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Light-Confining Nanoporous Anodic Alumina Microcavities by
Apodized Stepwise Pulse Anodization

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KEYWORDS: Nanoporous Anodic Alumina, Optical Microcavity, Light Confinement, Apodized Anodization, Quality Factor.

ABSTRACT: This study presents an innovative approach to fabricate nanoporous anodic alumina optical microcavities (NAA-\(\mu\)CVs) with enhanced quality factor and versatile optical properties. An apodization strategy using a logarithmic negative function is applied to a stepwise pulse anodization process in order to engineer the effective medium of NAA so it confines light efficiently. The architecture of these light-trapping photonic crystals is composed of two highly reflecting mirrors with asymmetrically apodized effective medium. Various anodization parameters such as anodization time, anodization period, current density offset, and pore widening time are systematically modified to assess their effect on the optical properties of NAA-\(\mu\)CVs in terms of quality factor and position of resonance band. We demonstrate that this fabrication approach enables the generation of NAA-\(\mu\)CVs with high quality factor (~113) and well-resolved and tunable resonance bands across the spectral regions, from UV to NIR, through the manipulation of the anodization parameters. These results represent a comprehensive rationale for the development of high quality NAA-\(\mu\)CVs with enhanced light-confining capabilities, providing new opportunities for further fundamental and applied research across a broad range of fields and disciplines such as photonics and optical sensing.
INTRODUCTION

New materials and structures that effectively confine light to small volumes are central for the development and advancement of nanophotonic applications such as quantum communication and computing\textsuperscript{1}, nanolasers\textsuperscript{2}, ultra-small photonic filters\textsuperscript{3}, and optical sensing.\textsuperscript{4} Photons possess no charge or rest mass and are prone to escaping when trapped in photonic structures.\textsuperscript{5,6} The confinement of light within small volumes comparable to the wavelength of light is challenging. However, high quality optical microcavities with strong light confinement capabilities to attain the precise control of light emission and propagation have been realized.\textsuperscript{7,8} Photonic crystals (PCs) have emerged as the most promising platforms to develop efficient optical microcavities with high quality factor and small cavity volume.\textsuperscript{9,10}

Optical microcavities (µCVs) are photonic crystal structures that can guide and build up optical signals by light confinement.\textsuperscript{6} Typically, µCVs consists of two plane-parallel mirrors positioned apart at a fixed distance with the objective of capturing and storing light indefinitely, until the system is triggered to release the confined light from the cavity in a controlled fashion.\textsuperscript{6,11,12} µCVs can be produced in different materials, including polymers\textsuperscript{13}, semiconductors such as GaAs, InP, GaInAsP and Ga\textsubscript{N}\textsuperscript{14-17} and silicon\textsuperscript{4,18,19}. Usually, µCVs are fabricated by a combination of lithographic and etching techniques, and chemical or physical vapor deposition.\textsuperscript{17} However, alternative materials such as porous silicon produced by electrochemical etching of silicon opened new opportunities to develop nanoporous µCVs with tunable optical properties and nanoporous architectures for different applications, including light-emitting devices, solar cells, optical filters, biosensors, drug delivery and theranostics.\textsuperscript{20-22} The modulation of porosity in depth by the anodizing current allows the effective engineering the optical properties of porous silicon µCVs, the composite air-silicon matrix of which acts as a versatile effective medium.\textsuperscript{23-27} Porous silicon has outstanding optoelectronic properties, however it has poor chemical stability and mechanical strength and
its fabrication process requires the use of extremely hazardous HF-based electrolytes.\textsuperscript{28,29} To date, different alternative/complementary nanoporous materials have been explored to overcome the intrinsic limitations of porous silicon. Of these, nanoporous anodic alumina (NAA) produced by anodization of aluminum has superior properties to those of porous silicon in respect of mechanical, thermal and chemical stabilities as well as versatile nanopore geometry. Furthermore, anodization of aluminum is a well-established electrochemical process performed in mild acid electrolyte solutions that is economical and fully scalable process and requires minimum safety measures.\textsuperscript{30-36}

