ABSTRACT: Strong-coupling effects alter the polaritonic states of metal–dielectric nanostructures and, therefore, can be used to tailor the response of infrared (IR) photonic elements. We report on the development of a simple IR double-nanoantenna platform that achieves strong coupling between plasmon and phonon polaritons using extreme aspect ratio Al and amorphous SiO2 antennas of modest quality-factor, equaling coupling performance of platforms using novel materials. Our spatially resolved spectroscopy studies reveal Rabi splitting (26 meV) and offer a detailed study of the strongly coupled mode structure within the nanoantenna, with unprecedented spatial sensitivity (<10 nm). We imaged the spatial distribution of strongly coupled modes, accessing the local electromagnetic density of states of the system, obtaining key information on photonic population. Our study obtains strong-coupling behavior in hybrid nanosystems using geometry, rather than materials properties, promising high performance using cheaper and more abundant materials.

KEYWORDS: plasmon–phonon coupling, strong-coupling, Rabi states, terahertz photonics, mid-IR photonics, vibrational EELS

Strong-coupling effects are one of the most fascinating manifestations of light–matter interaction, observable using a plethora of experiments in atomic physics, solid-state physics, biophysics, and so on.1−10 Significant progress on the understanding of strong coupling between different types of excitations has been achieved in several solid-state hybrid systems, resulting in drastic modifications of their energy states, which can impact the development of transformative applications, including optical switches for quantum computing,11 polaritonic devices,12 single-photon sources,13 and platforms for control of chemical reactions.14

Taking advantage of strong-coupling processes in the terahertz range, by including changes in shape, size, and doping,9−11 would provide unique opportunities to modify the energy states of surface plasmon–phonon polaritons beyond the standard tunability approaches. Strong plasmon–phonon coupling can modify the energy states, as recently explored in a few hybrid platforms with simple geometries using novel materials.15−17 However, building robust hybrid platforms for the realization of strong plasmon–phonon coupling in the mid-infrared (IR) range is a difficult task due to challenges imposed by the fabrication of hybrid nanostructures.18 Also, investigations into the role of spatial constraints in hybrid nanostructures will permit us to assess the significance of geometry over materials properties, seeking to identify additional tuning elements of the photonic response in terahertz systems. Better understanding of geometry will lead to new strategies for engineering efficient strong-coupling nanodevices with polaritonic tunability in a manner currently used in plasmonic nanocavity coupling investigations.18

Atom-wide electron probes have been recently used to probe phonons,19 plasmon–phonon coupling,20 and plasmon–exciton coupling20 due to improvements in the energy resolution for electron energy loss spectroscopy (EELS).21 In particular, the coupling of plasmonic antennas with phononic films has been investigated experimentally by electron16 and optical12 techniques, illustrating the potential of each technique to study excitation coupling. Optical probes dominate strong-coupling studies, where plasmon–phonon coupling has been measured unequivocally using extinction-like spectroscopy methods.22 But recent EELS studies have shown that electron beams bring some advantages, because they can probe single nanostructures with (sub-)nanometric resolution, providing access to excitations confined to subregions of nanostructures.23−25 Also, EELS scattering probability is related to the dynamic form factor, which encodes information about the excitations sustainable in terahertz systems.

Received: March 4, 2021
Published: May 7, 2021
matter in the absence of the probe, representing a clean method to assess strongly coupled excitations.

Furthermore, EELS scattering maps are linked to the local density of electromagnetic states (LDOS), driven by the passing electron, projected along the direction in which the electron travels, and thus offer fundamental insights into the LDOS of hybrid systems. However, measuring the spatial distribution of strongly coupled modes in an isolated IR hybrid device remains to be achieved. Progress in this direction will improve significantly our understanding of the interaction of strongly coupled modes with photons, molecules, and with other elementary excitations sustained in hybrid nanosystems.

Extending our understanding of the spatial distribution of coupled hybrid modes should shed light on the dynamics of energy-driven processes in mid-IR photonic devices.

We discuss here a hybrid plasmon–phonon double-antenna design based on a combination of infrared plasmonic and phononic materials, specifically aluminum (Al) and amorphous silica (a-SiO₂). The plasmonic response of Al is well-studied, while a-SiO₂ provides a unique platform for phonon excitations.

