

Enhanced and Spectrally Selective Near Infrared Photothermal Conversion in Plasmonic Nanohelices

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The photothermal conversion in plasmonic nanohelices is studied, unveiling how helical nanostructures made from metals with a notable interband activity -such as cobalt (Co) and nickel (Ni)- exhibit a remarkable temperature rise ΔT up to ≈ 1000 K under illumination. Such outstanding ΔT values exclusively occur at wavelengths close to their localized plasmon resonances (ΔT is significantly lower off resonance), and therefore the photothermal conversion of these nanoparticles is spectrally selective. The exceptional and spectrally selective temperature rise is demonstrated at near infrared (NIR) wavelengths, which prompts the use of Co and Ni helical nanoparticles in a wide range of photothermal applications including solar energy conversion, seawater desalination, catalysis, or nanomedicine.

1. Introduction

In recent years, plasmonic photothermal conversion has emerged as an attractive energy transformation technique with potential use in a wide range of applications.^[1–4] The effect takes advantage of localized surface plasmon resonances (LSPRs) occurring in different nanostructured substrates across the ultraviolet (UV), visible (Vis) and NIR regions of the electromagnetic spectrum. Such resonances allow the effective absorption of

electromagnetic energy in the nanomaterials, which is ultimately converted into heat via nonradiative plasmon decay.^[3–5]

Despite being a well-understood effect, the realization of functional plasmonic nanostructures with efficient photothermal conversion is not a straightforward task, especially when operating at NIR frequencies. In particular, an effective transformation of electromagnetic energy into heat is commonly achieved in nanoparticles with small sizes (tens of nm in all spatial directions).^[4,5] Nonetheless, these nanostructures commonly exhibit LSPRs at UV and Vis frequencies, and thus their optimal photothermal conversion is limited to

such energy ranges. Larger nanoparticles (exceeding hundreds of nm in a spatial direction) do present LSPR at NIR frequencies, however, they predominantly exhibit a radiative plasmon decay rather than an efficient light-to-heat conversion.^[4,5] Strategies to design plasmonic nanoparticles with a large photothermal conversion at NIR frequencies should therefore not only consider the particle morphology (size or shape), but also additional and relevant parameters such as the material composition.^[6]

In this study, we show outstanding photothermal conversion efficiencies at NIR frequencies in weakly coupled nanohelical particles made from transition metals such as cobalt (Co) and nickel (Ni). Such enhanced photothermal response can be ascribed to the joint contribution of three distinct factors. First, the unique (helical) shape of the nanoparticles allows to easily position LSPRs of the nanostructured substrates at the desired frequencies (NIR in this study).^[7,8] Second, the weak interparticle plasmon coupling existing in arrays of nanohelices, separated at distances δ comparable to the diameter of the wire forming the nanohelix d_w ($\delta \approx d_w$), is able to increase the overall light-harvesting efficiency of the nanoparticles.^[9,10] Third, we demonstrate that, by using metals with relevant interband transitions up to IR frequencies (Co and Ni),^[11,12] the photothermal conversion efficiency of metal nanohelices is notably enhanced and an outstanding temperature rise ΔT is achieved in these nanostructures. Indeed, ΔT reached when illuminating Co and Ni nanohelices at 785 nm (wavelength close to the position of the LSPRs of these nanoparticles) is estimated to be up to ≈ 1000 and ≈ 650 K, respectively. This is in clear contrast with the notably lower values of ΔT measured in metal nanohelices with a similar shape but made of more conventional plasmonic materials free of interband transitions at IR frequencies such as silver (Ag). Moreover, we demonstrate that the photothermal conversion in Co and Ni nanohelices is spectrally selective. This is reflected in the

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DOI: 10.1002/adfm.202401599

considerably smaller temperature rise measured when illuminating these samples at wavelengths away from the LSPR (ΔT values for Co and Ni nanohelices measured at 633 nm are only ≈ 20 and ≈ 60 K, respectively).