Recent studies have demonstrated that the effective refractive index of NAA can be precisely modulated in a multi-dimensional fashion to create a broad range of PC structures with finely tuned optical properties (e.g. distributed Bragg reflectors, gradient-index filters, bandpass and linear variable bandpass filters, encoded photonic tags, etc.). The realization of NAA-based $\mu$CVs has been demonstrated in a few pioneering studies.\textsuperscript{37-40} The fabrication of NAA-$\mu$CVs involves the introduction of defect modes in the PC structure, which can be achieved by various approaches such as the insertion of a thin layer of nanopores with constant effective refractive index between two highly reflective Bragg mirrors, a phase shift of effective refractive index between Bragg mirrors, or a progressive asymmetric modulation of the effective medium in depth.\textsuperscript{37,38,41} However, the maximum quality factors of NAA-$\mu$CVs reported by Wang \textit{et al.} (~24)\textsuperscript{38}, Lee \textit{et al.} (~55)\textsuperscript{37} and Yan \textit{et al.} (~45)\textsuperscript{41} were found to be significantly lower than those of porous silicon-based $\mu$CVs (~1500-3400)\textsuperscript{19,42,43} due to the low refractive index of alumina ($\text{Al}_2\text{O}_3 - n_{\text{Alumina}} \approx 1.70$).\textsuperscript{37-40} Despite this limitation, the development of new pulse-like anodization strategies and novel NAA-PC architectures provides new opportunities to improve the quality of NAA-$\mu$CVs and explore new strategies to attain strong light confinements by a precise control of light–matter interactions at the nanoscale.\textsuperscript{37-59} Recently, we identified sharp resonance bands within the photonic stopband.
(PSB) of NAA-PCs produced by stepwise pulse anodization when a logarithmic negative apodization function was applied under certain conditions.  

Motivated by these results, we decided to explore this nanofabrication approach to develop high-quality NAA-µCVs.

**Figure 1.** Fabrication of NAA-µCVs by apodized stepwise pulse anodization (ASPA). a) Representative ASPA profile (left) and structure of NAA-µCVs (right) showing details of the existing relationship between nanopore geometry and effective refractive index \(n_{\text{eff}}\) distribution between high (alumina) and low (air) values along the nanopore depth. b) Schematic showing the confinement of light within the structure of NAA-µCVs (left) and representative transmission spectra showing the characteristic photonic stopband (PSB) and the resonance band at its center in NAA-µCVs. Insets show a digital picture of that NAA-µCVs with the characteristic green interferometric color denoting the position of the photonic stopband and a magnified view of the red rectangle showing details of the resonance band (note: NAA-µCV produced with \(T_p = 1300\) s, \(\Delta t_J = 0.210\) mA cm\(^{-2}\), \(J_{\text{Offset}} = 0.280\) mA cm\(^{-2}\), \(t_{\text{An}} = 25\) h, and \(t_{\text{pw}} = 6\) min).

In this study, a new architecture of NAA-µCVs that enables high quality confinement of light by means of a rationally designed apodized stepwise pulse anodization (ASPA) approach is presented. A negative apodization function is implemented into the stepwise pulse anodization profile with the aim of modulating the effective refractive index of NAA in depth and engineering the photonic stopband (PSB) of the Bragg mirrors (Figure 1).  

Various anodization parameters including anodization time, anodization period, current density offset, and pore widening time are systematically modified in order to maximize and
tune the resonance band of NAA-µCVs across the spectral regions. Our study establishes a comprehensive rationale towards the fabrication of NAA-µCVs with high quality factor and optimized optical properties. These PCs will enable new opportunities to expand the applicability of NAA-µCVs across disciplines such as ultra-sensitive sensors, light harvesting/emitting devices, and optical filters.

EXPERIMENTAL SECTION

2.1. Materials. High purity (99.9997%) aluminum (Al) foils of thickness 0.32 mm were supplied by Goodfellow Cambridge Ltd. (UK). Sulfuric acid (H₂SO₄), perchloric acid (HClO₄), copper (II) chloride (CuCl₂), hydrochloric acid (HCl), phosphoric acid (H₃PO₄), and ethanol (EtOH-C₂H₅OH) were supplied by Sigma-Aldrich (Australia) and used as received, without further purification steps. Aqueous solutions used in this study were prepared with Milli-Q® water (18.2 mΩ·cm).

