) in the rectenna. The distance between two adjacent peaks in the horizontal axis is $\approx 2.7$ ms, corresponding to a modulation frequency of 371 Hz (see Supporting Information). The applied bias varies with time between 0.11 and 0.15 V (see Experimental Section). c) Photocurrent versus polarization angle. d) Photocurrent versus laser power measured by applying a phase lock-in technique (see Supporting Information). e) Friction (topography) map acquired on the substrate (left) and the concurrently acquired photocurrent map (center). The relation between the friction map (red line) and the corresponding photocurrent (green line) is also shown (right). See Supporting Information for details.
direct electron-hole pairs excitation (non-plasmon mediated) in the bulk of the M1 metal. By considering the fast electron-electron thermalization (the few nanometers long eMFP in Au), it can be argued that only the IPE excitons generated at the tip apex could contribute to the photocurrent. It can be then concluded that the number of IPE-generated e·h pairs contributing to the total current becomes negligible when considering that it results from the product of the impinging radiation intensity, the quantum coupling efficiency, and the M1-I contact area \( (C_r = 1.3 \, \text{nm}) \).\[50\] Furthermore, if the frequency of the incoming electromagnetic radiation is sufficiently high, IPE excitons could also comprise vertical interband transitions, where electrons energetically located at inner energy bands in M1 are brought slightly above the Fermi level, at the expense of most of the absorbed electromagnetic energy (specifically for Au, the transition from d-band to sp-band would require 1.8–2.4 eV \( \approx 500–700 \, \text{nm} \)).\[51\] In this case, the promoted electrons barely possess enough energy to go through the insulator barrier, hence limiting the overall current flow.\[52\]

Apart from the transport mechanism, we argue that the optical absorption efficiency enhancement of the plasmonic nanocone likely improves the performance of the rectenna, especially in terms of output current, particularly by confining light at the apex region. The experimental confirmation of the resonant nature of the rectification process occurring in the nanorectenna device is provided by the polarization measurements depicted in Figure 3c. The figure shows the \( \cos^2 \theta \) dependence of the photocurrent, where the value \( \theta = 0 \) represents the polarization along the \( Z \)-axis (see inset). The result demonstrates the maximum outcome for light polarized along the nanocone main axis, namely for a maximum value of the SPR coupling. The two aspects of maximal absorption efficiency and photocurrent for light polarized along the cone axis, bring about two major considerations: i) the cones should be kept sufficiently apart to avoid any reciprocal shadowing effect, a situation which would increase the rectenna device footprint; ii) the sunlight is non-polarized therefore part of it would not be captured by the conical antenna. These are two interconnected challenges that need to be addressed when designing future conical rectenna devices, for example by envisioning a non-resonant and polarization-free solution based on specific mode generation.\[60\] Figure 3d highlights the dependence of the photogenerated current on the laser power, showing a clear linear dependence. This result agrees with previous works,\[24,49,53,54\] and it confirms the main role of tunneling processes in photocurrent generation as described by the photon-assisted tunneling theory (see Section 2.3).

Besides the nanocone dimensions, material composition, and the impinging radiation wavelength responsible for the SPRs formation, the topography of the IM2 also influences the photocurrent amplitude. In this regard, to determine the role of the substrate morphology on the measured photocurrent, we simultaneously mapped the friction and the corresponding photocurrent over a randomly chosen region of TiO\(_2\)/Ti-50 nm under gentle mechanical contact condition, as shown in Figure 3e. The correlation between these two quantities is plotted, indicating that the highest photocurrents are recorded on top of the TiO\(_2\)/Ti-50 nm grains. This result suggests that the best performance can be achieved only when the outmost end of the nanocone apex is in contact with the substrate, corresponding to a minimized contact area.\[49\] Furthermore, in the Supporting Information we show the photocurrent maps obtained by applying different contact forces to the IM2 nanorectenna component, suggesting a signal decrease with the increase of the contact force (i.e., bigger contact radius). This result highlights the importance of a controlled contact force to maximize the nanorectenna photocurrent.

