Supporting Information:
The 3D-nanoprinted anti-resonant hollow-core micro-gap waveguide - an on-chip platform for integrated photonic devices and sensors

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Contents

List of Figures .......................................................... S-2

List of Tables .......................................................... S-3

1 Simulation of Fabrication Inaccuracies ......................... S-4

2 Determining the Size of the Voxel from Waveguide Transmission Measurements .......... S-6

3 Analytical models ..................................................... S-7
   3.1 Fabry-Pérot model ............................................. S-7
   3.2 Leaky slab waveguide model ............................... S-10

4 Two-thickness Fabry-Pérot model ............................... S-16

5 Ammonia gas absorption measurement with micro-gap waveguides ................................. S-17

6 Fraction of modal power present inside the polymer wall ............................................. S-21

References ............................................................. S-22

List of Figures

S1 Numerical simulation of fabrication inaccuracies. ................. S-5
S2 Estimation of the transverse voxel size. .......................... S-7
S3 Sketch of the wavevector components and zig-zag length Z for the Fabry-Pérot model ........ S-9
S4 Geometry for the infinitely extended slab waveguide model. .......... S-11
S5 Sketch of the wavevector components for the leaky slab waveguide model. . . S-15
S6 Two-thickness Fabry-Pérot model. .................................... S-17
S7 Normalized transmission spectrum of waveguide used for the gas sensing experiment recorded in air. S-18
S8 Reference measurement of ammonia absorption without micro-gap waveguide. S-19
S9 Impact of small change in wall width on optical properties. S-22

List of Tables

S1 Coefficients of linear calibration curves for the ammonia absorbance measurements with and without waveguide. S-19
S2 Overview of the geometric parameters of the waveguides used in the dynamic experiments. S-20
Here, we report additional results from the simulations, models and experiments including explanations about the double dip structure of the transmission spectrum of micro-gap waveguides and the details of the ammonia absorption experiment.

1 Simulation of Fabrication Inaccuracies

The impact of surface roughness and imperfect waveguide corners was studied numerically. Due to the fabrication via 3D laser-nanoprinting, which builds up the waveguide in a rasterized fashion, the waveguide walls feature a roughness with a periodicity equal to the slicing distance (200 nm) for the vertical walls and equal to the hatching distance (150 nm) for the horizontal walls. The amplitudes for the sinusoidal roughness added on both sides of the wall were chosen much larger than what could be observed experimentally under the SEM to obtain an upper bound for the effects of surface roughness on the waveguide’s transmission properties. In particular, an amplitude of 100 nm was used for the vertical walls and of 200 nm for the horizontal walls. Two different amplitudes were chosen to account for the ellipsoidal shape of the voxel. In order to compensate for the additional material, the wall thickness of the vertical walls was reduced to 856 nm and to 793 nm for the horizontal walls.

The values were compared to simulations for a pristine square waveguide and a square waveguide with rounded corners (Fig. S1). The rounding radius was chosen as 2 µm, which is larger than what could be observed experimentally.

Overall, none of the simulated fabrication inaccuracies has a strong impact on the off-resonance loss of the waveguide. In reality, additional losses are caused by surface roughness which is non-uniform along the waveguide axis. However, the required 3D model to simulate such an effect cannot be practically implemented due to computational limitations.
However, two effects of the simulated inaccuracies can be observed: (1) Surface roughness can lead to a splitting of the resonances, which is more pronounced towards shorter wavelengths. (2) The loss spectrum of the waveguide with the rounded cross section features less azimuthal sub-resonances than the square waveguide. In the limit of a completely round tube-type waveguide, theoretical investigations show that azimuthal resonances vanish completely and only the main radial resonances are observable.\textsuperscript{1,2}