Our hybrid double-antenna design consists of a plasmonic Al antenna and a phononic a-SiO₂ antenna joined side by side, as indicated in Figure 1A. The dielectric responses of isolated rod-like antennas have been intensely studied in the past, revealing a large variety of modes sustained in the structure, primarily driven by the antenna cross-section shape and aspect ratio. While the plasmonic response of rod-like antennas could be tuned over a wide energy range by adjusting its length, the large variety of surface phonon modes in rod-like phonon antennas remains constrained within the Reststrahlen band (RB). We present a description of the mid-IR response of isolated Al and a-SiO₂ rod-like antennas in the Supporting Information (SI), thus, complementing studies in the visible/near-IR and setting the starting point of our analysis. The proposed double-antenna design seeks to exploit the interaction of the dipole Fabry–Perot mode (m = 1) of the Al antenna with the Fabry–Perot phonon modes and other surface phonon modes of the a-SiO₂ antenna.

We built the double-antenna structure illustrated in Figure 1A following a careful nanofabrication approach, described in the Methods section of the SI. Figure 1B shows a low-magnification annular dark-field (ADF) STEM image of a fabricated Al/a-SiO₂ double-antenna that is suspended in vacuum, minimizing interaction with the support. The vertical line indicates the scattering from the support.

Figure 1. Plasmon–phonon coupling platform and EELS spectroscopy studies of hybrid Al/a-SiO₂ double-antennas. (A) Schematic picture illustrating the coupling between one plasmonic and one phonon excitation within the Rabi splitting model. At resonance conditions ($\omega_{pl} = \omega_{vib}$), the plasmonic and vibrational energy modes coincide, interact, and form two new hybrid modes ($\omega^+$, $\omega^-$) spaced by the Rabi energy ($\hbar \Omega$). For simplicity, other polaritonic modes of the antennas are not shown. (B) ADF-STEM image of a fabricated Al/a-SiO₂ double-antenna that is suspended in vacuum, minimizing interaction with the support. (C) EELS spectra acquired on hybrid Al/a-SiO₂ antennas of different lengths (L) revealing energy splitting within the PB (gray band) of the amorphous silica, as a result of the plasmon–phonon coupling. Inset shows the probe location. The vertical line indicates the scattering from the support.
antenna is about 35 nm, while the Al nanoantenna width varies from 100 to 250 nm, without affecting the plasmon–phonon coupling.

To achieve pl-ph coupling, the plasmonic response of the Al antennas was spectrally shifted by adjusting its length in such a way that its dipole Fabry–Perot plasmon mode \((m = 1)\) frequency \(\omega_{\text{pl}}\) coincides with frequencies of vibrational modes \(\omega_{\text{ph}}\) within the RB of the silica.\(^{23}\) Zero detuning \(\delta = 0\) conditions are achieved with antennas of \(\sim 3.1\) \(\mu\)m in length, resulting in strong spectral modifications within the RB. To study closely the evolution of the pl-ph interaction in the small detuning range \(\delta \rightarrow 0\), we fabricated structures of slightly different lengths ranging from 2.4 to 3.7 \(\mu\)m. This results in phononic antennas of extreme aspect-ratio (up to \(\sim 90\)) at resonance conditions, which favors coupling with IR light and stronger lateral interaction with the plasmonic antenna.

Figure 1C shows background-subtracted EELS spectra acquired in hybrid double-antennas of different lengths \((L)\) that were probed by locating the electron beam 10 nm away from the tip of the structures (see inset of Figure 1C). We notice that the dominant EELS peaks move toward lower energies as the length of the antenna increases and that the formation of a double-peak resonance becomes visible near/within the RB, revealing an energy splitting for the 3.1 \(\mu\)m long structure. These two peaks are formed due to the excitation of the new coupled modes due to pl-ph interaction. In the absence of coupling and at zero detuning conditions \(\delta = 0\),
the spectra would simply display an overlap of peaks of different intensities, without indication of an energy separation. Other resonances also appear in the spectra, indicating the excitation of higher-order \((m \geq 2)\) surface plasmon polaritons (SPP) of the Al structure and surface phonon polariton (SPhP) modes of the SiC support. The frequencies of those polaritons differ from the vibrational modes of the SiO₂ antenna, so they do not participate in the pl-ph coupling.

We measured the dispersion curve of the surface polaritonic modes sustained in the hybrid systems (Figure 2A) using a well-established methodology. The dispersion curve includes a range dominated by the pl-ph excitations between 120–180 meV, while most of the high-order SPP modes appear above 220 meV. The formation of two branches within the upper RB of the silica highlights the Rabi energy splitting (≈26 meV) behavior. It should be noted that the energy gap persists over a finite range of wave-vectors \((\Delta q > 0.3 \mu m^{-1})\), as typically expected for coupling between different excitations. Each branch corresponds to the excitation of one of the coupled pl-ph modes, which are denominated symmetric and antisymmetric modes. Each coupled mode exhibits a particular surface charge configuration according to our simulations (see top-view schematics, Figure 2A, inset).

