

Article

Photonic–Chemical Coupling in Confined Catalytic Nanocavities for Selective Energy Conversion

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Abstract

Selective energy conversion in confined catalytic nanocavities is examined through a coupled reactive–photonic framework. The practical target is a combustor-integrated selective emitter for thermophotovoltaic (TPV) conversion and cascaded thermoelectric (TEG) recovery, in which Pt-coated anodic porous alumina (APA) functions simultaneously as a catalytic reactor, a cavity-modified electromagnetic environment and a heat-routing structure. Visible/near-infrared spectra (380–780 nm) show that Pt-coated APA exhibits a substantially stronger non-grey red-edge depression than a smooth zirconia reference. This observation establishes a spectral contrast in the measured window but is not used to identify an experimental cutoff wavelength, because a finite, open, lossy and array-coupled pore does not exhibit the abrupt edge predicted for an ideal cylindrical waveguide. For the mid-infrared, analytical scaling shows that the principal H₂O and CO₂ bands at 2.7, 4.3, 6.3 and 15.0 μm all lie deep in the evanescent regime relative to the ideal TE₁₁ cutoff wavelength $\lambda_c \approx 0.513 \mu\text{m}$ for a 300 nm pore. A converged finite-difference time-domain benchmark at the CO₂ 4.3 μm band yields a source-local Purcell factor $F_p \approx 0.38$, indicating suppression of the total local density of optical states, while aperture flux is more than six orders of magnitude smaller than the near-field power budget. The specific contribution is therefore not the established fact of below-cutoff attenuation, but the co-design and separate quantification of a catalytic nanocavity as a reactive compartment, photonic environment and energy-branching element. The results provide a bounded mechanistic basis for combustor-integrated TPV and hybrid TPV/TEG architectures.

Keywords: confined combustion; anodic porous alumina; nanocavities; photonic–chemical coupling; selective energy conversion; thermophotovoltaics; thermoelectrics



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1. Introduction

Portable and distributed power systems continue to motivate interest in small-scale combustion because liquid and gaseous fuels remain high-energy-density carriers. Fernandez-Pello identified heat loss, flame stabilisation and system integration as central constraints for combustion-based micropower generation [1]. The immediate application considered here is a combustor-integrated selective emitter for TPV conversion with cascaded TEG recovery, so that reaction, spectral control and heat recovery are treated within one architecture.

Ju and Maruta reviewed the scaling laws, quenching phenomena and stabilisation strategies that govern microscale combustion [2]. Maruta analysed ignition, extinction and

flame dynamics across micro- and mesoscales [3]. Ahn et al. experimentally compared gas-phase and catalytic combustion in heat-recirculating burners [4]. These studies establish the thermal and chemical challenges of miniaturised combustion, but they do not treat the combustor wall as an electromagnetic mode-selection element.

A complementary literature shows how subwavelength structures can control thermal radiation. Li and Fan described the use of nanophotonics to tailor thermal spectra for energy applications [5]. Baranov et al. reviewed the design principles of far-field thermal emitters [6]. Zhang et al. surveyed recent methods for controlling the coherence, directionality and polarisation of thermal radiation [7]. Sakakibara et al. examined the practical constraints that selective emitters must satisfy in thermophotovoltaic systems [8]. The present proposition is to bring this spectral-selection function inside the catalytic combustor rather than adding a separate emitter or filter.

The Pt-coated APA platform is distinctive because the confinement length scale is submicrometric while the pores remain high aspect ratio. The wall is therefore not only a catalyst support and thermal boundary; it also sets the electromagnetic boundary conditions experienced by emitting products. Bykov first formulated spontaneous-emission modification in periodic structures [9]. Yablonovitch demonstrated inhibited spontaneous emission in a photonic environment [10], while John established photon localisation in structured dielectrics [11]. Chang and Campillo systematised microcavity optical processes [12], and Qian et al. later reviewed spontaneous-emission control in micro- and nanophotonic structures [13]. In this manuscript, “geometric LDOS control” denotes this boundary-condition-driven modification of available optical channels without invoking vibrational strong coupling or an ideal photonic band gap.

Biological Inspiration: Active Compartments as Selective Energy Routers

Biological systems are used here as a design analogy rather than as evidence for the combustion mechanism. Mitchell’s chemiosmotic framework showed how membrane-defined gradients direct energy conversion [14]. Bar-Peled and Kory described metabolic compartmentalisation as a means of separating reactions and controlling transport [15]. Flori et al. demonstrated that thylakoid architecture can optimise photosynthetic function [16]. Together, these examples motivate treating geometry as an active variable in energy routing.

The firefly lantern provides a more direct example of co-located chemistry, mass transfer and optics. Trimmer et al. identified nitric-oxide-mediated control of flashing through oxygen delivery [17]. Kim et al. translated firefly cuticular nanostructures into a bioinspired light-extraction lens [18], and Bay et al. quantified improved optical extraction in a Photuris lantern [19]. More broadly, Yao et al. reviewed how bioinspired photonic architectures can meet complex spectral requirements in thermal management [20].

The engineering implication is methodological: the catalytic pore should be considered as an active compartment that co-locates reaction, wall interaction and optical boundary conditions. This analogy is retained in a concise form because it motivates the integrated architecture, but the quantitative claims of the manuscript rest on the measured spectra, analytical cutoff scaling and electromagnetic modelling.

Within this scope, the experimental visible/NIR spectra establish that Pt-coated APA and smooth zirconia do not follow the same grey-body trend. They do not, by themselves, locate a waveguide cutoff or identify a unique absorption mechanism. The mid-infrared propagation regime is therefore treated separately through idealised cutoff scaling across the principal H₂O and CO₂ bands and through a converged FDTD benchmark at 4.3 μm .