### 2.3. Photon-Assisted Tunneling Theory

Among the fundamental parameters determining the actual photocurrent generated by the nanorectenna device, we shall recognize the barrier height, barrier thickness, and tunneling area. In this regard, as demonstrated in previous theoretical and experimental studies,\[17,22–24,55\] studies, when a tunnel junction is illuminated with radiation of energy \( h\omega_{\text{ph}} \), an AC voltage of the form \( V_{\text{opt}} = \cos(\alpha_{\text{ph}} \cdot t) \) develops across the junction which leads to a net DC current component. This DC component, following Tien-Gordon and Tucker formulation, is described by the time-averaged Photon-Assisted Tunneling (PAT) theory: \[56–58\]

\[
I_{\text{dark}}(V) = \sum_{k=-\infty}^{\infty} j_k \left( \frac{e V_{\text{opt}}}{\hbar \omega_{\text{ph}}} \right) \left( V + \frac{k \hbar \omega_{\text{ph}}}{e} \right)
\]

where \( k \) referring to the number of quanta exchanged in the electron tunneling process, \( j_k \) being the Bessel function of \( k \)-th order whose square describes the probability of an electron transition from its initial state to an energy level modified by \( k \)-quanta, and \( V \) is the applied DC voltage. Under the assumption of \( eV_{\text{opt}} < \hbar \omega_{\text{ph}} \), it results to be \( k \approx -1, 0, 1 \), which simplifies Equation (1) (this assumption is realistic at high incident frequencies \( \omega_{\text{ph}} \), such as the visible range). Furthermore, the characteristic \( I_{\text{dark}} \) reflects the transport mechanisms in dark conditions (i.e., no light)—direct or Fowler-Nordheim (FN) tunneling—and it depends on the employed materials (M1, I, and M2), their geometry, the voltage applied to the junction and temperature. In particular, the transition voltage\[59\] between direct and FN tunneling is estimated by the position of the local minimum (inflection point\[6,52,59\]) in the FN representation of the \( I_{\text{dark}}(V) \) curve.

The experimentally measured \( I_{\text{dark}} \) depicted in the FN representation of Figure 4a (blue dots) highlights the absence of any inflection points, suggesting direct tunneling as the preferred transport mechanism across the nanorectenna. A fit of the experimental \( I_{\text{dark}}(V) \) characteristic (Figure 4a, black lines) was then performed by employing the Simmons’ model\[60\] (see Supporting Information), and it was used to determine the effective parameters of the junction band diagram. We obtained an average effective barrier height of 3.94 eV, an effective barrier thickness of 1.5 nm (in agreement with ellipsometry data, see Supporting Information) and an effective tunneling area of 1 nm\(^2\). This last value is consistent with small tunneling electrical contacts reported in the literature,\[61\] where it is shown that electrical contact area is usually smaller than the mechanical contact area (~5 nm\(^2\), contact radius of 1.3 nm, see Supporting Information). The parameters obtained from the
dependence between laser power intensity and generated power agrees with the aforementioned results of Figure 3d on the transport mechanisms in pc-M1IM2 nanorectennas. It also that the PAT theory may indeed be employed to describe the dark and illumination conditions. This result strongly suggests theoretical/experimental matching shown in Figure 4b, both under

\[
V_{	ext{opt}} = 10 \text{ mV}
\]

was used to achieve the theoretical/experimental matching shown in Figure 4b, both under dark and illumination conditions. This result strongly suggests that the PAT theory may indeed be employed to describe the transport mechanisms in pc-M1IM2 nanorectennas. It also agrees with the aforementioned results of Figure 3d on the dependence between laser power intensity and generated power current, where a linear relationship was depicted. 

\[
I_{	ext{dark}}(V) \quad \text{fitting were finally employed within the PAT expression (Equation (1)) to calculate the } I-V \text{ characteristic under illuminated conditions compared with the experimental data. In particular, a } V_{	ext{opt}} \text{ equal to } 10 \text{ mV was used to achieve the theoretical/experimental matching shown in Figure 4b, both under dark and illumination conditions.}
\]

2.4. Thermal Effects

In order to confirm PAT as the main mechanism occurring in the pc-M1IM2 nanorectenna, it is crucial to rule out any other effects that might be expected under illumination conditions. In particular, thermal effects such as thermal expansion, Seebeck effect, and thermal assisted photoemission due to temperature rise in the illuminated nanocone, might negatively influence the conduction outcome of the nanorectenna by partial or even complete suppression of the optical rectification. In this regard, the first clue about the limited presence of any thermal effect is provided by the reasoning that a structural expansion of the nanocone should occur upon a significant increase in temperature. This modification would especially affect the nanocone along its main axis, pushing the nanocone tip into the 1M2 substrate, possibly reducing the oxide thickness. By assuming a strong thermal effect due to the illumination conditions, the current should, over time, show an amplitude change over the whole considered bias range with a directionality related to the applied bias: positive in the first quadrant and negative in the third quadrant. This behavior is not observed in Figure 3a where a bias independent illuminated \( I-V \) characteristic is instead shown hence suggesting the limited, if not absent, thermal expansion effect on the measured current.