The high-order SPP modes \((m \geq 2)\) exhibit the typical linear dispersive character of plasmon polaritons in the near IR (Figure 2A), and the smaller slope than that of the light line indicates that those polaritons travel with a group velocity smaller than the speed of light. That linearity also shows that the coupled modes possess a photon-like component in their dispersive nature, indicating their ability to couple to mid-IR photons. To bring further insight in the pl-ph coupling, we plotted the excitation energy as a function of the double-antenna length (Figure S1). We observe a linear behavior for each SPP mode \((m = 2\) and 3), as well as two hybrid anticrossing branches spaced by an energy gap formed as a result of the repulsion between them. This anticrossing is one of the key characteristics of coupling between excitations.

Simulated curve dispersions of isolated Al and a-SiO₂ rod-like antennas (Figure S4) show that, in the long-wavelength limit \((qL \ll 1, L > 1 \mu m)\), the Al antennas exhibit photonic-like dispersive behavior, while the phononic a-SiO₂ antennas show an undispersive behavior confined within the RB. For the hybrid double-antenna systems (Figure 2B), the simulated dispersion shows the formation of an anticrossing region over a band of wave vectors \((\Delta q > 0.1 \mu m^{-1})\) with a minimum energy gap of ≈15 meV. Figure 2D shows the calculated EELS probability curves corresponding to antennas under nearly on-resonance conditions \((\delta \rightarrow 0)\). Notice that the gap splitting decreases as the detuning approaches zero, reaching values of 19 meV (curve “a”) and 15 meV (curve “b”). The scattering amplitude of each coupled mode varies as a function of the detuning parameter, in agreement with experiment (Figure 1C). Under conditions of large detuning \((|\delta| > 30 \text{ meV})\), the pl-ph coupling does not hold and enters a weak coupling regime, resulting in the excitation of decoupled SPPs and vibrational modes (curve “d”), with very small electron scattering intensities from the silica spreading across the spectral gap and strong surface plasmon scattering signal.

We measured the spectroscopic properties of the coupled modes by performing spectral fitting using the Rabi splitting model (Figure 1A). Within this model the coupling occurs between Al and a-SiO₂ modes of the same (or similar) energy and results in two new different modes \((\omega', \omega'')\) spaced by an amount of energy proportional to the Rabi frequency \((\Omega)\). The energy of each hybrid state is given by the following relationships:

\[
\hbar \omega' = \hbar (\omega_{pl} + \omega_{sib})/2 - i\hbar (\gamma_{pl} + \gamma_{sib})/2 \\
\pm \left( \sqrt{\hbar^2 - (\delta - i\hbar(\gamma_{pl} - \gamma_{sib}))^2} / 2 \right)
\]

where \(\hbar\) is the reduced Planck’s constant, \(\gamma\) is the coupling constant, \(\delta\) is the detuning parameter, and \(\omega_{pl/sib}\) and \(\gamma_{pl/sib}\) are the oscillation frequency and damping rate of the plasmonic/phononic antenna before coupling, respectively.

We performed a fitting analysis in several EELS spectra containing the double-peak spectra feature using Lorentzian functions. A detailed description is presented in the SI (Methods). Our general findings are illustrated in Figure 2C, which shows the symmetric and antisymmetric peaks at ≈130 and 156 meV, respectively. From the fit analysis, we find that both coupled modes have similar line widths \((\approx 30 \text{ meV})\), which represents the mean value of the line widths of each constituent of the coupled system before coupling. Also, the line widths of the plasmon \((\hbar \omega_{pl})\) and vibrational \((\hbar \omega_{sib})\) resonances before coupling are about 45 and 15 meV, respectively. We also find the smallest energy splitting \((\hbar \Omega)\) of ≈26 meV for the 3.1 and 3 μm long antennas, indicating an exchange transition rate of 6.3 THz between coupled modes. In this reversible process, the energy is exchanged between the coupled modes with a rate faster than any decay rate of the hybrid system, therefore, lasting for several exchange cycles before a complete decay takes place. Tuning the energy gap should be possible using other combinations of materials for the double-antenna constituents or using other geometries (e.g., array of plasmon wires embedded in a matrix, plasmonic rod coated with a phononic layer, or a single molecule attached to a plasmonic rod).