The wider interpretation is consistent with modern studies of chemistry under confinement. Grommet et al. reviewed how nanoconfinement can alter concentrations, adsorp-

tion, transport and reaction selectivity [21]. Dong et al. resolved confinement-dependent molecular orientation and intermediates at the single-molecule level [22]. McCormack et al. surveyed phase, flow and reactivity changes in nanoconfined fluids [23]. Wang et al. demonstrated accelerated water formation under interfacial confinement [24]. Roelli et al. clarified the competing radiative, absorptive and quenching channels of molecular nanocavities [25], while Garner et al. showed theoretically that resonant cavity coupling can modify hydrogen-tunnelling dynamics [26]. Those last studies concern resonant molecular-cavity regimes; the present APA platform instead addresses an open, lossy, geometrically below-cutoff regime.

2. Nanocavity Interaction and Redistribution of Rovibrational Emission

2.1. Theoretical Framework

The core physical claim of this paper is that nanocavities modify not only the local temperature field but also the radiative phase space available to excited combustion products. A photonic–chemical coupling framework is therefore adopted: nanocavities modify the local photonic density of states (LDOS), which in turn changes the branching between radiative decay, wall-assisted quenching, phonon generation and surface-mediated chemical relaxation.

The spectral energy density of a cavity mode is related to the LDOS through:

$$S(\omega, T) = \rho(\omega) W(\omega, T), \quad (1)$$

where $\rho(\omega)$ is the local photonic density of states at the emitter position and $W(\omega, T)$ is the Planck mean energy per mode:

$$W(\omega, T) = \frac{\hbar\omega}{\exp(\hbar\omega/k_B T) - 1}. \quad (2)$$

The corresponding free-space spectral power per unit volume is:

$$S_p(\omega, T) = \rho_v(\omega) V W(\omega, T), \quad \rho_v(\omega) = \frac{\omega^2}{\pi^2 c^3}, \quad (3)$$

where $\rho_v(\omega)$ is the free-space modal density per unit volume.

$$G(\omega, T) = \frac{S(\omega, T)}{S_p(\omega, T)} \quad (4)$$

The ratio measures the cavity-induced modification: $G < 1$ denotes inhibited radiative output and $G > 1$ denotes enhancement.

The geometric requirement for strong modification is that the pore diameter be of the same order as the wavelength inside the medium, $d \sim \lambda/n$, while the cavity remains high aspect ratio ($h/d \gg 1$), so that the pore behaves as a reflective quasi-waveguide rather than as a shallow rough surface [12].

The cavity-modified radiative decay rate is given by:

$$k_{\text{rad}}^{\text{cav}}(\omega) = F_p(\omega) k_{\text{rad}}^0(\omega), \quad (5)$$

following the formalism of Purcell (1946) [27], where $F_p(\omega)$ is the Purcell factor quantifying cavity-induced LDOS modification. The total decay rate is:

$$k_{\text{tot}} = k_{\text{rad}}^{\text{cav}} + k_{\text{wall}} + k_{\text{nr}} + k_{\text{chem}}, \quad (6)$$

where k_{wall} collects wall-assisted absorption and quenching processes, k_{nr} is non-radiative molecular relaxation, and k_{chem} is chemically coupled dissipation or reactivity-assisted relaxation at the catalytic interface. The radiative branching fraction is therefore:

$$\Phi_{\text{rad}}(\omega) = \frac{k_{\text{rad}}^{\text{cav}}(\omega)}{k_{\text{tot}}}. \quad (7)$$

The key distinction in the present framework is between total LDOS and free-space escape. The source-local total LDOS, and hence the Purcell factor F_p , can be either enhanced or suppressed relative to free space depending on the balance between wall-coupled (evanescent, surface and absorptive) channels and the cutoff-limited radiative continuum (Equations (5)–(7)); in the deeply below-cutoff lossy pore considered here it is suppressed. Independently of the sign of the total-LDOS modification, the operationally relevant quantity for energy conversion is the fraction of power that escapes into free space: the cavity redirects most of the emitted energy into wall-coupled channels rather than into aperture escape.

2.2. Idealised Cutoff and the Finite-Pore Response

For a perfectly conducting circular waveguide, the first characteristic wavelengths follow from the zeros of the Bessel functions [12]. The commonly used approximations are $\lambda_{\parallel} \approx 1.31D$ and $\lambda_{\perp} \equiv \lambda_{\perp} \approx 1.71D$, where D is the internal diameter and λ_c is the TE_{11} cutoff wavelength. For $D = 300$ nm, $\lambda_c \approx 513$ nm; for $D = 400$ nm, $\lambda_c \approx 684$ nm. These values are ideal modal references. Table 1 shows the idealised cylindrical-waveguide parameters for the two nanocavity geometries. They are not predictions of an abrupt experimental edge in a finite, open, rough, lossy and array-coupled pore.

Table 1. Idealised cylindrical-waveguide parameters for the two nanocavity geometries.

Platform	D (nm)	$\lambda_{\parallel} \approx 1.31D$ (nm)	$\lambda_{\perp} \approx 1.71D$ (nm)	Interpretation
Metallic cavity array	400	524	684	Ideal TE_{11} cutoff reference at 684 nm; the 2–15 μm molecular bands are in the deep-evanescent regime.
Pt-coated APA pore	300	393	513	Ideal TE_{11} cutoff reference at 513 nm; this value is not an onset prediction for the finite Pt-coated array.

Note: The values in this table are modal references for an ideal circular guide. They describe the propagation condition but do not predict the onset of the measured vis/NIR deviation.