To further confirm these considerations, light-induced thermal effects in a nanocone are carefully addressed by performing numerical FEM-based simulations where Maxwell and heat diffusion equations were simultaneously solved. The results, illustrated in the Supporting Information, show that with the parameters employed in the experiment (light power, focal spot, polarization), a temperature rise of less than 2 K was achieved, making any thermal expansion and thermally assisted photoemission negligible. Finally, the presence of thermoelectric contributions through the Seebeck effect can also be neglected in our nanorectenna as these contributions were only reported in MIM samples characterized by linear \( I-V \), which is not the present case. These arguments confirm negligible thermal effects on the electric behavior of the nanorectenna, pointing to PAT as the primary working mechanism.

Another possible mechanism that could in principle occur is related to the thermal-induced electro-chemistry modification of TiO\(_2\), in particular in creating oxygen vacancy filaments. However, Figure S3, Supporting Information, reveals an unchanged morphology for the three different maps performed over the same area with different amounts of force, infering that no physical deformation/electroformation occurred in our samples. Small thickness, low working voltage range and negligible thermal changes (see Figure S6, Supporting Information) altogether eliminate the possibility of electroformation in our nanoscale configuration. This is further confirmed by the absence of any memristive behavior since our \( I-V \) measurements on multiple samples under identical conditions always returned a behavior without any memory effect/hysteresis.

2.5. Multi-Tip Nanorectenna

In order to investigate the scaling-up potential of the nanorectenna architecture, an array of tips (multi-tip) was fabricated on an AFM cantilever probe. In this regard, a square array of \( 3 \times 3 \) tips was realized (Figure 5a,b) with a separation of 300 nm, hence with an area covering the entire focal spot region. This configuration was then tested to verify whether an enhanced photocurrent is retrieved with respect to the single nanorectenna. The resulting \( I-V \) characteristic obtained with a multi-tip nanorectenna on top of TiO\(_2\)/Ti-50 nm is shown in Figure 5c, which confirms the same optical rectification signature of a single nanorectenna. Importantly, the histograms of Figure 5d remarkably demonstrate that the zero-bias photocurrent generated with several nanocones is statistically larger than a single nanocone, therefore supporting that an actual nanorectenna device could indeed result from the integration of many nanocones on the same chip.
However, a multi-tip probe of this kind introduces some experimental challenges, as all the tips need to be in controlled contact with the underneath substrate for best operation conditions. SEM images found that the fabricated tips have indeed ±5 nm differences in height, which was also sensed by the AFM feedback system during electrical measurements. This fabrication limitation, together with the tilting of the cantilever, suggests that different approaches should be taken into consideration for the fabrication of nanorectenna integrated chips, where a geometrically static device would likely operate with better performance.[70] Regardless of the actual final geometrical configuration, these measurements indicate that under the assumption of proper electrical connection between the tips and the underneath material, if all the tips undergo the same kind of optical excitation, the resulting overall photocurrent should scale up linearly with the number of tips.

2.6. Efficiency

One of the most important quantities for evaluating the performance of an energy conversion device is its efficiency, here linked with the capability to convert electromagnetic energy into collectable current. In this regard, the quantities which have to be taken into account to assess the efficiency are the open-circuit voltage $V_{OC}$ and the short-circuit current $I_{SC}$, whose product provides the theoretical power $P_T$, similarly to photovoltaic solar cells. Specifically, for the nanorectenna device, these values are expected to be read in the second quadrant of the $I-V$ characteristic, as shown in Figure 3a, and in agreement with the PAT theory (differently from semiconductor solar cells). In particular, the full cone—geometrical efficiency aims at a straight comparison to the works of Sharma et al. and Anderson et al.,[22–24] which report the best to date efficiencies of $\approx 10^{-6}$ % (for $\lambda = 532, 638,$ and 1064 nm). Our configuration provides an improved efficiency $2.3 \times 10^{-4}$ % at $\lambda = 1064$ nm and FF = 0.25 (as resulting from the triangle shape of Figure 3a). This value was calculated for the experimental values $I_{SC,1064nm} = 23.5$ pA and $V_{OC,1064nm} = 151.5$ mV obtained under an input intensity of 12.95 MW m$^{-2}$ (see Figure 3a) and considering a geometrical absorption based on the effective area corresponding to the 2D projection of a cone of height 300 nm, base diameter 200 nm and apex-deposited Au layer of 20 nm thick coating, as depicted in Figure 2d (for $\lambda = 780$ nm refer to Supporting Information). Even though this result is an important step forward in efficiency, it should be stressed that these values are still far away from representing devices with actual practical applications.