Figure S1: Numerical simulation of fabrication inaccuracies. The effect of rounded corners (red) and surface roughness (blue) on the real part of the effective index (a) and the attenuation (b) of the fundamental core mode is compared to the ideal square waveguide (black). The black and blue curves are shifted by an offset of $14 \cdot 10^{-4}$ (a) and a factor of 1000 (b) for reasons of clarity. Insets show the data without shifts. All structures feature the same core size $D = 20 \, \mu m$ and (effective) wall thickness $W = 1 \, \mu m$. In the gap between 1100 nm and 1200 nm the fundamental mode could not be determined.
2 Determining the Size of the Voxel from Waveguide Transmission Measurements

As shown in Fig. 3b of the main text, the positions of the resonances of structures with different wall widths are well described by Eq. 1, which depends on the known refractive index of the polymer and the wall thickness. Therefore, we can determine the wall thickness of the waveguides from the optical measurements through the spectral position of the transmission minima. We noticed that the measured wall thickness differs from the designed wall thickness by a constant offset for all different wall thicknesses that we investigated. As shown in the sketch-insets of Fig. S2, this deviation can be attributed to the lateral extent of the voxels that form the wall. The designed wall thickness here refers to the distance between the inner- and outermost hatch lines of the vertical walls.

We extracted the lateral voxel size from a linear fit of the experimental versus the designed wall width (Fig. S2) for six samples with different wall widths (the same samples that were reported in Fig. 3b of the main text). Previously, we determined fabrication related chip-to-chip variations in the feature size of 3D-nanoprinted waveguides to be 15 nm for a different type of hollow-core waveguides (i.e., the light cage\textsuperscript{S3}). This value was used here as the standard deviation of the experimentally determined wall width. The y-intercept of the linear fit is then an estimate of the lateral voxel size. An upper bound for the error in the voxel size is estimated by the min-max method, which in this case is the sum of the fabrication related standard deviation of 15 nm and the error of y-intercept of the linear fit, which is 8 nm. This results in a lateral voxel size of (358 ± 23) nm. To note here is that this size is only valid for the used printing parameters and is affected by the close proximity of the voxels within the wall. It is not an estimate for the size of an isolated voxel and the given error does not reflect the variation of the size of individual voxels.
3 Analytical models

3.1 Fabry-Pérot model

According to Fresnel’s equations, even low-index dielectrics become highly reflective under near-grazing incidence ($D \gg \lambda$) angles enabling light guidance with low loss in square core hollow antiresonant waveguides. However, the finite thickness of the dielectric slab results in interference of waves inside the material creating Fabry-Pérot-type resonances where the confining material becomes completely transparent. Based on these observations, a simple model for the effective index of such waveguides can be derived.

First, we focus on the antiresonance points, where the reflectivity of the walls is high and therefore, the wavevector of the fundamental mode can be approximated to be that of a perfectly reflecting waveguide with field nodes at the wall surface:
\[ k = \begin{pmatrix} \kappa \\ \kappa \\ \beta \end{pmatrix} \]  \hspace{1cm} (1)

where \( \kappa = \frac{\pi}{D} \) is the transverse wavevector component, \( \beta = \sqrt{k_0^2 - 2\kappa^2} \) is the propagation constant and \( k_0 \) is the free space wavevector. This step fixes the angle of incidence at the core cladding boundary. In the next step, we take into account the finite reflectivity of the walls, describing them as Fabry-Perot resonators yielding reflection coefficients for TE and TM waves as:

\[ r_{TE/TM}^{FP} = r_{TE/TM} \frac{1 - e^{2i\phi}}{1 - r_{TE/TM}^2 e^{2i\phi}} \]  \hspace{1cm} (2)

\[ r_{TE} = \frac{\kappa - \kappa_W}{\kappa + \kappa_W} \]  \hspace{1cm} (3)

\[ r_{TM} = \frac{\kappa - \kappa_W}{\kappa + \kappa_W} \]  \hspace{1cm} (4)

\[ \kappa_W^2 = k_0^2 n_W^2 - \beta^2 \]  \hspace{1cm} (5)

\[ \phi = W \kappa_W \]  \hspace{1cm} (6)

\[ T_{TE/TM}^{FP} = 1 - |r_{TE/TM}^{FP}|^2 \]  \hspace{1cm} (7)

where \( r_{TE} \) and \( r_{TM} \) are the reflection coefficients for TE and TM polarized waves at an air-dielectric interface obtained from Fresnel’s equations, \( n_W \) is the refractive index of the dielectric, \( \kappa_W \) is the transverse wavevector component in the wall, \( \phi \) is the phase acquired
by the waveguide mode in a single pass through the wall and $T_{TE/TM}^{FP}$ is the transmission through the Fabry-Pérot slab.