For wavelengths longer than λ_c , the axial propagation constant becomes imaginary and the ideal modal field decays as $\exp(-\alpha z)$, where α is given by Equation (8). Table 2 evaluates the dimensionless detuning and decay parameter for the principal combustion-product bands identified in molecular spectroscopy [28]. All four bands lie far beyond cutoff, with λ/λ_c ranging from 5.3 to 29.2 and $\alpha L \approx 240$ –245 for a 20 μm pore. Thus, the entire 2.7–15 μm set belongs to the same deep-evanescent propagation regime, although realistic LDOS and loss partitioning can still vary with wavelength, source position and material dispersion.

Table 2. Idealised multi-band cutoff scaling for a $D = 300$ nm, $L = 20$ μm pore ($\lambda_c = 0.513$ μm).

λ (μm)	Principal Molecular Relevance	λ/λ_c	αL	Modal Implication
2.7	H ₂ O/CO ₂ stretching region	5.26	240.5	Deep evanescent regime
4.3	CO ₂ asymmetric-stretch band	8.38	243.2	Deep evanescent regime; converged FDTD benchmark
6.3	H ₂ O bending band	12.28	244.1	Deep evanescent regime
15.0	CO ₂ bending band	29.24	244.8	Deep evanescent regime

The decay parameter αL is calculated from Equation (8). It is used only to classify the ideal axial propagation regime; the realistic open-cavity LDOS and aperture flux are assessed separately by FDTD.

$$\alpha(\lambda) = [(2\pi/\lambda_c)^2 - (2\pi/\lambda)^2]^{\frac{1}{2}}, \quad \lambda > \lambda_c. \quad (8)$$

The approximately 650–680 nm separation between the measured Pt-coated APA spectrum and its grey-body fit should therefore not be equated with the ideal 513 nm cutoff. Finite pore length, diameter dispersion, wall roughness, Pt absorption, aperture coupling, array interactions and temperature-dependent emissivity can broaden or shift the spectral response. Figure 2 is used only to establish non-grey behaviour in the measured window; it is not presented as an experimental validation of a 513 nm cutoff.

2.3. Engineering Relevance

For a downstream TPV cell, the relevant radiative quantity is the power that leaves the pore and reaches the converter. For a TEG stage, the relevant quantity is the heat delivered to the surrounding solid. A reduced aperture channel does not by itself prove that all non-escaping power becomes useful heat; it indicates that the source couples predominantly to non-aperture channels, including lossy wall and near-field channels. This distinction motivates, rather than presupposes, a hybrid TPV/TEG architecture.

Figure 1 summarises the proposed branching concept. Shorter-wave channels that are supported by the finite structure may outcouple, whereas long-wave rovibrational channels lie in a deep-evanescent axial regime. The proposed engineering objective is to co-design the pore geometry, catalytic interface and downstream converters so that radiative and wall-coupled outputs are both used productively.

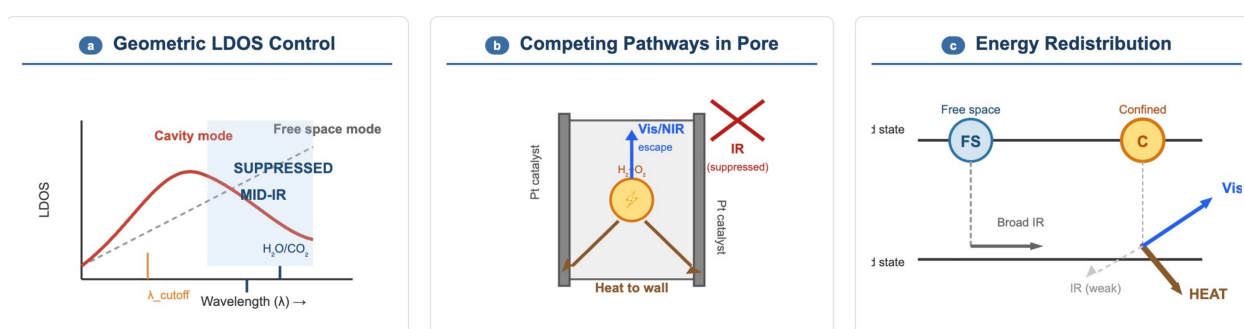


Figure 1. Photonic–chemical coupling concept. (a) Cavity geometry modifies the available optical channels. (b) Within a pore, long-wave axial escape is restricted while wall-coupled channels remain available. (c) The proposed architecture routes radiative output toward TPV conversion and wall-coupled heat toward TEG recovery.

3. Experimental Basis and Quantitative Indicators

3.1. Experimental Platform

3.1.1. APA Substrate Preparation

Self-ordered anodic porous alumina (APA) substrates were prepared by two-step anodisation of electropolished aluminium foils (99.999% purity, Goodfellow, Huntingdon, UK) in 0.3 M oxalic acid at 40 V and 5 °C. The first anodisation step (12 h) was followed by selective removal of the resulting oxide layer in a 1.8 wt% CrO₃ + 6 wt% H₃PO₄ solution at 60 °C. The second anodisation step (4 h under identical conditions) produced ordered pore arrays with nominal diameter $D \approx 300$ nm and interpore spacing $a \approx 430$ nm. Pore depth was controlled to ≈ 20 μ m by anodisation time; depth uniformity was verified by cross-sectional scanning electron microscopy. The preparation route follows established APA processing principles previously used by the authors [29].

Ion-beam-defined metallic cavity arrays with nominal diameter $D \approx 400$ nm and depth ≈ 20 μ m were fabricated by focused ion beam (FIB) milling of gold-coated silicon substrates (FEI Strata DB235, 30 kV Ga⁺ beam, beam current 1–10 nA). The metallic reference-cavity route follows the subwavelength fabrication approach reported by Pullini et al. [30].