2.2. Fabrication of Nanoporous Anodic Alumina Microcavities. NAA optical microcavities (NAA-µCVs) were produced by apodized stepwise pulse anodization (ASPA) under current density control conditions. 1.5 x 1.5 cm Al square chips were cleaned under sonification in EtOH and Milli-Q® water for 15 min each, then dried under air stream. Prior to anodization, these Al substrates were electropolished in a mixture of EtOH and HClO₄ 4:1 (v:v) at 20 V and 5°C for 3 min. The anodization process of Al substrates was carried out in an electrochemical reactor at a constant temperature of -1°C, using an aqueous solution of 1.1 M H₂SO₄ with 25 v% of EtOH as electrolyte. The galvanostatic anodization process started with a constant current density step at 1.120 mA cm⁻² for 1 h to create a starting nanoporous oxide layer that acts a shuttle for achieving a homogenous pore growth rate preceding the ASPA step. The anodization profile was subsequently set to apodized stepwise pulse mode. A logarithmic negative apodization function was implemented into conventional stepwise pulse
anodization. The current density-time ASPA profiles were produced by a custom-designed Labview®-based software according to \textbf{Equation 1.}

\begin{equation}
J(t) = 2A_J(t) + J_{offset}
\end{equation}

where \( A_J(t) \) is the time-dependent current density amplitude, which follows a logarithmic negative apodization function as defined in \textbf{Equations 2 and 3.}

For \( t \leq t_{An}/2 \)

\begin{equation}
A_J(t) = A_{max} + \left( \frac{A_{max} - A_{min}}{\log\left(\frac{t}{t_{An}}\right) + 1} \right) \cdot (\log(t + 10) - 1)
\end{equation}

For \( t > t_{An}/2 \)

\begin{equation}
A_J(t) = \left( \frac{A_{max} - A_{min}}{\log\left(\frac{t}{t_{An}}\right) + 1} \right) \cdot \left( \log(t + 10) - \log\left(\frac{t_{An}}{2} + 10\right) \right) + A_{min}
\end{equation}

where \( A_{max} \) and \( A_{min} \) are the maximum and minimum amplitudes and \( t_{An} \) is the total anodization time at ASPA.

Note that \( T_P \) in the ASPA profile was defined as the total time length of high and low anodization current density pulses (\textbf{Equation 4}):\[ T_P = t_{high} + t_{low} \]

where \( t_{high} \) and \( t_{low} \) are the time duration at high and low current density values, respectively. The ratio between \( t_{high} \) and \( t_{low} \) was set to \( t_{high}:t_{low} = 1:4 \).

To gain a better understanding of the light-confining capabilities of NAA-\( \mu \)CVs produced by ASPA, different anodization parameters (i.e. anodization time \( -t_{An} \), anodization period \( -T_P \), current density offset \( -J_{offset} \), and pore widening time \( -t_{pw} \)) were systematically manipulated.
to assess their effects on the optical characteristics of NAA-µCVs, such as interferometric color, position of the resonance band ($\lambda_R$), full-width at half maximum of the resonance band ($FWHM_R$) and quality factor of cavity ($Q_C$), as defined by Equation 5.

$$Q_C = \frac{\lambda_R}{FWHM_R}$$

2.3. Optical Characterization. Prior to optical characterization, the remaining aluminum substrate was selectively dissolved from the backside of these aluminum chips by wet chemical etching in a saturated solution of HCl/CuCl$_2$, using an etching cell with a Viton® mask with a circular window of 5 mm in diameter. These etched NAA-µCVs were then optically characterized. The optical transmission spectra of NAA-µCVs fabricated at various conditions were obtained at normal incidence (i.e. $\theta = 0^\circ$) from 200–1000 nm with a resolution of 1 nm and 5 mm slit using a UV-vis-NIR spectrophotometer (Cary 60, Agilent, USA), and from 200–1500 nm with a resolution of 1 nm in a UV-vis-NIR spectrometer (UV-3600 Plus, Shimadzu, Japan). The interferometric color displayed by these NAA-µCVs as a function of the different fabrication parameters was characterized through digital images acquired by a Canon EOS 700D digital camera equipped with a Tamron 90 mm F2.8 VC USD macro mount lens with autofocus function under natural illumination. A black card was used as background for the digital image acquisition. The pore size of NAA-µCVs was widened by isotropic chemical etching in an aqueous solution of 5 wt% H$_3$PO$_4$ at 35°C at different pore widening times (i.e. $t_{pw} = 0, 2, 4,$ and 6 min) and their transmission spectra and digital images were recorded after each pore widening step. Note that the features of the resonance band of these NAA-µCVs (i.e. position of resonance band $-\lambda_R$, full-width at half maximum of the resonance band $-FWHM_R$, and baseline of resonance band $-y_0$) were estimated using OriginPro 8.5®, applying Gaussian fittings over the resonance bands shown in the transmission spectra of NAA-µCVs and using as a baseline the lower lobe of the
photonic stopband (PSB), as illustrated in Figure 1. The obtained results were summarized in contour maps generated using OriginPro 8.5®, using a triangulation algorithm in which the coordinates of the intersection point were computed with linear interpolation.