We determined a coupling constant \((\gamma)\) of about 18 meV at the smallest energy separation. An evaluation of the conditions for different regimes of coupling indicates that the pl-ph interaction is in the strong regime, fulfilling the two typical relationships: \(2 \gamma > h\Omega_{pl} - h\Omega_{sib}/2\) (or \(36 > 15\)) and \(2 \gamma > h\Omega_{pl} + h\Omega_{sib}/2\) (or \(36 > 30\)). This finding is very important because it demonstrates that the coupling conditions achieved using antennas of modest quality factors (Al and SiO₂) in the proposed double-antenna geometry are as strong as the ones obtained using higher quality-factor structures (Al and SiO₂) in configurations involving phononic layers and antennas/ resonators \((\gamma = 7–19 \text{ meV})\). Schematics of the different strong-coupling platforms presented in refs 12, 16, and 17 are shown for comparison in Figure S5. Based on the electrostatic eigenmode model, most of the interaction between those structures can be accounted for the dipole–dipole contribution to the coupling constant \((\gamma)\). For double-antennas, the consideration of dipole–dipole interactions leads to modest plasmon–phonon coupling due to the weak dipole moments of the SiO₂, suggesting that additional multipole terms (e.g., quadrupole) of the SiO₂ nanoantenna are also contributing actively to enhance pl-ph coupling. Indeed, due to its shape the silica nanoantenna exhibits a larger variety of modes than phononic layers (only two Fuchs-Kliewer modes), thus, offering more available channels for plasmon–phonon interaction. The contribution of each phononic mode to the coupling constant was not assessed. Our experimental study provides evidence that the geometry of each constituent plays a role in the design of strong-coupling terahertz platforms.
desirable behavior can be also obtained by use of an intelligent set of spatial constraints, rather than relying only on qualities of materials with low damping.

To study the spatial distribution of the two strongly coupled modes and to gain insight into the LDOS distribution in a single hybrid antenna, we mapped the scattering intensities of the EELS resonances. We initially probed systems (L = 3 and 3.1 μm) in a loof mode within subwavelength distances, keeping the electron beam traveling in vacuum at ∼20 nm from the double-antenna edge. Figure 3A shows the space-dependent scattering intensities of the symmetric and antisymmetric coupled modes extracted from EELS spectra. This distribution reveals two maxima near the structure ends that are spaced by a minimum in the middle region, resembling a dipolar pattern of a traditional optical antenna. This suggests that a large population of photonic modes is concentrated near the ends of the double-antenna, implying a drastic modification of LDOS imposed by the hybrid system. At larger distances, the signal decays due to the evanescent character of the response fields, extending up to several hundreds of nanometers.

We mapped the internal section of the double-antenna including the adjacent regions from Al and SiC structures (see ADF image of the mapped area in Figure 3B). Figure 3C shows spatially resolved EELS maps for the modes in the double-antenna. To render a better visualization of maps with different amplitudes over a wide energy range, an arbitrary multiplicative energy-loss dependent factor (4.5 (ΔE)^1/2) was applied to each map, which preserved the original intensity trend before scaling (SI). Notice that the strongly coupled symmetric/antisymmetric modes reveal a large intensity variation along the antenna. This spatial distribution clearly reveals a dipole-like configuration with the stronger signal near the ends of the double-antenna and a weaker signal in the middle, in agreement with the measurements obtained in vacuum (Figure 3A). The slight asymmetry between the maximum scattering intensities might be due to thickness variations of the structure. Interestingly, the maps of the strongly coupled modes share a lot of similarities in EELS scattering distribution along the antenna, but subtle scattering variations across the interfaces can be noticed in the regions of stronger intensity. The strongly coupled mode maps within the silica were obtained by subtracting the purely bulk contribution of the silica (see description in SI).

EELS maps for two multipolar SPP modes (296 and 444 meV) of the Al antenna show distinctive patterns that exhibit a signal intensity decrease as the probe moves farther away from the plasmonic structure, pointing out the evanescent character of the plasmonic fields. Also, we generated a map for a SPhP mode of the SiC support, which shows an increase of the electron scattering near the SiC/SiO₂ interface (horizontal dotted line) and the formation of a dipole-like pattern along that interface. For the 3.1 μm long hybrid antennas, our results showed that the suspended double-antenna minimizes the interaction of the strongly coupled modes with the SiC support. Nevertheless, simulations including triple-antenna