Using ray-optics, we estimate the real and imaginary parts of the effective index of the fundamental waveguide mode. Therefore, we define the zig-zag length $Z$ along the waveguide axis over which the fundamental mode undergoes two reflections, one on a horizontal wall and one on a vertical wall (Fig. S3).

$$Z \approx \frac{k_0 D}{\kappa} \text{ (for } D >> \lambda) \quad (8)$$

Figure S3: Sketch of the wavevector components and zig-zag length $Z$ for the Fabry-Pérot model shown for simplicity in two dimensions only. Light is propagating along the $z$-direction with propagation constant $\beta$. Wavevector $\mathbf{k}$, transverse wavevector component $\kappa$, inclination angle $\alpha$ of the ray and core size $D$ are also shown.

From this, the waveguide loss and the imaginary parts of the effective index can be estimated to be:

$$\alpha = \frac{2T_{av}}{Z} \quad (9)$$

$$\text{Im}(n_{\text{eff}}) = \frac{\lambda^2 T_{av}}{4\pi D^2} \quad (10)$$

with $T_{av} = \frac{T_{TE} + T_{TM}}{2}$ describing the polarization averaged transmission coefficient of the Fabry-Pérot slab.

Furthermore, the resonance wavelengths where the losses become maximal are evident from Eq. 2 as:
\[
\lambda_{\text{Res}} = \frac{2W}{m} \sqrt{n_W^2 - 1} \quad \forall \ m \in \mathbb{N}
\] (11)

The effect of the resonances on the real part of the effective index can be approximated by calculating the additional phase shift \(\Delta \phi\) due to the imperfect reflections on the walls resulting in a modification \(\Delta \beta\) of the propagation constant compared to the ideal waveguide:

\[
\Delta \phi = \arg \left( -\frac{r_{TE}^{FP} + r_{TM}^{FP}}{2} \right)
\] (12)

\[
\Delta \beta = \frac{2\Delta \phi}{Z}
\] (13)

Therefore, the real part of the effective index can be expressed as:

\[
\text{Re}(n_{\text{eff}}) = \sqrt{1 - \frac{\lambda^2}{2D^2} + \frac{\lambda^2 \Delta \phi}{2\pi D^2}}
\] (14)

### 3.2 Leaky slab waveguide model

A more advanced model takes into account that the walls of the waveguide are not perfectly reflecting and therefore the field nodes of the fundamental mode are not exactly at the core-cladding boundary. However, a completely analytical model for such a geometry has not yet been reported. Here, we present an approximation to this solution by deriving the exact solution for an infinitely extended hollow slab waveguide (Fig. S4) and then superposing the solutions for the \(TE_0\) and \(TM_0\) modes. This corresponds to crossing two infinitely extended slab waveguides at right angle and neglecting the interference of the solutions at the corners of the waveguide where the field intensity is low. Our analysis follows the argument in.\textsuperscript{86}
Figure S4: Geometry for the infinitely extended slab waveguide model. The two slabs (regions 2 and 4) are made of a material with refractive index $n_W$ while the material of the core (region 3) and background (regions 1 and 5) has an index $n_C < n_W$. Light is propagating along the $z$-direction with propagation constant $\beta$.