Overall, the temperature rise attained by these nanostructured substrates is substantially larger than those reported in other nanomaterials, including plasmonic nanoparticles consisting of diverse combinations of morphology and constituting materials,^[1,2,13] as well as other nanostructures exhibiting state-of-the-art photothermal efficiency based on different (non-plasmonic) light-to-heat conversion mechanisms.^[14] As such, our work reveals nanohelices made from metals with large inter-band activity as promising nanostructures to be used in a wide range of applications including biomedicine, catalysis or areas related to solar energy harvesting.^[1–4]

2. Results

2.1. Photothermal Conversion in Co and Ni Nanohelices

We estimate the temperature of arrays of Co and Ni nanohelices upon illumination by measuring the surface-enhanced Raman scattering (SERS) spectra of graphene as a common probing molecule placed on top of metal nanoparticles (methods).^[1,15,16] In nanomaterials without or with a small SERS enhancement factor EF (≈ 1 , case of Co and Ni nanohelices)^[16] the Stokes/anti-Stokes intensity ratio ($\frac{I_S}{I_{aS}}$) of the Raman spectrum of probing molecules depends primarily on the population of the vibrational levels involved in the inelastic scattering processes, which is a function of the local temperature of the sample T :^[1,17,18]

$$\frac{I_S}{I_{aS}} = e^{\frac{\hbar\omega}{k_B T}} \quad (1)$$

where k_B is the Boltzmann constant and $\hbar\omega$ is the energy of the Raman mode in consideration.

The two most prominent features of the Raman spectra of graphene are the so-called G and 2D modes which lie ≈ 1580 and ≈ 2650 cm^{-1} , respectively.^[19] We use the G mode (energy $\hbar\omega_G \approx 195$ meV) to estimate the local temperature of the graphene sample T and therefore record both Stokes and anti-Stokes Raman lines at ≈ 1580 and ≈ -1580 cm^{-1} , respectively.

Prior to study the spectra of graphene placed on the fabricated nanohelices, we measure (methods) the Raman spectrum of graphene flakes on two reference substrates:^[15,16,19] a Si substrate with 300 nm SiO_2 on top and polydimethylsiloxane, PDMS. The measured ratio of the Raman peaks of graphene on both Si/ SiO_2 and PDMS (see measurements in Note S1, Supporting Information) is $\frac{I_S}{I_{aS}} \approx 45\text{--}47$, which corresponds to a sample temperature $T \approx 600$ K (value which is consistent with those measured in literature for graphene-based materials under similar measurement conditions).^[1] Moreover, we have also measured the Stokes to anti-Stokes intensity ratio of the Raman G band of graphene on a 50 nm Co thin film (see measurements in Note S1, Supporting Information), obtaining similar $\frac{I_S}{I_{aS}}$ between 40–50. The fact that the estimated local temperature values are $T \approx 600$ K for graphene on all these non-structured substrates (Si/ SiO_2 , PDMS and Co film, three materials with different thermal con-

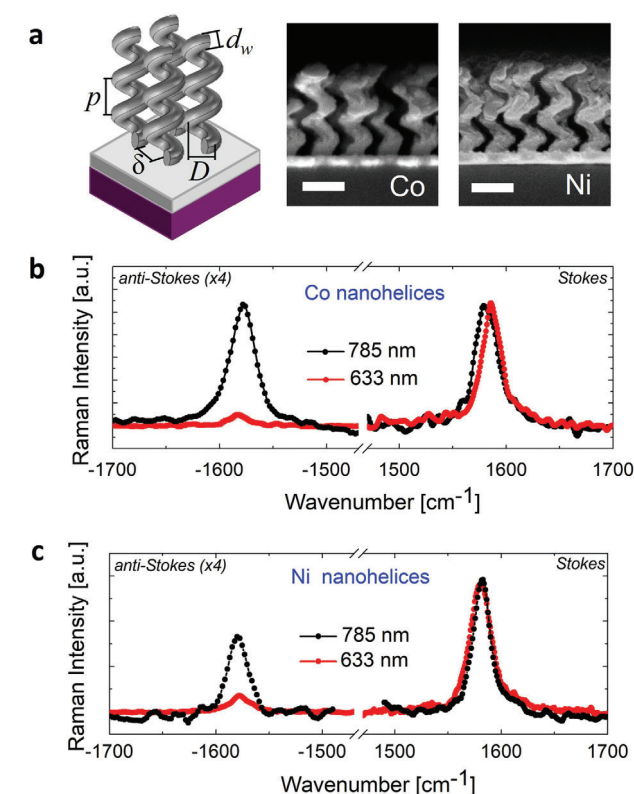


Figure 1. a) Left panel: schematic showing the main parameters of the helical array including the helical diameter D , pitch p , wire diameter d_w and separation between helices δ . Middle and right panels show scanning electron micrograph images of arrays of Co and Ni nanohelices, respectively. Scale bars in both insets are 150 nm. b) anti-Stokes and Stokes Raman G-line of graphene on Co nanohelices and for 633 (red) and 785 nm (black) laser wavelengths. c) anti-Stokes and Stokes Raman G-line of graphene on Ni nanohelices and for 633 (red) and 785 nm (black) laser wavelengths.