3.1.2. Pt Coating by Electroless Deposition

Platinum coating was deposited conformally onto the APA pore walls by electroless deposition. Substrates were sensitised with SnCl₂ (0.1 g L^{−1}, Sigma-Aldrich, $\geq 98\%$) in 0.1 M HCl for 5 min, rinsed in deionised water, then activated with PdCl₂ (0.01 g L^{−1}, Sigma-Aldrich, $\geq 99.9\%$) in 0.1 M HCl for 5 min. Pt deposition was carried out in an aqueous bath containing H₂PtCl₆ (0.5 g L^{−1}, Sigma-Aldrich, $\geq 37.5\%$ Pt basis), dimethylamineborane (DMAB, 1.5 g L^{−1}, Sigma-Aldrich, 97%) as reducing agent, and Na₂SO₄ (10 g L^{−1}) as stabiliser, at pH 9 (adjusted with NaOH) and 70 °C for 30 min. Target coating thickness was $t_{\text{pt}} \approx 50$ nm, confirmed by transmission electron microscopy cross-sections. A microwave-assisted annealing step was performed in a CEM Discover SP microwave reactor (CEM Corporation, Matthews, NC, USA; maximum power 300 W, single-mode cavity, 10 mL vessel capacity) at 150 °C for 10 min to improve coating adhesion and crystallinity.

3.1.3. Visible/NIR Spectral Characterisation

Spectral radiance measurements were performed using a fibre-coupled spectrometer (Ocean Optics USB4000, wavelength range 350–1000 nm, 3648 CCD pixels) coupled to an integrating sphere (Labsphere 6-inch, Spectralon interior coating, reflectance $> 98\%$ from 350 to 2500 nm). Samples were mounted on a temperature-controlled stage and brought to thermal equilibrium at $T = (1000 \pm 5)$ °C as measured by a type-K thermocouple embedded in the substrate holder. Spectra were acquired with 100 ms integration time, 10-scan average, and corrected for dark counts and instrument response. Grey-body fits were performed by least-squares minimisation of $|S_{\text{exp}}(\lambda) - \epsilon \cdot B(\lambda, T)|^2$, where $B(\lambda, T)$ is the Planck spectral radiance and ϵ is the fitted emissivity.

The structural parameters from the APA platform ($D \approx 300$ nm, interpore spacing $a \approx 430$ nm, depth ≈ 20 μ m) directly define the representative geometry used in the FDTD simulations of Section 4. Figure 3 shows representative SEM images of the two experimental nanocavity platforms: (a) ion-beam-defined metallic cavity arrays ($D \approx 400$ nm, depth ≈ 20 μ m) and (b) self-ordered APA pores ($D \approx 300$ nm, interpore spacing ≈ 430 nm).

Figure 2 shows that the smooth zirconia reference remains comparatively close to its fitted grey-body trend, whereas Pt-coated APA develops a pronounced negative red-edge deviation. The contrast establishes non-grey radiative behaviour of the Pt-coated structured sample within 380–780 nm. It does not, however, identify a unique electromagnetic mechanism or locate the ideal waveguide cutoff.

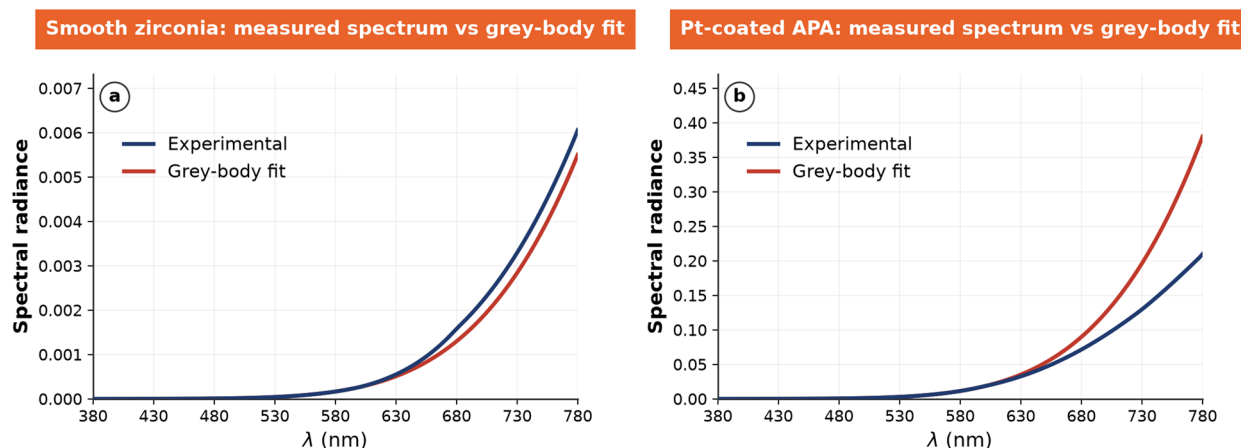


Figure 2. Experimental visible/NIR spectral comparison against grey-body fits. (a) Smooth zirconia reference. (b) Pt-coated APA nanocavity sample. The different red-edge trends establish a measurable spectral contrast; the approximately 650–680 nm separation point is not interpreted as the ideal TE_{11} cutoff.