We start with Maxwell’s equations in linear nonmagnetic media with refractive index $n$ and make an Ansatz for the electric and magnetic fields $\mathbf{\tilde{E}}$ and $\mathbf{\tilde{H}}$ propagating along the $z$-direction:

\[
\nabla \times \begin{pmatrix} \tilde{E}_x \\ \tilde{E}_y \\ \tilde{E}_z \end{pmatrix} = -\mu_0 \frac{\partial}{\partial t} \begin{pmatrix} \tilde{H}_x \\ \tilde{H}_y \\ \tilde{H}_z \end{pmatrix} \tag{15}
\]

\[
\nabla \times \begin{pmatrix} \tilde{H}_x \\ \tilde{H}_y \\ \tilde{H}_z \end{pmatrix} = \epsilon_0 n^2 \frac{\partial}{\partial t} \begin{pmatrix} \tilde{E}_x \\ \tilde{E}_y \\ \tilde{E}_z \end{pmatrix} \tag{16}
\]

\[
\tilde{E} = \mathbf{E}(x,y)e^{i(\omega t - \beta z)} \tag{17}
\]

\[
\tilde{H} = \mathbf{H}(x,y)e^{i(\omega t - \beta z)} \tag{18}
\]
We use the Ansatz to solve Maxwell’s equations in each of the five regions of the slab waveguide individually and then impose boundary conditions to combine them. With this approach, we can neglect the variation of \( n \) at the boundaries and set \( n = \text{const.} \) in the following. Since the geometry is homogeneous along \( y \), we use that \( \frac{\partial E}{\partial y} = \frac{\partial H}{\partial y} = 0 \). Furthermore, we separate the solutions in two branches according to their polarization by setting \( E_z = 0 \) (TE modes) or \( H_z = 0 \) (TM modes). Plugging the Ansatz in Eqs. (15) to (20) and using these conditions, we obtain a simplified set of equations:

**TE:**

**Eqs. (16), (18):**

\[ E_x = E_z = H_y = 0 \]  \hspace{1cm} (23)

**Eq. (15):**

\[ H_x = -\frac{\beta}{\omega \mu_0} E_y \]  \hspace{1cm} (24)

**Eq. (17):**

\[ H_z = i \frac{\omega \mu_0}{\omega \mu_0} \frac{\partial E_y}{\partial x} \]  \hspace{1cm} (25)

**Eqs. (19), (24), (25):**

\[ \frac{\partial^2 E_y}{\partial x^2} + (k_0 n^2 - \beta^2) E_y = 0 \]  \hspace{1cm} (26)

**TM:**

S-12
Eqs. (15), (19): \[ H_x = H_z = E_y = 0 \] 

Eq. (18): \[ E_x = \frac{\beta}{\omega \epsilon_0 n^2} H_y \] 

Eq. (20): \[ E_z = -\frac{i}{\omega \epsilon_0 n^2} \frac{\partial H_y}{\partial x} \] 

Eqs. (16), (28), (29): \[ \frac{\partial^2 H_y}{\partial x^2} + (k_0^2 n^2 - \beta^2) H_y = 0 \] 

According to Eqs. (26) and (30) both \( E_y \) and \( H_y \) are oscillatory functions of \( x \) and all other field components can be derived from them. Based on this observation we make the following Ansatz for the TE solution:

\[
E_y = \begin{cases} 
A_1 \exp(i\kappa_C x) & \text{for region 1} \\
A_2 \sin(\kappa_W x) + A_3 \cos(\kappa_W x) & \text{for region 2} \\
A_4 \cos(\kappa_C x) & \text{for region 3}
\end{cases}
\] 

with \( \kappa_C = k_0 \sqrt{n_C^2 - n_{eff}^2} \) and \( \kappa_W = k_0 \sqrt{n_W^2 - n_{eff}^2} \) using the effective mode index \( n_{eff} = \frac{\beta}{k_0} \).

Here, we used the symmetry of the waveguide around its center line at \( x = 0 \), which al-
allow to calculate the solution for regions (4) and (5) via \( E_y(x) = E_y(-x) \).