2.4. Structural Characterization. The nanoporous structure of NAA-µCVs was characterized by a field emission gun scanning electron microscope (FEG-SEM FEI Quanta 450). The obtained FEG-SEM images were analyzed using ImageJ (public domain program developed at the RSB of the NIH).  

RESULTS AND DISCUSSION

3.1. Fabrication and Structural Characterization of Nanoporous Anodic Alumina Microcavities. Figure 1a illustrates the fabrication process of NAA-µCVs by ASPA. The structure of these PC structures is composed of two highly reflective distributed Bragg reflector (DBR) mirrors with asymmetrically modulated effective refractive index in a stepwise fashion in depth following a logarithmic negative window. The amplitude of the current density pulse is logarithmically reduced during the fabrication process of the first half of the NAA-µCV (i.e. from \( t = 0 \) to \( t = t_{As} / 2 \)) (Equation 2). At \( t = t_{As} / 2 \), the current density amplitude is progressively increased according to the mathematical expression shown in Equation 3. The transmission spectrum of these PC structures is characterized by a relatively broad PSB with a strong and narrow resonance band at approximately its central position (Figure 1b). This resonance band denotes a strong confinement of light within the NAA-µCV at that narrow range of wavelengths, which is established by the geometric features of the NAA-DBR mirrors. Figures 2a-c show a set of representative FEG-SEM images of NAA-µCVs produced by ASPA. These images reveal that the structure of these PCs is composed of stacked layers of NAA with a porosity modulation in depth that follows the ASPA current density profile applied during the anodization process. Figure 2a depicts a
representative top view FEG-SEM image of a NAA-µCV, revealing nanopores with an average pore diameter \( (d_p) \) of 15 ± 2 nm that are randomly distributed across the surface.

**Figure 2.** Nanoporous structure of NAA-µCVs produced by ASPA. a) Representative top view FEG-SEM image of a NAA-µCV showing a random distribution of nanopores with \( d_p = 15 ± 2 \) nm (scale bar = 500 nm). b) General cross-sectional view FEG-SEM image of a NAA-µCV showing a top layer of straight nanopore diameter (constant anodization = CA – thickness = 1.4 ± 0.1 µm) and the PC microcavity layer with nanopore diameter modulation (ASPA – thickness = 11.0 ± 0.1 µm) with details showing the areas where the period length \( (L_{TP}) \) was estimated (i.e. from 0-2 µm to 8-10 µm) (scale bar = 5 µm). c) Magnified view of the white rectangle shown in (b) revealing the porosity modulation in depth in NAA-µCVs (scale bar = 1 µm). d) Magnified views at different cross-sectional positions (i.e. 0-2, 4-6, and 8-10 µm) showing details of the period length modulation (scale bar = 500 nm). e) Illustration representing the idealized nanoporous structure of NAA-µCVs, where the period length \( (L_{TP}) \) is modified in depth to create an optical microcavity structure with a logarithmically modulated effective refractive index composed of two NAA-DBRs with asymmetrically modulated effective refractive index. f) Bar chart showing the period length distribution in NAA-µCVs produced by ASPA along the nanopore depth (note: NAA-µCV produced with \( T_p = 800 \) s, \( \Delta J_f = 0.210 \) mA cm\(^{-2}\), \( J_{Offset} = 0.280 \) mA cm\(^{-2}\), \( t_{An} = 20 \) h, and \( t_{pw} = 6 \) min).
**Figure 2b** shows a general cross-sectional view of a NAA-µCV produced with \( T_p = 800 \) s, \( J_{offset} = 0.280 \) mA cm\(^{-2}\), \( AA_J = 0.210 \) mA cm\(^{-2}\), \( t_{An} = 10 \) h, and \( t_{pw} = 6 \) min. That image reveals that the structure of these NAA-µCVs is composed of a top layer 1.4 ± 0.1 µm thick with constant nanopore diameter, which results from the first anodization stage at constant anodizing current density (CA – \( J = 1.120 \) mA cm\(^{-2}\) for 1 h), and a much thicker layer (i.e. 11.0 ± 0.1 µm) with nanopore diameter modulation in depth corresponding to the ASPA stage (**Figures 2c and d**). A pore branching effect can be observed at the bottom part of the NAA-µCV structure (**Figure 2d**; 8-10 µm), which can be associated with the non-self-organization conditions used in our study. A closer analysis of the period length (i.e. \( L_{TP} \) – distance between adjacent layers in the ASPA section of the NAA-µCVs) reveals a direct dependency with the anodization amplitude (\( AA_J \)) (**Figure 2e**). For instance, we estimated the average \( L_{TP} \) along the ASPA cross-section of a NAA-µCV produced with \( T_p = 800 \) s, \( J_{offset} = 0.280 \) mA cm\(^{-2}\), \( AA_J = 0.210 \) mA cm\(^{-2}\), \( t_{An} = 10 \) h, and \( t_{pw} = 6 \) min every 2 µm by FEG-SEM image analysis. Our results indicate that \( L_{TP} \) varies along the nanopore depth following the apodization function applied during anodization, with an estimation of 115 ± 9 nm at 0–2 µm, 112 ± 6 nm at 2–4 µm, 96 ± 8 nm at 4–6 µm, 111 ± 6 nm at 6–8 µm, and 113 ± 5 nm at 8–10 µm (**Figure 2f**). From this analysis it is apparent that \( L_{TP} \) is reduced at the center of the ASPA section of the NAA-µCVs (i.e. \( t \sim t_{An}/2 \)), which is expected due to the significant reduction of the anodization amplitude at \( t = t_{An}/2 \). Furthermore, FEG-SEM image analysis denote a modulation of porosity in depth with the pulse anodizing current density. For instance, the porosity at \( J = 0.280 \) and 1.120 mA cm\(^{-2}\) (i.e. minimum and maximum values of current density) was estimated to be 18 ± 9 and 32 ± 13%, respectively.\(^8\) Apodization is a filtering technique broadly used in optics to narrow the PSB of photonic structures. The direct relationship between the geometric features of NAA-µCVs and the anodization parameters...
enables the apodization of the optical signals of these PCs by structural engineering of their effective medium (i.e. effective refractive index modulation).