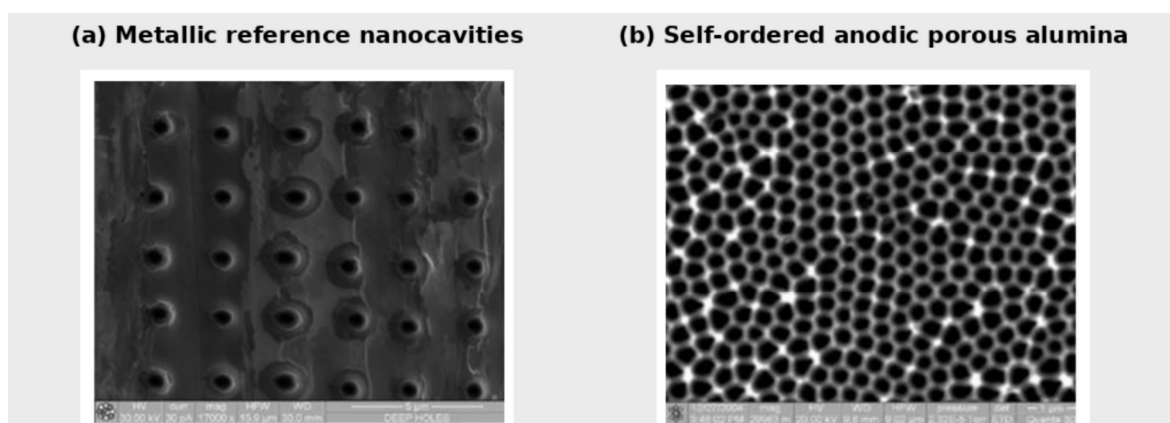


Figure 3. Experimental nanocavity platforms. (a) Ion-beam-defined metallic cavity arrays, $D \approx 400$ nm and depth ≈ 20 μm . (b) Self-ordered anodic porous alumina, $D \approx 300$ nm and interpore spacing ≈ 430 nm.

The experimental archive therefore supplies two inputs to the present analysis: a measurable non-grey contrast in the vis/NIR window and the structural dimensions used in the electromagnetic model. The mid-infrared mechanism is evaluated independently through Table 2 and the FDTD benchmark of Section 4.

3.2. Approximate Quantitative Indicators from Visible/NIR Spectra

Approximate indicators were extracted by digitising the curves in Figure 2 and reported in Table 3. They quantify the relative red-edge departure of the two samples without assigning that departure to a specific cutoff, absorption or catalytic-heating mechanism.

These indicators quantify the stronger non-grey response of Pt-coated APA relative to zirconia. They neither prove suppression in the unmeasured 2–15 μm band nor establish that the 650–680 nm separation point is a cutoff wavelength.

Table 3. Approximate figure-derived indicators extracted from the experimental spectra.

Sample	Pointwise Deviation in Measured Window	Integrated 680–780 nm Radiance/Grey-Body Fit	Crossover Behaviour	Interpretation
Smooth zirconia	+25% at 680 nm, +17% at 730 nm, +9% at 780 nm	≈ 1.15	No strong inversion relative to fit in the red tail	Reference remains comparatively close to grey-body behaviour within the experimental window.
Pt-coated APA	−15% at 660 nm, −34% at 730 nm, −45% at 780 nm	≈ 0.67	Experimental and fitted curves approach near 660–680 nm, then diverge strongly	Pt-coated APA exhibits the stronger non-grey red-edge depression; this spectrum alone does not identify the underlying mechanism.

3.3. Scope of the Present Evidence

The present evidence combines preserved vis/NIR spectra, structural information, analytical multi-band cutoff scaling and a converged mid-infrared electromagnetic benchmark. The four components are intentionally kept distinct: the spectra establish sample-to-sample contrast, the geometry fixes the model, Table 2 classifies the molecular bands as deeply evanescent in the ideal guide, and FDTD evaluates source-local LDOS and aperture escape for one representative band.

4. Targeted FDTD Assessment of Mid-Infrared Radiative-Channel Redistribution

4.1. Relationship Between the Measured Spectrum, Multi-Band Scaling and FDTD

The visible/NIR data establish a non-grey spectral contrast but do not identify the ideal cutoff. Table 2 separately shows that the principal 2.7, 4.3, 6.3 and 15.0 μm molecular bands all occupy the same deep-evanescent axial regime for the representative 300 nm pore. The role of FDTD is then narrower and more specific: it tests how a realistic lossy pore modifies the source-local LDOS and partitions power between the near-field budget and the aperture channel.

Although FDTD is a time-domain method capable of broadband excitation, the present calculation is performed as a set of single-frequency evaluations. The 4.3 μm CO₂ band is used as the physically representative benchmark within the deep-cutoff set, and the calculation is repeated at the other computed bands (2.7 and 6.3 μm) to confirm the trend across the deep-cutoff set. Generality across the molecular bands is supported both by the dimensionless analytical scaling in Table 2, which spans the full 2.7–15.0 μm set, and by these single-frequency benchmarks.

4.2. Model Assumptions and Numerical Setup

A single cylindrical pore is simulated in cylindrical symmetry using the open-source MEEP FDTD solver [31], with the benchmark evaluated at a single azimuthal order, $m = -1$. This choice is dictated by the source symmetry: a radially polarised dipole projects negligibly onto the $m = 0$ azimuthal channel, so that an $m = 0$ evaluation yields a near-vanishing and ill-conditioned vacuum LDOS in the denominator of F_p , whereas the $m = -1$ channel carries the dominant radial-dipole coupling and provides a positive, well-conditioned vacuum reference. The cavity is embedded in an Al₂O₃ matrix with refractive index $n = 1.63$ and lined by a conformal Pt coating of thickness $t_{\text{pt}} = 50$ nm. The representative benchmark

geometry uses nominal pore diameter $D = 300$ nm, cavity depth $L = 20$ μm , and lattice pitch $a = 430$ nm, consistent with the structural scale of the experimental APA platform. The effective free cavity diameter is $D_{\text{eff}} = D - 2 t_{\text{Pt}} = 200$ nm.

Platinum is described by a Drude dielectric function ($\omega_p = 9.59$ eV, $\gamma = 0.048$ eV), using optical-constant data and Drude-Lorentz parameters reported for metallic films [32]. The source is a radially polarised point dipole placed at the cavity mid-plane at a radial distance of approximately 50 nm from the Pt wall. In the cylindrical MEEP simulation, a radially polarised dipole—i.e., an oscillating current oriented along the radial (ρ) direction—represents the emission geometry of a molecule located near the Pt wall and radiating toward the cavity axis; this is distinct from the linear polarisation of a free-space Hertzian dipole. The 50 nm radial distance represents a molecule adsorbed on or near the Pt catalytic surface—a representative near-wall source location for probing coupling to the Pt boundary.

