Supporting Material

Frozen “tofu” effect: engineered pores of hydrophilic nanoporous materials

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1. Fabrication of polymer porous photonic crystal

The pre-polymer solution contains a mixture of an acrylate monomer: dipentaerythritol hydroxy penta acrylate (DPHPA), photoinitiator: Rose Bengal (RB), coinitiator: N-Phenylglycine (NPG), reactive solvent: N-vinylpyrrolidinone (NVP), liquid crystal: TL213 and toluene as non-reactive solvent. The composition of each compound was 0.2 wt% RB, 1 wt% NPG, 16 wt% NVP, 45 wt% DPHPA, 20 wt% Toluene, 17.8 wt% TL213. The TL213 was purchased from EMD Chemicals Inc. and the RB was purchased from Spectra Group Limited. All other chemicals were purchased from Sigma Aldrich. The prepolymer syrup was mixed to ensure homogeneity with a mixer for 60 minutes and then sandwiched between two parallel glass slides separated by 8 μm spacers. The sandwiched sample was then attached to a right-angle prism (Thorlabs) with index matching oil and exposed to the holographic interference pattern for 60 s using a 532 nm CW solid state laser with 0.5 W exposure power (Verdi V6, Coherent). After laser exposure, the sandwiched sample was post-cured under an Hg lamp (100 W, Sylvania) for 24 hours. The reflection notch could be observed after removing the glass slide from the cell and allowing the incorporated solvent to evaporate. The incident angle of the laser beam will determine the reflection resonance. For instance, Figure S1 shows the reflection spectrum of a grating fabricated under the incident angle of 35° (i.e. the raw data for curve 1 in Figure 2a of the main text).

![Figure S1](image_url)

**Figure S1** Measured reflection spectrum of nanoporous polymer PhC structure with the reflection peak at 548.8 nm, corresponding to curve 1 in Figure 2a.

2. Spectral tuning of porous polymer PhC using wet-drying
Figure S2 Reflection spectra of the PhC sample with freeze-wet-drying treatments for the 3rd and 4th cycles. The dashed lines and numbers on the top panel indicate the peak wavelength position for each step.

3. Extraction of geometric features of polymer porous photonic crystals using matrix analysis

According to transfer matrix theorem [S1], the matrix for a single dielectric layer on semi-infinite substrate is

\[
M = \begin{bmatrix}
    c_i & q_l^{-1} s_l \\
    -q_l s_l & c_i
\end{bmatrix}
\]  

(S1)

where \( q_s = (\varepsilon \omega^2/c^2 - K^2)^{1/2} \) is the local value of the normal component of the wave vector; \( c_i = \cos \delta_i \); \( s_i = \sin \delta_i \); \( \varepsilon \) is the refractive index of dielectric layer; and \( K = n_1 (\omega/c) \sin \theta_1 \). \( \delta_i = q_d_i \) where \( d_i \) is the thickness of the dielectric layer. \( n_1 \) and \( \theta_1 \) are the refractive index and incident angle of the environmental medium. As an extension to this equation, the matrix of a unit cell (i.e. a high-low refractive index bilayer) for a periodically stratified media with high-low refractive index configuration for s-polarized wave is

\[
M = M_l M_h = \begin{bmatrix}
    m_{11} & m_{12} \\
    m_{21} & m_{22}
\end{bmatrix}
\]

\[
= \begin{bmatrix}
    c_l & q_l^{-1} s_l \\
    -q_l s_l & c_l
\end{bmatrix}
\begin{bmatrix}
    c_h & q_h^{-1} s_h \\
    -q_h s_h & c_h
\end{bmatrix}
\]

\[
= \begin{bmatrix}
    c_l c_h - q_l^{-1} q_h s_l s_h & q_l^{-1} c_l s_h + q_l^{-1} s_l c_h \\
    -q_l s_l c_h - q_h s_h c_l & c_l c_h - q_l q_h^{-1} s_l s_h
\end{bmatrix}
\]  

(S2)

For \( N \) period high-low index bilayers, the matrix elements are those of the \( N_{th} \) power of the unit-cell matrix: i.e.,

\[
\begin{bmatrix}
    m_{11} & m_{12} \\
    m_{21} & m_{22}
\end{bmatrix}^N = \begin{bmatrix}
    m_{11} S_N - S_{N-1} & m_{12} S_N \\
    m_{21} S_N & m_{22} S_N - S_{N-1}
\end{bmatrix}
\]  

(S3)

where
\[ S_N = \frac{\sin(N\emptyset)}{\sin\emptyset}, \cos\emptyset = 1/2(m_{11} + m_{22}) \]

For s-polarized wave, \(\cos\emptyset_s\) is defined as a half of the trace of this unit-cell matrix
\[ \cos\emptyset_s = c_l c_h - 1/2 s_l s_h (q_l^{-1} q_h + q_l q_h^{-1}) \]  

(S4).