The boundary conditions for the tangential components of \( \tilde{E} \) and \( \tilde{H} \) state that \( E_y \) and \( H_z \propto \frac{\partial E_y}{\partial x} \) are continuous across the interfaces. Considering the two interfaces for \( x > 0 \), this condition yields four independent equations of which we consider the real part.

This linear system can be written in the form of a matrix \( \mathbf{M} \) such that \( \mathbf{M} \mathbf{P} = 0 \) with \( \mathbf{P} = (A_1, A_2, A_3, A_4) \). For the solution to be nontrivial, it is required that \( \text{det}(\mathbf{M}) = 0 \) which yields the following analytical equation for \( n_{TE} \) that we solved numerically:

\[
\begin{vmatrix}
\cos(\kappa_C b) & -\sin(\kappa_W b) & -\cos(\kappa_W b) & 0 \\
0 & -\sin(\kappa_W a) & -\cos(\kappa_W a) & \cos(\kappa_C a) \\
-\kappa_C \sin(\kappa_C b) & -\kappa_W \cos(\kappa_W b) & \kappa_W \sin(\kappa_W b) & 0 \\
0 & -\kappa_W \cos(\kappa_W a) & \kappa_W \sin(\kappa_W a) & -\kappa_C \sin(\kappa_C a)
\end{vmatrix} = 0 \quad [TE] \quad (32)
\]

where \( a = \frac{D}{2} \) and \( b = \frac{D}{2} + W \) denote the interface locations.

The TM solution \( n_{TM} \) can be obtained with a similar Ansatz for \( H_y \) and the boundary condition that \( H_y \) and \( E_z \propto \frac{\partial H_y}{\partial x} \) are continuous across the interface which results in the following equation:

\[
\begin{vmatrix}
\cos(\kappa_C b) & -\sin(\kappa_W b) & -\cos(\kappa_W b) & 0 \\
0 & -\sin(\kappa_W a) & -\cos(\kappa_W a) & \cos(\kappa_C a) \\
-\frac{\kappa_C}{n_C^2} \sin(\kappa_C b) & -\frac{\kappa_W}{n_{wC}^2} \cos(\kappa_W b) & \frac{\kappa_W}{n_{wC}^2} \sin(\kappa_W b) & 0 \\
0 & -\frac{\kappa_W}{n_{wC}^2} \cos(\kappa_W a) & \frac{\kappa_W}{n_{wC}^2} \sin(\kappa_W a) & -\frac{\kappa_C}{n_C^2} \sin(\kappa_C a)
\end{vmatrix} = 0 \quad [TM] \quad (33)
\]
To obtain an approximation for the real part of the propagation constant $\beta_{\text{Square}}$ and the effective index $n_{\text{eff}}^{\text{Square}}$ of the square waveguide, we calculate and combine the transverse wavevector components $k_{TE}$ and $k_{TM}$ of the TE and TM solution of the slab waveguide as shown in Fig. S5.

\[ k_{TE/TM}^2 = k_0^2 \left( 1 - \text{Re}^2 \{ n_{TE/TM} \} \right) \]  

\[ \text{Re}^2 \{ \beta_{\text{Square}} \} = k_0^2 - k_{TE}^2 - k_{TM}^2 \]  

\[ \Rightarrow \text{Re}^2 \{ n_{\text{eff}}^{\text{Square}} \} = \text{Re}^2 \{ n_{TE} \} + \text{Re}^2 \{ n_{TM} \} - 1 \]

Figure S5: Sketch of the wavevector components for the leaky slab waveguide model. Light is propagating along the $z$-direction. The middle column shows the case for an infinitely extended slab waveguide with the two confining walls located perpendicular to the x-axis (top) and y-axis (bottom). Right column shows the square waveguide with four confining walls.