In particular, after further in our analysis by considering two additional scenarios associated with more realistic situations. Here, instead of considering a geometrical absorption of the incident radiation impinging on the Au nanocone, the optical absorption spectra were employed as depicted in Figure 6a,b. In particular: i) Full cone—optical, with $P_{in} = 0.37 \mu$W at 1064 nm, results from the absorption cross-section of the entire cone,
our results show an efficiency improvement of at least two orders of magnitudes with respect to the best reported high-frequency result to date. Still, importantly, our work suggests that through a proper device engineering (e.g., matching between wavelength and antenna geometry or adoption of multi-resonant rectennas), it is possible to improve the efficiency further, possibly reaching values appealing for commercial light-harvesting rectifying devices. In this respect, it is stressed the need for an analytical/numerical predictive tool capable of providing the rectenna I–V characteristic even in the visible range. A tool of this kind would be beneficial for understanding and engineering high frequency rectenna operation.

4. Experimental Section

Numerical Simulations: The Pt-C core nanocone top-coated with =20 nm of Au and in contact with a TiOx/Ti substrate was simulated with 3D electromagnetic FEM simulation software Comsol Multiphysics. As design parameters were considered the diameter of the nanocone base, its height, the nanocone apex diameter, and thickness of the Au layer together with the thickness and materials forming the underneath layer. A linearly polarized light with a polarization angle of 12° with respect to the X-axis (mimicking the experimental arrangement) was assumed as excitation source, as shown in Figure 1a. The refractive of TiOx was taken equal to 2.3 (similar to the ellipsometry data), the refractive index of Ti was implemented by adopting a Drude-Lorentz formalism as in Rakic et al., while Au was taken from Alabastri et al.

Fabrication of the pc-M1IM2 Nanorectenna: The nanocone antenna, as resulting from the numerical simulations, was fabricated using FIB milling (FEI Nanolab 600 dual beam) with Ga ion beam. A contact mode silicon AFM cantilever probe (MikroMasch CSC38-Al) with a long cone/pyramid was chosen as platform for the nanocone fabrication (lever length 350 µm, lever thickness 1 µm, and probe height 15 µm). In particular, the Si cantilever probe was coated with a 7 nm Ti layer to increase its adhesion capability followed by a further coating of 15 nm of Au to create a uniform conductive layer. Afterward, the AFM tip was etched creating a plateau where a Pt-C nanocone was grown via GIS milling (FEI Nanolab 600 dual beam) with Ga ion beam. A contact mode silicon AFM cantilever probe (MikroMasch CSC38-Al) with a long cone/pyramid was chosen as platform for the nanocone fabrication (lever length 350 µm, lever thickness 1 µm, and probe height 15 µm).

In particular, the Si cantilever probe was coated with a 7 nm Ti layer to increase its adhesion capability followed by a further coating of 15 nm of Au to create a uniform conductive layer. Afterward, the AFM tip was etched creating a plateau where a Pt-C nanocone was grown via GIS milling. An over-layer of ~20 nm of Au, thick enough to support SPPs, was then deposited via Ar ion sputter on the structure followed by 20 min of annealing process at 195 °C characterized by a fast heating ramp and a slowly decaying cooling ramp. This final procedure was set in order to smooth as much as possible the nanocone surface, necessary condition for improved electric contact with the underneath substrate.

The nature of the nanorectenna assembly and characterization procedure requires a reduced surface roughness for the IM2 substrate, as it could minimize the variability in the rectified current yield. Due to this necessity and considering that the substrate morphology strongly influences the roughness of the coating materials, quartz with a surface roughness of 0.6 nm was used as substrate material. In particular, the quartz was first cleaned with Piranha solution, then with acetone, followed by isopropanol. Afterward, the clean quartz substrate was dried with nitrogen, washed again with a piranha solution, and finally dried with nitrogen once again. Immediately after the conclusion of this procedure, 50 nm of Ti were deposited on top of the quartz with an electron beam evaporator (Kurt J. Lesker Company PVD 75) adopting a deposition rate as slow as 0.02 nm s⁻¹, a rate chosen to minimize the surface roughness.

Afterward, the growth of the native TiOx through the surface oxidation of Ti was induced by inserting the sample inside an ISO 6 cleanroom at room temperature for ~1 h before characterization measurements.

The Optical System: A commercial AFM (Veeco AFM-Multimode V) was utilized as core component of the optical and electronic systems. The AFM was used in contact mode to perform conducting atomic force spectroscopy of the IM2 nanorectenna component. The main advantage
Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

energy harvesting, metal-insulator-metal diodes, optical rectifiers, plasmonic diodes

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Supporting Information

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