At the benchmark wavelength, the LDOS is quantified through $F_p = \text{LDOS}_{\text{cav}}/\text{LDOS}_{\text{vac}}$ (Equation (5)), a source-local quantity evaluated at the dipole position rather than a spatial average. The same dipole is simulated in the cavity and in vacuum using identical excitation, domain and stopping criteria, so that the ratio is free of source-normalisation bias. A closed-box monitor surrounding the source records the local power budget, including radiative and evanescent contributions, while an aperture monitor is placed at the pore exit. No far-field projection is used; consequently, $P_{\text{box}}/P_{\text{aperture}}$ is interpreted as an aperture-escape ratio relative to the near-field source budget, not as a direct far-field intensity ratio.

The calculation was performed for $D = 300$ nm at three of the four principal molecular bands (2.7, 4.3 and 6.3 μm , spanning $\lambda/\lambda_c \approx 5.3$ –12.3), each as a single-frequency evaluation carried to full temporal convergence of the source-local response (field-decay threshold 10^{-6}), at a spatial resolution of 300 px/ μm with complex fields and epsilon averaging. Each cavity evaluation is paired with a matched vacuum evaluation under identical conditions. The multi-band scope of the propagation argument is provided analytically in Table 2 across all four bands and confirmed by the FDTD benchmarks at these three wavelengths.

4.3. Benchmark Results

The source-local benchmark for the representative Pt-coated cavity provides the following results:

- At the 4.3 μm CO₂ band the LDOS-based Purcell factor is $F_p \approx 0.38$, i.e., the source-local total LDOS is suppressed (to ≈ 0.38 of the vacuum value) rather than enhanced. The vacuum reference LDOS is positive and well-conditioned, and the value is robust to spatial resolution and to the perfectly matched layer padding at the percent level.
- The same suppression is found across the computed bands: F_p remains below unity throughout 2.7–6.3 μm and rises monotonically with wavelength ($F_p \approx 0.17, 0.38$ and 0.73 at 2.7, 4.3 and 6.3 μm ; Table 4), consistent with a deeply below-cutoff pore in which the radiative continuum is suppressed while non-radiative wall channels dominate.
- The box-integrated power exceeds the aperture signal by six to nearly nine orders of magnitude across the computed band ($P_{\text{box}}/P_{\text{aperture}} \approx 6.6 \times 10^6$ at 2.7 μm rising to $\approx 9.7 \times 10^8$ at 6.3 μm), the confinement strengthening as the band moves deeper below cutoff. Because the box monitor lies in the near field, this ratio demonstrates restricted aperture escape relative to the local power budget; it is not equated with a far-field suppression factor or a direct calorimetric measurement of wall heating.

Table 4. Single-frequency FDTD source-local results across the computed molecular bands (2.7, 4.3 and 6.3 μm ; Pt-coated cavity, $D = 300\text{ nm}$, $L = 20\text{ }\mu\text{m}$, $t_{\text{pt}} = 50\text{ nm}$, azimuthal order $m = -1$, resolution $300\text{ px}/\mu\text{m}$).

λ (μm)	Purcell Factor F_p ($\text{LDOS}_{\text{cav}}/\text{LDOS}_{\text{vac}}$)	Ratio $P_{\text{box}}/P_{\text{aperture}}$	Interpretation
2.7	0.17	6.6×10^6	LDOS suppressed; aperture escape $\ll$ near-field budget
4.3	0.38	1.4×10^8	LDOS suppressed; representative CO_2 benchmark
6.3	0.73	9.7×10^8	Deep-evanescent regime; suppression weakening toward unity

The Purcell factor is the source-local LDOS ratio at the dipole position; the vacuum LDOS is obtained from a matched vacuum evaluation. The box monitor is in the near field, so $P_{\text{box}}/P_{\text{aperture}}$ is an aperture-escape ratio relative to the local source-power budget, not a far-field radiation ratio. The $15.0\text{ }\mu\text{m}$ band is classified analytically in Table 2 and is not evaluated by FDTD here.

Figure 4 presents the source-local Purcell factor and the aperture-escape ratio across the computed molecular bands. Panel (a) shows the LDOS-based Purcell factor $F_p < 1$ across 2.7–6.3 μm . Panel (b) compares the near-field box-integrated power with the aperture escape on a logarithmic scale.