The imaginary part of the effective index is obtained by summing the imaginary parts of the effective indices of the TE and TM mode. The fact, that the losses are not averaged arithmetically is due to the change in geometry. This can be illustrated in the ray model. By adding two more confining walls to an infinitely extended waveguide (making it a square waveguide), the ray has to undergo twice as many reflections over the same axial distance.
\[ \Rightarrow \text{Im}\{n_{\text{eff}}^{\text{square}}\} = \text{Im}\{n_{TE}\} + \text{Im}\{n_{TM}\} \] (37)

4 Two-thickness Fabry-Pérot model

In all experimentally recorded transmission spectra, the resonances show up with a pronounced double dip substructure. This is in contradiction to the theoretical models and the numerical simulation, where resonances feature a single dip only. The deviations can most likely be attributed to a non-uniformity in wall width because resonance wavelengths scale proportional to the wall width. To estimate the wall nonuniformity, a Fabry-Pérot model with two different wall widths is considered, where the transmission through the waveguide is calculated as

\[ T_{av} = \sqrt{T_{W_{\text{short}}} \cdot T_{W_{\text{long}}}} \]

with the two wall widths \( W_{\text{short}} \) and \( W_{\text{long}} \). Fitting the model with an experimental spectrum shows that a deviation of \( \pm 25 \) nm in an average wall width of 1.5 \( \mu \)m would explain the observed double dip structure (Fig. S6).
Figure S6: Two-thickness Fabry-Pérot model. The short and the long wavelength dips of each resonance are fitted separately with the Fabry-Pérot model and the two resulting wall thicknesses $W_{\text{short}} = 1519$ nm and $W_{\text{long}} = 1571$ nm are combined to a two-thickness model by: $T_{\text{av}} = \sqrt{T_{W_{\text{short}}} \cdot T_{W_{\text{long}}}}$. Therefore, the double dip structure could be explained by a variation in the wall thickness of about 50 nm along the axis of a single wall or in between different walls. Differences in the absolute value of the transmission arise due to imperfect and wavelength dependent coupling to the waveguide (coupling efficiency $< 0.5$) and scattering on fabrication inaccuracies. Grey bar indicates the part of the transmission spectrum that could not be recorded experimentally. The transmission spectrum is taken from Fig. 3a (L = 5 mm).

In order to improve the uniformity of the walls, two different fabrication approaches were tried. First, hatching and slicing distances were reduced which is known to lower potentially present surface roughness.\textsuperscript{87} Second, the mechanical stability of the waveguide was increased by using a single supporting block that extends over the whole length of the waveguide. However, both approaches did not have an impact on the structure of the resonances.

5 Ammonia gas absorption measurement with micro-gap waveguides

To perform the gas sensing experiment a waveguide with a wall width of $W = 1.67$ µm was used such that the targeted ammonia absorption line at $\lambda_0 = 1501.74$ nm lies within one of the transmission bands of the sample. The complete transmission spectrum of the used
sample is shown below (Fig. S7).

Figure S7: Normalized transmission spectrum of waveguide used for the gas sensing experiment recorded in air ($G = 10$ µm $L = 176$ µm $D = 20$ µm $W = 1.67$ µm total length: 5 mm). Targeted ammonia absorption line at $\lambda_0 = 1501.74$ nm is shown in red. Grey region could not be investigated because a notch filter was required to block the intense pump laser of the white light source.

Evaluating the data from the ammonia gas absorption experiment we found a deviation of the linear increase in the absorbance with ammonia concentration for concentrations larger than 50 %. A linear increase is expected according to Lambert-Beer’s law stated in Eq. 2 of the main text. To exclude that this effect arises from the waveguide, we repeated the experiment with the same gas chamber but without the waveguide. The retrieved transmission (Fig. S8) and absorbance data (Fig. 5d) matches well with results obtained with the waveguide. The data points from the two measurements are expected to overlap since light travels the same distance through the ammonia gas. Again, we used the absorbance data for concentrations between 10 % and 50 % to obtain a linear calibration curve of the form:

$$A = a \cdot c_r + b$$  \hspace{1cm} (38)