ductivities) indicates that, regardless of the substrate, in-plane heat transfer predominantly occurs in graphene flakes. Such behavior is a consequence of the high thermal conductivity of this 2D material.

Figure 1a shows a schematic of the helical arrays used in the study (left panel), together with scanning electron microscopy images of the fabricated Co and Ni nanohelices (middle and right panels, respectively). The nanohelices exhibit a relatively uniform pitch p and diameter D ($p \approx 140$ nm and $D \approx 95$ nm, respectively) and have a similar number of turns $N \approx 2.5$. The plasmonic behavior of metallic nanohelices is dominated by a longitudinal LSPR approximately placed at a wavelength λ_p equal to the total length of the wire composing the nanohelix,^[7,8]

$$\lambda_p \sim N \sqrt{(\pi D)^2 + p^2} \quad (2)$$

and thus the longitudinal LSPR in the samples presented in Figure 1b,c is located at NIR frequencies (≈ 824 nm). Reflectance measurements have been additionally carried out in our samples to experimentally verify the position of their longitudinal LSPR (see Note S2, Supporting Information).

As reported in the literature,^[7,9,10,16] at wavelengths close to their longitudinal LSPR, the near-field distribution of multiple-turn nanohelices consists of periodic dipoles (with an effective length of half a pitch, $p/2$) along the length of the nanostructures. The interaction between these dipoles induces a notable light absorption in the individual nanohelices at wavelengths close to the LSPR.^[7,9] Moreover, the nanohelices presented in this study are weakly coupled since they are arranged in an array configuration with a separation distance between nanoparticles ($\delta \approx 75$ nm) which is comparable with the diameter of the wire forming the nanohelices d_w . Metal nanohelices with these aspect ratios $\delta/d_w \approx 1$ provide an increased light-harvesting efficiency w.r.t. the individual nanoparticle.^[9,16] Such absorbed electromagnetic energy can be ultimately re-radiated or converted into heat depending on, for instance, the interband activity of the metals constituting the nanostructures.^[7,9,16]

Figures 1b,c depicts the measured Stokes and anti-Stokes G mode Raman lines of graphene placed on arrays of Co and Ni nanohelices, respectively, at two different laser wavelengths (785 and 633 nm). At a first glance, both arrays of Co and Ni nanohelices show much smaller $\frac{I_S}{I_{AS}}$ ratios at 785 nm than at 633 nm laser wavelengths. This fact stems from an enhanced light-harvesting occurring in arrays of nanohelices at wavelengths close to the position of their LSPR,^[7] (≈ 824 nm) and it makes evident the spectrally selective photothermal conversion provided by these nanostructures. In particular, the estimated temperatures of graphene on nanohelices at 633 nm wavelengths (i.e., away from the position of the LSPR) are $T \approx 620$ K ($\frac{I_S}{I_{AS}} \approx 38$) and $T \approx 660$ K ($\frac{I_S}{I_{AS}} \approx 30$) for Co and Ni nanohelices, respectively. Therefore, helical nanostructures induce a minimal temperature rise ΔT of 20 (Co nanohelices) and 60 K (Ni nanohelices) at 633 nm. Instead, the estimated temperatures for graphene on Co and Ni nanohelices at 785 nm wavelength are notably larger, $T \approx 1600$ K ($\frac{I_S}{I_{AS}} \approx 4$) and $T \approx 1250$ K ($\frac{I_S}{I_{AS}} \approx 6$), respectively. The temperature rise ΔT induced by Co and Ni nanohelices at 785 nm is then 1000 and 650 K, respectively. These values are notably larger than those obtained at 633 nm, despite the fact that the laser irradiance I at 785 nm ($0.12 \text{ mW } \mu\text{m}^{-2}$) is an order of magnitude smaller than the one at 633 nm ($6.6 \text{ mW } \mu\text{m}^{-2}$), see methods for further measurement details. We remark at this point that the estimated ΔT values for Ni and Co nanohelices are accurate: the temperature rise of the nanoparticles is the primary factor contributing to a decrease in the measured $\frac{I_S}{I_{AS}}$ ratio in plasmonic nanostructures with SERS EF ≈ 1 ,^[17,18] which is the case of Ni and Co nanohelices.^[16] Moreover, we highlight that i) the temperature rise ΔT increases approximately linearly with the irradiance of the laser I (see Note S3, Supporting Information) and ii) the temperature rise obtained for both Co and Ni nanohelices at 785 nm and an irradiance $0.12 \text{ mW } \mu\text{m}^{-2}$ is large, roughly half of the melting point temperatures of the bulk materials (1768 and 1726 K for Co and Ni, respectively). In fact, following these two observations, one can also understand that disintegration of these nanohelices occurs below the laser spot when increasing the irradiance of the 785 nm laser to $0.3 \text{ mW } \mu\text{m}^{-2}$ (see Note S4, Supporting Information).