### 3.2. Effect of Anodization Time ($t_{An}$) on the Optical Properties of Nanoporous Anodic Alumina Microcavities.

To understand the effect of $t_{An}$ on the optical characteristics of NAA-$\mu$CVs, a set of NAA-$\mu$CVs was fabricated using logarithmic negative ASPA with varying $t_{An}$ from 5 to 25 h at an interval of 5 h. Other anodization parameters such as anodization period ($T_P$), current density offset ($J_{offset}$), and amplitude difference ($\Delta A$) were fixed at 1200 and 1300 s, 0.280 mA cm$^{-2}$, and 0.210 mA cm$^{-2}$, respectively. **Figures 3a and b** show representative anodization profiles for NAA-$\mu$CVs fabricated at different $t_{An}$ (i.e. 5, 10, 15, 20, and 25 h) for $T_P$ = 1200 and 1300 s, respectively. These ASPA profiles denote that, under the anodization conditions used in our study, the anodizing current density profile is precisely translated into modulations of voltage throughout the whole process, resulting in an internal modulation of $d_p$ in depth. The transmission spectra of NAA-$\mu$CVs produced at $T_P$ = 1300 s as a function of $t_{An}$ and pore widening time ($t_{pw}$) are displayed in **Figures 4a-e**. The optical properties of these NAA-$\mu$CVs were characterized in terms of $\lambda_R$, $FWHM_R$, $Q_c$, and interferometric color. **Figure 4** shows that the PSB of these NAA-$\mu$CVs is located within visible-NIR range and it undergoes a blue shift and increases its intensity and width with $t_{pw}$, from 0 to 6 min. The interferometric color is a result of the selective and constructive reflection of light by the NAA-$\mu$CV structure and denotes the position of the PSB within the UV (transparent), visible (color), or NIR (transparent) spectral regions. The transmission spectra of these NAA-$\mu$CVs shows a resonance band located at approximately the center of the PSB, which indicates the presence of an optical microcavity within the structure of these PCs.
Figure 3. Representative anodization profiles of NAA-µCVs produced by ASPA at different anodization times and anodization periods (note: NAA-µCVs produced with $T_P = 1200$ and $T_P = 1300$ s, $\Delta J = 0.210$ mA cm$^{-2}$ and $J_{Offset} = 0.280$ mA cm$^{-2}$). a) Anodization profiles of NAA-µCVs produced with $T_P = 1300$ at $t_{An} = 5$, 10, 15, 20, and 25 h. b) Anodization profiles of NAA-µCVs produced with $T_P = 1200$ at $t_{An} = 5$, 10, 15, 20, and 25 h.