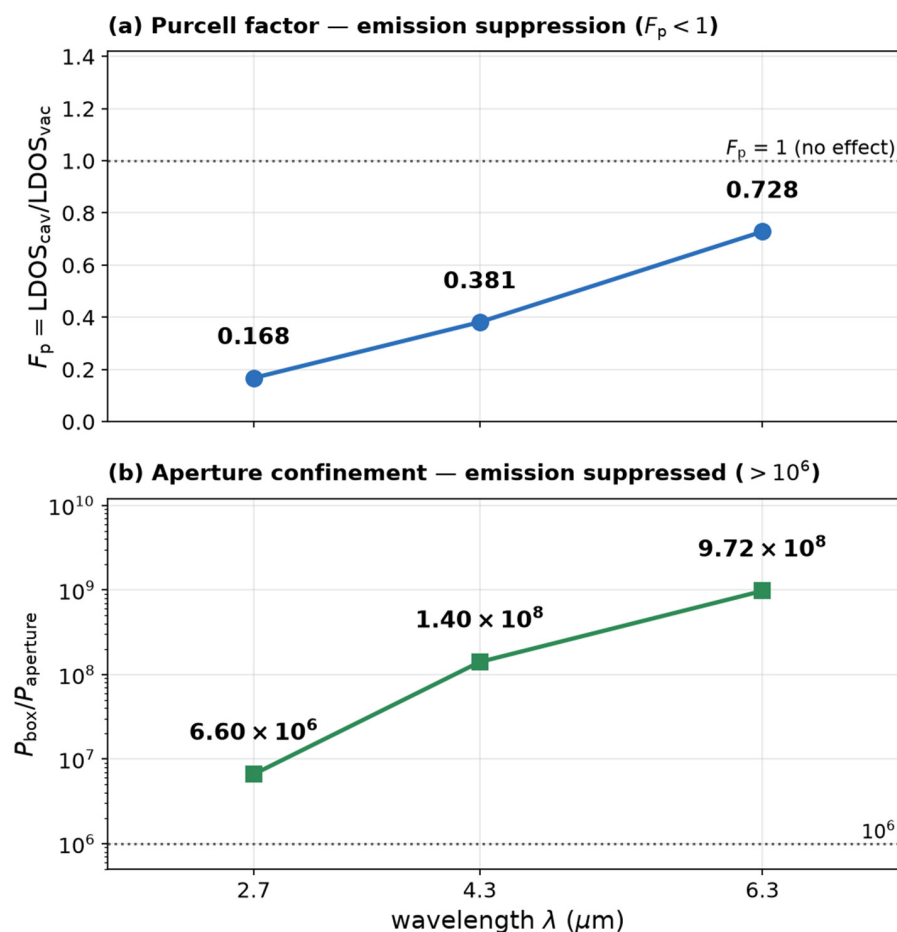


Figure 4. FDTD source-local benchmark across the computed molecular bands (2.7, 4.3 and 6.3 μm) for the representative Pt-coated nanocavity ($D = 300\text{ nm}$). (a) Source-local LDOS-based Purcell factor as a function of wavelength, showing suppression ($F_p < 1$) throughout the 2.7–6.3 μm set. (b) Aperture-escape ratio $P_{\text{box}}/P_{\text{aperture}}$ —the near-field box-integrated power divided by the power crossing the pore aperture—as a function of wavelength on a logarithmic scale. The ratio exceeds 10^6 across the whole computed band and increases with wavelength (6.6×10^6 at 2.7 μm to 9.7×10^8 at 6.3 μm), indicating progressively stronger aperture confinement deeper below cutoff. Because the box monitor lies in the near field, this is an aperture-escape ratio relative to the local source-power budget, not a far-field projection.

4.4. Interpretation and Spectral Generality

The analytical and numerical results answer different questions. Equation (8) and Table 2 show that all four molecular bands lie deep beyond the ideal TE₁₁ cutoff, so the 4.3 μm benchmark is not an isolated near-threshold case. The FDTD result then shows that a realistic open metallic pore suppresses the source-local total LDOS ($F_p < 1$) while the aperture channel remains weaker still, so that the emitted energy is redirected into wall-coupled channels rather than escaping into free space.

The mechanism is therefore a strong restriction of free-space escape accompanied by suppression of the total source-local LDOS, consistent with the deep-evanescent, lossy regime. The present monitor configuration supports the statement that suppressed total source-local LDOS coexists with even more strongly restricted aperture escape. It does not, by itself, quantify the fraction ultimately converted to lattice heat, which would require explicit absorption and thermal transport accounting.

4.5. Established Principle and Specific Contribution of This Work

Below-cutoff attenuation and dissipation in metallic waveguides are established principles and are not claimed here as new. Likewise, the microcombustion studies cited in Refs. [1–4] established heat loss, catalytic stabilisation and heat recirculation, but did not report source-local LDOS together with an independent aperture-flux diagnostic for a Pt-coated APA catalytic pore.

The specific contribution is the integrated framework: an experimentally grounded catalytic pore geometry is treated simultaneously as a reactive compartment, an electromagnetic environment and an energy-branching element; source-local LDOS and aperture escape are kept as distinct quantities; and their coexistence is connected to a dual-output TPV/TEG architecture. This reframing prevents the familiar cutoff-heating principle from being presented as the novelty and locates the contribution in the coupled catalytic-photonic system design and its diagnostic separation of channels.

The single-pore benchmark establishes this local mechanism. Array coupling, pore-size dispersion and far-field outcoupling may change the quantitative device response and remain appropriate subjects for future modelling, but they do not alter the bounded conclusion reported here: the selected geometry suppresses the source-local LDOS and strongly restricts aperture escape at 4.3 μm , while all principal molecular bands are analytically deep beyond cutoff.

5. Relevance for Selective Energy Conversion

The device context is supported by several distinct lines of prior work. Gentillon et al. experimentally characterised a porous-media combustion TPV system with controlled emissions [33]. Sakakibara et al. reviewed the materials and durability requirements of practical TPV emitters [8]. LaPotin et al. demonstrated TPV conversion efficiency above 40% at the cell level [34], while Chen et al. reviewed TPV technology for heat recovery [35]. Federici et al. integrated catalytic microcombustors with thermoelectric elements for portable power [36], and Ismail et al. examined porous-burner micro-cogeneration [37]. Wang et al. analysed a hybrid TPV/TEG heat-recovery configuration [38]. Against this background, the present work proposes that the catalytic nanocavity itself provides the first stage of spectral and thermal branching.

The 4.3 μm benchmark identifies a potentially useful regime rather than a completed device performance result: the source-local LDOS is suppressed while aperture escape is even more strongly restricted relative to the near-field power budget. The non-aperture channels include lossy wall and evanescent coupling, which motivates placing a TEG in thermal contact with the solid matrix, while any useful outcoupled radiation can be directed

to a TPV cell. Figure 5 illustrates this architecture without assigning an experimentally measured conversion efficiency to either branch.