Figure 3. Mapping of strongly coupled plasmon-phonon modes in hybrid antennas. (A) Scattering intensity modulation of plasmon—phonon modes (∼130 and 156 meV) extracted from EELS spectra acquired in vacuum along antennas of 3.0 and 3.1 μm in length. Curves were shifted vertically for better visualization. (B) ADF STEM image indicates a region (90 × 3100 nm) of the antenna probed by the electron beam. The image was elongated in the vertical direction for better visualization. The SiC support appears at the bottom of the image. The arrow indicates the position in Figure 4. (C) Experimental two-dimensional EELS scattering maps showing the spatial distribution of plasmon-phonon modes, surface plasmon polariton modes and a surface phonon polariton mode. The white dotted line indicates the SiC/SiO₂ interface. Black horizontal lines located on the map sides indicate interfaces between materials. The color scale in (C) indicates the normalized scattering intensity in arbitrary units.
systems (Al/SiO2/SiC) indicate that coupling between Al and SiC antennas can occur for longer antennas (Figure S6) and point out that these hybrid platforms can be built to explore interactions between strongly coupled modes and other type of polaritons.

We also investigated locally the response of the strongly coupled modes by performing spatially resolved EELS studies across the hybrid double-antenna. An overview of the polaritonic response when probing each layer of the hybrid system is presented in Figure S7. Figure 4 shows several spectra acquired across interfaces, an ADF STEM image of the region under analysis, and the cross-section views of the surface charge configuration of each coupled mode. The two-peak resonances (130 and 156 meV) can be easily distinguished in the Al and SiC regions (black curves), but a drastic spectral modification is visible in the SiO2 region (gray curves), which manifests as an apparent shift of the antisymmetric mode toward lower energy. These variations occur within short distances (<10 nm) across the interfaces, thus, providing vital spatial information which is not accessible with traditional optical techniques. This variation is mainly due to a decrease of the antisymmetric surface scattering and an increase of the bulk SiO2 vibrational contributions (~148 meV), and it illustrates the power of the technique to probe both vibrational surface and bulk modes in solids. A comparison of the scattering intensity associated with the strongly coupled modes (Figure S8) reveals a variation of the antisymmetric mode near the Al/SiO2 interface (~10 nm), forming a small dip-like feature, which is not present for the symmetric mode. This finding gives support to the hypothesis of the formation of a dipole-like charge configuration (antisymmetric mode) across the Al/SiO2, in contrast to the symmetric mode that displays a uniform charge distribution.

In summary, we designed and built a hybrid double-antenna platform using low-cost materials to reveal the key role played by spatial boundary constraints driving specific strong-coupling behavior. EELS investigations reveal strongly coupled modes behavior with high-spatial sensitivity and show the spatial distribution of strongly coupled modes in hybrid nanosystems. EELS maps reveal the richness of IR polaritonic modes storing electromagnetic energy within subwavelength ranges in the hybrid antenna. These results extend our physical understanding of LDOS of strongly coupled states. Specifically, it brings insights into how electromagnetic energy could be distributed through the nanoscale photonic structure during an energy exchange process (e.g., Rabi oscillation). Our results should motivate further studies to derive temporal information from EELS data to study dynamics of hybrid modes with...
The experimental data was obtained using a Nion-Ultra Scanning Transmission Electron Microscope (STEM) equipped with a monochromator operated at 60 kV. The EELS spectroscopy work was performed using a probe of 30 mrad convergence semiangle at a resolution of 10 meV, producing a probe size of about 1.5 Å. The collection semiangle is 20 mrad. The STEM imaging work was also conducted using an electron beam with convergence semiangle of 30 mrad. The transmitted scattered electrons were collected to form annular dark-field (ADF) images, using an annular detector with inner/outer collection angles of 80 and 200 mrad, respectively. Theoretical simulations were conducted to evaluate the polaritonic response of infinite hybrid antennas induced by a swift electron using the boundary element method. Further details regarding the experimental and simulation parameters are presented in the Supporting Information.

**Author Contributions**

M.J.L. conceived the ideas, designed the infrared double-antennas, performed the EELS experiments, and analyzed the results. P.E.B. and M.J.L. advised on the results analysis and interpretation. Z.L. assisted on the EELS map processing. U.H. performed theoretical calculations. M.J.L. wrote the paper with input from all the authors. All the authors read and commented on the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

M.J.L. acknowledges the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC) under a Discovery Grant. P.E.B. acknowledges the financial support of the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award #DE-SC0005132. The authors also thank G. A. Botton for discussions regarding infrared plasmons; V. Amarasinghe, L. C. Feldman, and A. Knights for providing samples; and H. Yang, I. Bicket, and A. Trigler for providing support on some experiments and simulations. We also thank the Canadian Centre for Electron Microscopy (CCEM) for providing assistance with the fabrication of hybrid double-antennas.

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