For the p-polarized wave, the arguments of the trigonometric function remain unchanged. But \(q_l\) and \(q_h\) are replaced by \(Q_l = q_l/\varepsilon_l\) and \(Q_h = q_h/\varepsilon_h\), respectively, in the matric elements. Therefore,
\[ \cos\emptyset_p = c_l c_h - 1/2 s_l s_h (Q_l^{-1} Q_h + Q_l Q_h^{-1}) \]  

(S5)

The transmission and reflection amplitude \(t_s, r_k\) \((k=s, p)\) are determined by matrix elements \(m_{ij}\) in Eq. (S3), which can be expressed by
\[
\begin{pmatrix}
  t_s \exp(i q_{2b}) \\
  i q_2 \exp(i q_{2b})
\end{pmatrix}
= \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix}^N \times \begin{pmatrix} \exp(i q_1 a) + r_s \exp(-i q_1 a) \\ i q_1 \exp(i q_1 a) - r_s \exp(-i q_1 a) \end{pmatrix}
\]

(S6)

\[
\begin{pmatrix}
  n_2 t_p \exp(i q_{2b}) \\
  i q_2 n_1 t_p \exp(i q_{2b})
\end{pmatrix}
= \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix}^N \times \begin{pmatrix} \exp(i q_1 a) + r_p \exp(-i q_1 a) \\ i q_1 \exp(i q_1 a) - r_p \exp(-i q_1 a) \end{pmatrix}
\]

(S7)

where \(q_1 = n_1 (\omega/c) \cos\theta_1; q_2 = n_2 (\omega/c) \cos\theta_2; \theta_2\) is the angle between the wave vector and the normal in the homogeneous substrate with the index of \(n_2\). \(Q_1 = q_1/\varepsilon_1; Q_2 = q_2/\varepsilon_2\). \(a\) and \(b\) are the start and end point coordinates along \(z\) direction for a single period.

By solving Eq. (S6) and (S7), the reflection coefficients for s- and p-polarized wave are shown as:
\[
r_s = \frac{q_1 q_2 m_{12} + i q_1 (m_{22} - \sigma_N) - i q_2 (m_{11} - \sigma_N)}{q_1 q_2 m_{12} - i q_1 (m_{22} - \sigma_N) + i q_2 (m_{11} - \sigma_N)}
\]

(S8)

\[
-r_p = \frac{q_1 q_2 m_{12} + i q_1 (m_{22} - \sigma_N) - i q_2 (m_{11} - \sigma_N)}{q_1 q_2 m_{12} - i q_1 (m_{22} - \sigma_N) + i q_2 (m_{11} - \sigma_N)}
\]

(S9)

where
\[
\sigma_N = \frac{S_{N+1}}{S_N} = \frac{\sin[(N-1)\emptyset]}{\sin(N\emptyset)} = \cos\emptyset - \sin\emptyset \cot(N\emptyset)
\]

(S10)

Based on Eq. (S8) and (S9), we can calculate the resonant wavelength at different incident angle. The typical experimental angular dependent reflection spectra of a PhC grating (i.e. the wet-dried sample in Figure 2 in the main text) are shown in Figure S3a. The maximum reflection was achieved at 35°, corresponding to the Bragg condition. By fitting the experiment data using Eq. (S8) (as shown by the solid curve in Figure S3b), the refractive indices and thicknesses for P-rich region and V-rich region can then be extracted (i.e., the 4th and 5th columns in Table 1 in the main text). Since the polymer grating contains P-rich and V-rich regions, a two-component Bruggeman model was employed to calculate the volume fraction of different materials: i.e.,
\[
\sigma_p G_p + \sigma_v G_v = 0
\]

(S9)

where
\[
G_p = \frac{n_p^2 - n^2}{n_p^2 + 2n^2}, \quad G_v = \frac{n_v^2 - n^2}{n_v^2 + 2n^2}
\]

(S10)
\(\sigma_p, \sigma_v,\) and \(n_p, n_v\) are volume fractions and refractive indices for DPHPA polymer and voids, respectively. \(n\) is the effective refractive index for porous polymer structure. The volume fractions are listed in the last two columns in Table 1 in the main text.
Figure S3 (a) Angle dependent reflection spectra of the PhC sample in Figure 2a. (b) Measured (blue circles) and fitted peak wavelengths (red line) at different incident angles based on matrix analysis.

4. Accurate spectral tuning of porous polymer PhC using partially filled frozen ‘tofu’ process.

Figure S4 The reflection spectra of the PhC sample with water condensation freeze-wet-drying treatment for the 3rd and 4th cycles. The dashed lines and numbers on the top panel indicate the peak wavelength position for each step.

References
[S1] J. Lekner, Light in periodically stratified media, JOSA A 11, 2892-2899 (1994).