Next, we show that the combined effect of helical nanostructures made from metals with relevant interband transitions are the primary cause of the efficient light-to-heat conversion in Ni

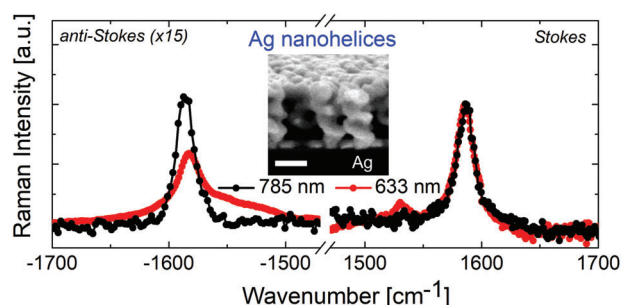


Figure 2. Anti-Stokes and Stokes Raman G-line of graphene on Ag nanohelices for 633 (red) and 785 nm (black) laser wavelengths. Inset shows a scanning electron micrograph image of the array of Ag nanohelices. The scale bar in the inset is 150 nm.

and Co nanohelices. To do so, we estimate the temperature rise of an array of nanohelices made from a different metal, Ag. Contrary to Co and Ni, Ag is a conventional plasmonic material with no major interband activity at wavelengths above ≈ 400 nm,^[20] and the plasmonic decay in Ag nanohelices is predominantly radiative through scattering.^[7,9,16] In this sense, it is expected that the local temperature reached in arrays of Ag nanohelices is notably lower than the one attained in arrays of Co and Ni nanohelices. **Figure 2** shows the measured Stokes and anti-Stokes Raman lines of graphene placed on the array of Ag nanohelices. Ratios $\frac{I_S}{I_{AS}} \approx 30$ at 633 nm wavelength and $\frac{I_S}{I_{AS}} \approx 15$ at 785 nm wavelength are extracted for these samples, which correspond to estimated temperatures ≈ 660 and ≈ 830 K and ΔT of 60 and 230 K, respectively. We further highlight that these estimated temperature values are an upper limit for the case of Ag nanohelices: factors other than a temperature rise of the nanohelices contribute to a decrease in the measured $\frac{I_S}{I_{AS}}$ ratio^[17,18] in plasmonic nanostructures with SERS EF $\gg 1$ such as Ag nanohelices^[9,16] (see further information in Note S5, Supporting information).

2.2. Performance of Co and Ni Nanohelices as Efficient Photothermal Conversion Devices for Applications

The remarkable temperature rise ΔT achieved in Co and Ni nanohelices at 785 nm (≈ 1000 and ≈ 650 K at a laser irradiance $0.12 \text{ mW } \mu\text{m}^{-2}$, respectively) promotes these nanostructured substrates as effective photothermal conversion devices at NIR frequencies. These nanomaterials are particularly interesting for high temperature photothermal applications, systems where typical working temperatures > 500 K are required.^[3–5] In fact, ΔT values reached in Co and Ni helical nanoparticles are larger than state-of-the-art nanostructures reported in literature.^[14]