Geometry-driven energy branching schematic

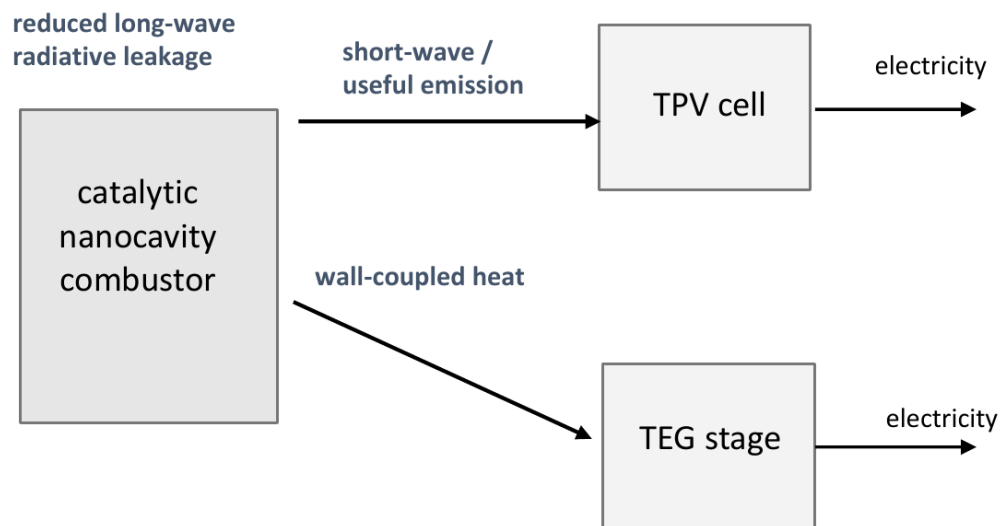


Figure 5. Geometry-driven energy-branching concept for hybrid TPV/TEG conversion. Restricted long-wave aperture escape motivates recovery of wall-coupled heat by a TEG, while useful outcoupled radiation is directed toward a TPV cell. The diagram is an architectural concept rather than a measured energy balance.

Table 5 provides an illustrative sensitivity calculation for an emitter temperature of 1700 K and a GaSb-like bandgap cutoff near 1.8 μm . The temperature and suppression levels are parametric assumptions selected to show the direction of the spectral effect; the table is not derived from the FDTD monitor ratio or from a device experiment.

Table 5. Illustrative TPV spectral-efficiency sensitivity for assumed long-wave suppression scenarios (parametric assumptions, not derived from FDTD or experiment; $T = 1700\text{ K}$, $\lambda_g \approx 1.8\text{ }\mu\text{m}$).

Assumed Suppression of 2–15 μm Radiative Escape	Relative TPV Spectral Efficiency vs. Baseline	η_{spec} for $\lambda_g \approx 1.8\text{ }\mu\text{m}$
0%	1.00	0.29
10%	1.15	0.33
30%	1.23	0.36
50%	1.34	0.39

6. Outlook and Future Validation Toward Selective Energy-Conversion Devices

The present framework opens four complementary directions for future validation and device development:

1. Full-spectrum characterisation—extending spectral acquisition into the 2–15 μm thermal band under controlled operating conditions;
2. Geometric parameter mapping—varying pore diameter, depth and Pt thickness to relate structure to spectral branching;
3. Coupled chemical and thermal diagnostics—correlating spectral behaviour with wall temperature, product composition, conversion, stability and repeatability;

4. Converter integration—coupling the nanocavity platform to TPV and TEG elements to establish device-level electrical outputs.

On the modelling side, multi-pore simulations, explicit absorption accounting and far-field projection can extend the present local benchmark to the full array and converter geometry. These studies would refine the quantitative design while preserving the present paper's central separation between measured vis/NIR contrast, ideal multi-band propagation scaling and the converged 4.3 μm source-local benchmark.

This outlook is presented as a forward research pathway rather than as an extension of the current dataset.

7. Conclusions

Pt-coated APA exhibits a substantially stronger non-grey red-edge depression than smooth zirconia in the measured 380–780 nm window. The revised interpretation deliberately does not identify the approximately 650–680 nm separation point with the ideal 513 nm TE_{11} cutoff. In a finite, open, lossy and array-coupled pore, the ideal cutoff is a modal reference rather than an abrupt experimental onset.

Analytical scaling shows that the principal H_2O and CO_2 bands at 2.7, 4.3, 6.3 and 15.0 μm all lie deeply beyond the ideal cutoff for a 300 nm pore. The converged 4.3 μm FDTD benchmark then demonstrates that the source-local total LDOS is suppressed ($F_p \approx 0.38$) while aperture power lies more than six orders of magnitude below the near-field box-integrated power. This ratio is interpreted as restricted aperture escape, not as a direct far-field or calorimetric measurement.

The established phenomenon of below-cutoff attenuation is not claimed as the novelty. The contribution is the integrated catalytic–photonic architecture and the explicit separation of source-local LDOS from aperture escape, which together motivate a combustor-integrated TPV/TEG energy-branching concept. Future full-spectrum, array-level and converter-coupled studies can develop this bounded mechanism into a quantitative device design.

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Acronyms

Acronym	Meaning
APA	Anodic Porous Alumina
FDTD	Finite-Difference Time-Domain
IR	Infrared
LDOS	Local Density of Optical States
NIR	Near-Infrared

PML	Perfectly Matched Layer
NO _x	Nitrogen Oxides
Pt	Platinum
RCWA	Rigorous Coupled-Wave Analysis
TEG	Thermoelectric Generator
TPV	Thermophotovoltaic
Vis/NIR	Visible/Near-Infrared

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