The resulting coefficients and their standard deviation are summarised in Table S1 for the measurement with and without the waveguide. Both coefficients agree within a single standard deviation as expected.
Table S1: Coefficients of linear calibration curves for the ammonia absorbance measurements with and without waveguide.

| Coefficients     | a            | σ_a         | b            | σ_b         |
|------------------|--------------|-------------|--------------|-------------|
| With Waveguide   | 6.89 · 10^{-4} | 0.23 · 10^{-4} | 1.09 · 10^{-2} | 0.08 · 10^{-2} |
| Without Waveguide| 7.46 · 10^{-4} | 0.64 · 10^{-4} | 1.05 · 10^{-2} | 0.22 · 10^{-2} |

Since we did not record the ingoing laser power with a separate photodiode, power fluctuations are present in the raw data between measurements of different ammonia concentrations. Therefore each spectrum was normalized to an individual linear baseline, that connects the transmission values at the border of the region of interest (1501.57 - 1501.93 nm). This explains why some values in the transmission spectra exceed one and might be the reason for the deviation of the linear calibration curve from the measurement with 0 % ammonia (Fig. 5d). Oscillations in the spectra are caused by the coupling objectives.

Figure S8: Reference measurement of ammonia absorption without micro-gap waveguide. Transmission spectra of empty gas chamber with varying concentrations of ammonia indicated on the color gradient. The experiment was carried out under identical conditions as the one with the waveguide described in the main text. The green dots show the absorption data of ammonia according to the HITRAN database.\textsuperscript{88,89}

The specifications of the waveguides used in the dynamic measurements are listed in Table S2. They were all printed on the same chip with an extension of 4.908 mm. As the segment length was held constant at $L = 176 \, \mu\text{m}$ and the gap size $G$ was changed, the number of segments has been adjusted to reach a similar length of the waveguides (second
column of Table S2). The length where the light is confined is determined by the number and length of the segments and listed in the fourth column, whereas the unconfined space on the waveguide length is the result of the sum of gaps.

To compensate for the slight skew of the chips during printing, the waveguide printing starts and ends 150 µm from the edges of a chip. This, along with a 200 µm gap between the glass and the chip in the gas chamber to prevent glue from getting on the waveguides during assembly of the gas chambers, contributes to the free space shown in the sixth column. In addition, the seventh column shows the filling times determined during the dynamic measurements, which were calculated from the data recorded in Fig. 5e as the time difference between reaching 90 % and 20 % of the originally transmitted power.

Table S2: Overview of the geometric parameters of the waveguides used in the dynamic experiments.

| Gap Size [µm] | Waveguide Length [µm] | Total No. of Gaps | Confined Space [µm] | Unconfined Space (W) [µm] ¹ | Unconfined Space (C) [µm] ² | Filling Time [s] |
|---------------|-----------------------|------------------|---------------------|-------------------------------|-----------------------------|-----------------|
| 2             | 4448                  | 24               | 4400                | 48                           | 800                         | 3.84            |
| 5             | 4520                  | 24               | 4400                | 120                          | 800                         | 2.83            |
| 10            | 4454                  | 23               | 4224                | 230                          | 976                         | 2.28            |
| 15            | 4569                  | 23               | 4224                | 345                          | 976                         | 2.04            |
| 20            | 4488                  | 22               | 4048                | 440                          | 1152                        | 1.98            |

¹ Space along waveguide length. ² Space between glass wall of chamber and waveguide.