A detailed benchmarking between the here-reported Co and Ni nanohelices and other photothermal nanomaterials is provided in **Figure 3**. For a proper comparison, we only consider here substrates measured in similar conditions than our nanohelices (i.e., using monochromatic radiation and atmospheric conditions), excluding thus nanomaterials measured in solution or studies where polychromatic radiation was used.^[21,22] In particular, **Figure 3** depicts the temperature rise achieved in the different photothermal nanosystems normalized w.r.t. the irradiance I of the incident Vis or NIR radiation $\overline{\Delta T} = \Delta T/I$ (raw data

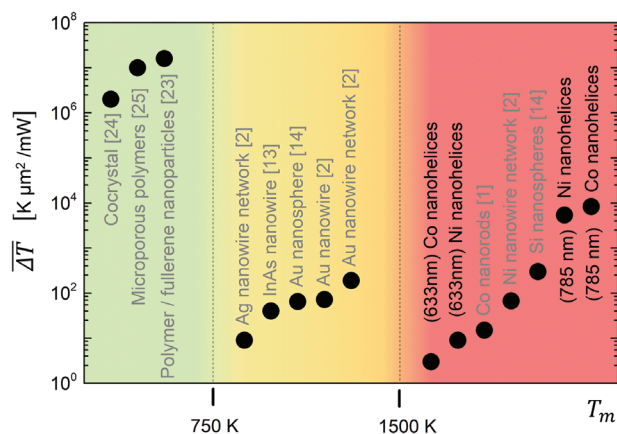


Figure 3. Temperature rise normalized w.r.t. the irradiance of the incident radiation for different photothermal systems: nanohelices reported in this work (black letters) and in literature (grey letters). The graph is separated in three regions, depending on the melting point of the constituting bulk materials: below 750 K (green part of the panel, left-hand side), between 750 and 1500 K (orange part of the panel, in the middle) and above 1500 K (red part of the panel on the right-hand side).

for composing this image is shown in Note S6, Supporting Information). The figure itself is separated into three regions depending on the melting point of the bulk materials constituting the nanostructures T_m : below 750 K (left-hand side of the panel, green region), between 750 and 1500 K (middle part of the panel, orange region) and above 1500 K (right-hand side of the panel, red region). In turn, these three regions classify photothermal conversion devices/substrates according to their ability to operate at low, medium or high working temperatures, respectively.

Intriguingly, Co and Ni nanohelices at 785 nm show the largest reported $\Delta \bar{T}$ of the substrates able to work at high temperatures (red region), surpassing state-of-the-art substrates such as silicon nanospheres by an order of magnitude.^[14] Nanostructured substrates based on polymers show the largest $\Delta \bar{T}$ among all substrates,^[23–25] however, they can only be utilized at much lower temperatures due to their low melting point (i.e., the temperature rise ΔT reached in these substrates is also low). Figure 3 also illustrates the fact that arrays of weakly coupled Co and Ni nanohelices excel at spectrally selective photothermal conversion, i.e., at efficiently converting electromagnetic radiation into heat only at specific wavelengths: the normalized temperature rise exhibited by the nanostructures at 633 nm is three orders of magnitude smaller than the temperature rise at 785 nm (close to the longitudinal LSPR).

Furthermore, we note that metals such as Ni and Co have lower surface diffusion than more conventional plasmonic materials such as Ag, aluminum (Al) or gold (Au).^[26,27] This fact minimizes the reshaping of Ni and Co nanohelices at temperatures close to their melting threshold and thus aids in the stability of these novel photothermal substrates.

In terms of applications, not only the fact of reaching a large temperature rise ΔT at specific wavelengths in the here reported Co and Ni nanohelices is important. We also remark the possibility of controlling such temperature rise in the surroundings of these nanostructured materials depending on the irradiance of the incoming light

(see Note S3, Supporting Information). Finally, we accentuate the fact that the plasmonic nanohelices disintegrate even at modest laser irradiances (above $0.30 \text{ mW } \mu\text{m}^{-2}$, see Note S4, Supporting Information), which makes these nanomaterials readily to be used in laser-induced explosion applications.^[28]

3. Conclusion

In conclusion, by using micro-Raman spectroscopy, we have demonstrated Co and Ni nanohelices to be efficient photothermal conversion devices at IR wavelengths. The measured temperature rise in these nanostructures when using a relatively low laser irradiance ($0.12 \text{ mW } \mu\text{m}^{-2}$) reaches 1000 K, value which is larger than the one reported in state-of-the-art photothermal nanomaterials able to operate at high temperatures.^[14] Such efficient light-to-heat conversion is achieved at specific wavelengths close to the LSPR of the nanostructures and thus spectrally selective. The simple tuning of the LSPR of metallic nanohelices,^[7] and the scalable fabrication of these nanomaterials,^[29] prompt the use of these novel photothermal substrates in a wide range of applications including solar energy conversion, photothermal signal generation in radiometry and nanomedicine or laser-induced explosion.^[1–5,28] Moreover, being chiral systems, nanohelices exhibit a different absorption of right-handed and left-handed circularly polarized light,^[30] behavior which can be potentially exploited to design unique and novel devices with chiral photothermal properties.

4. Experimental Section

Fabrication of Nanohelices: Periodic arrays of helical nanostructures made from Ni, Co, and Ag were engineered by oblique angle deposition, OAD.^[7,29] The OAD set-up for this study was implemented in a general-purpose evaporator by means of an in-house built retrofittable system that provides controlled substrate rotation. The OAD method was used on seeded substrates (150 nm separation) with a $\approx 50 \text{ nm}$ Ag film on top to produce the three regular nanohelical arrays made from Co, Ni, and Ag.^[29] The oblique angle and rotation speed were fixed at $\approx 88^\circ$ and 0.3 rpm , respectively for all the samples and the deposition rate was 1.5 nm s^{-1} . Scanning electron microscopy (SEM) was utilized to examine the structure and morphology of the grown metallic nanohelices.

Graphene Transfer on Nanohelices: Polymethyl methacrylate (PMMA) was spun on top of Monolayer CVD graphene on Cu foil (from Graphenea). The Cu was etched in a 1 M ammonium persulfate solution. Graphene supported with PMMA was then transferred on the helical nano-arrays. Finally, the PMMA layer was dissolved in acetone, and samples were rinsed in isopropanol and dried with N_2 gas.

Raman Measurements: Raman spectra were measured with a micro-Raman set-up (Horiba Jobin-Yvon Labram HR) with $\approx 2 \text{ cm}^{-1}$ spectral resolution, using a $100\times$ objective with numerical aperture N.A. 1.25. The excitation wavelengths were 633 (laser spot $\approx 1 \text{ } \mu\text{m}^2$) and 785 nm (laser spot $\approx 12 \text{ } \mu\text{m} \times 6 \text{ } \mu\text{m}$). Unless otherwise stated, by using a filter that transmits 10% of the incoming light, the laser power on the samples was set in the measurements to 6.6 mW for both laser lines and thus their irradiance was ≈ 6.6 and $\approx 0.12 \text{ mW } \mu\text{m}^{-2}$ for 633 and 785 nm wavelength, respectively. The acquisition time for each spectrum was 2 min and, to ensure reproducibility and stability, five Raman spectra were measured for each array of nanohelices. When needed (i.e., to undertake measurements at different laser powers), additional filters transmitting 1%, 5% or 25% of the incoming light were used in the Raman spectrometer.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Authors thank the support from the Ministry of Science and Innovation (MCIN) and the Spanish State Research Agency (AEI) under the grant PID2021-128154NA-I00 funded by MCIN/AEI/10.13039/501100011033 and by "ERDF A way of making Europe". This work has been also supported by Junta de Castilla y León co-funded by FEDER under the Research Grant number SA103P23. J.A.D.N. thanks the support from the Universidad de Salamanca for the María Zambrano postdoctoral grant funded by the Next Generation EU Funding for the Requalification of the Spanish University System 2021–23, Spanish Ministry of Universities. J.M.C. acknowledges financial support by the MCIN and AEI "Ramón y Cajal" program (RYC2019-028443-I) funded by MCIN/AEI/10.13039/501100011033 and by "ESF Investing in Your Future". J.M.C. also acknowledges financial of the European Research Council (ERC) under Starting grant ID 101039754, CHIOTRONICS, funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Research Council. Neither the European Union nor the granting authority can be held responsible for them. D.M.C. acknowledges funding under Science Foundation Ireland's Frontiers for the Future program grant no. 19/FFP/6745.

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

infrared photothermal devices, interband activity, metal nanoparticles, photothermal conversion, plasmonics

Received: January 26, 2024

Revised: March 26, 2024

Published online:

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