Even without using micro-gap waveguides for the gas absorption experiment, the transmission through the gas chamber does not change instantaneously when it is filled with ammonia because some time is required for the gas previously present inside the chamber to be replaced. To determine this filling time, a bulk measurement at the ammonia absorption line (λ₀ = 1501.74 nm) was done in the same setup. Unlike the dynamic measurements using different gap sizes, the light was focused onto one point in the gas chamber. Since the light travels the same distance through the gas as in the waveguide experiments, this measurement allows the bulk filling time (without waveguide) to be determined. The measurement started by changing the incoming gas from 100 % nitrogen to 100% ammonia, revealing a filling time of 1.92 s.
6 Fraction of modal power present inside the polymer wall

The power inside the polymer wall is calculated by integrating the axial component of the Poynting vector over the area of the polymer wall \( P_{\text{Wall}} = \iint_{\text{Wall}} S_z(x, y) \, dx \, dy \) while the total power of the mode is obtained by integrating over the complete simulation region \( P_{\text{Total}} = \iint_{\text{All}} S_z(x, y) \, dx \, dy \). The fraction of modal power present inside the polymer wall is then obtained as \( P_{\text{Wall}} / P_{\text{Total}} \).

For presenting this data in Fig. 2c we used a median filter which we want to justify here. As shown in Fig. S9b lots of small sub-resonances appear within the transmission bands where the power inside the polymer is suddenly ten to thousand times higher than at neighbouring wavelength points. However, when changing the wall width by just 5 nm these sub-resonances already shift substantially. Since fabrication-related inhomogenities in the feature size of nanoprinted waveguides are indeed on the order of a few nanometers,\textsuperscript{3} such sub-resonances will average out in real samples and do not affect the sensing performance.
Figure S9: Impact of small change in wall width on optical properties. Two simulations were performed for wall widths differing by 5 nm (blue: $W = 1.000 \, \mu m$; orange: $W = 1.005 \, \mu m$) for the standard core size of $D = 20 \, \mu m$. (a) Spectral distribution of the modal loss is mostly unaffected by the change in wall width. (b) Strong fluctuations are present in the fraction of the modal power present inside the polymer. Since these fluctuations change strongly with the small change in wall width, they average out due to the practical limitations in wall uniformity in realized samples.

References

(S1) Zeisberger, M.; Schmidt, M. Analytic model for the complex effective index of the leaky modes of tube-type anti-resonant hollow core fibers. Sci. Rep. 2017, 7, 11761.

(S2) Euser, T. G.; Schmidt, M. A.; Joly, N. Y.; Gabriel, C.; Marquardt, C.; Zang, L. Y.; Förtsch, M.; Banzer, P.; Brenn, A.; Elser, D.; Scharrer, M.; Leuchs, G.; Russell, P. S. Birefringence and dispersion of cylindrically polarized modes in nanobore photonic crystal fiber. J. Opt. Soc. Am. B 2011, 28, 193–198.

(S3) Bürger, J.; Kim, J.; Jang, B.; Gargiulo, J.; Schmidt, M. A.; Maier, S. A. Ultrahigh-aspect-ratio light cages: fabrication limits and tolerances of free-standing 3D nanoprinted waveguides. Opt. Mater. Express 2021, 11, 1046–1057.
(S4) Novotny, L.; Hecht, B. *Principles of Nano-Optics*, 2nd ed.; Cambridge University Press, 2012.

(S5) Yariv, P., A; Yeh *Optical Waves in Crystals: Propagation and Control of Laser Radiation*; Wiley, New York, 1984.

(S6) Okamoto, K. *Fundamentals of optical waveguides*; Academic press, 2006.

(S7) NanoGuide. [https://support.nanoscribe.com/hc/en-gb/articles/360003142594-Printing-Microoptics#Reducing_the_Roughness_of_3D_Micro-Optics](https://support.nanoscribe.com/hc/en-gb/articles/360003142594-Printing-Microoptics#Reducing_the_Roughness_of_3D_Micro-Optics) (accessed 2022-07-20).

(S8) HITRAN Database. [https://hitran.org/](https://hitran.org/) (accessed 2022-07-20).

(S9) Sung, K.; Brown, L.; Huang, X.; Schwenke, D.; Lee, T.; Coy, S.; Lehmann, K. Extended line positions, intensities, empirical lower state energies and quantum assignments of NH3 from 6300 to 7000 cm\(^{-1}\). *J. Quant. Spectrosc. Radiat. Transfer* **2012**, *113*, 1066–1083.