Figures 5a-e show magnified views of the resonance bands observed in the transmission spectra of these NAA-µCVs (Figures 4a-e) with details of Gaussian fittings used to estimate $\lambda_R$, FWHM$_R$, and $Q_c$. In general, it can be observed that the resonance band of these NAA-
μCVs rises as $t_{pw}$ increases, becoming more well-resolved and intense due to the effective refractive index contrast enhancement between adjacent NAA layers.

**Figure 4.** Combinational effect of anodization time ($t_{An}$) and pore widening time ($t_{pw}$) on the transmission spectrum of NAA-μCVs produced by ASPA at $T_P = 1300$ s (note: color rectangles denote the approximate position of the resonance band within the PSB and black dotted arrow lines indicate the blue shift of the resonance bands with $t_{pw}$). a) $t_{An} = 5$, b) $t_{An} = 10$, c) $t_{An} = 15$, d) $t_{An} = 20$, and e) $t_{An} = 25$ h. Insets in a-e display digital pictures of these photonic crystal structures showing vivid interferometric colors when the resonance band is located within the visible region and transparent when the band is within the UV or NIR spectral regions.
Figure 5. Combinational effect of anodization time ($t_{An}$) and pore widening time ($t_{pw}$) on the resonance band of NAA-$\mu$CVs produced by ASPA at $T_p = 1300$ s (note: horizontal dotted black lines denote the baseline ($y_0$) used for the Gaussian fittings, which correspond to the lower lobe of the PSB, and vertical dotted red lines indicate the central wavelength of the resonance band ($\lambda_R$) and the symmetry of the Gaussian fitting). a) $t_{An} = 5$, b) $t_{An} = 10$, c) $t_{An} = 15$, d) $t_{An} = 20$, and e) $t_{An} = 25$ h.
The stepwise modulation of nanopores within NAA-μCVs is more evident as the nanoporous structure of NAA is chemically etched, since those layers produced at lower anodizing current density dissolve at a faster rate than those produced at higher \( J \) (Figure S1 – Supporting Information). However, the over-etching of the NAA-μCVs’ structure \( (t_{pw} > 4 \text{ min}) \) results in a broadening of the resonance band and a decrement of its intensity due to light scattering by the overall PC structure (Figure S2 – Supporting Information). So, for NAA-μCVs produced at \( t_{An} = 5, 10, \text{ and } 15 \text{ h} \), the resonance band is almost vanished from the transmission spectrum at \( t_{pw} = 6 \text{ min} \). To further extend the analysis on the effect of \( t_{An} \) on the optical properties of NAA-μCVs produced by ASPA, we fabricated another set of NAA-μCVs under the same conditions (i.e. \( J_{\text{offset}} = 0.280 \text{ mA cm}^{-2}, \Delta A_J = 0.210 \text{ mA cm}^{-2} \), and \( t_{An} = 5, 10, 15, 20, \text{ and } 25 \text{ h} \)) but setting the anodization period at \( T_p = 1200 \text{ s} \). Figure 3b shows representative anodization profiles of these NAA-μCVs produced at \( T_p = 1200 \text{ s} \), showing how the anodizing current density (input) is directly translated into voltage (output) changes in a dynamic fashion, without apparent delay. Figures 6a-e show the transmission spectra of NAA-μCVs produced with \( T_p = 1200 \text{ s} \), which also include digital pictures displaying the characteristic interferometric color of these PC structures. As these graphs indicate, the PSB of these NAA-μCVs is located within the visible-NIR region of the spectrum, although slightly blue-shifted as compared to their \( T_p = 1300 \text{ s} \) counterparts. As demonstrated in previous studies, this blue shift is associated with the reduction of the anodization period, which results in a shorter period length \( (L_{TP}) \) within the nanoporous structure of NAA-μCVs.\textsuperscript{43-59} The transmission spectra of these NAA-μCVs displays a PSB that increases its intensity with \( t_{pw} \) and a well-defined resonance band at the center of the PSB. Figures 7a-e compile magnified views of the resonance bands observed in the transmission spectra of these NAA-μCVs (Figures 6a-e), with details of Gaussian fittings used to estimate \( \lambda_R, \text{FWHM}_R, \text{and } Q_c. \)
Figure 6. Combinational effect of anodization time ($t_{an}$) and pore widening time ($t_{pw}$) on the transmission spectrum of NAA-µCVs produced by ASPA at $T_p = 1200$ s (note: color rectangles denote the approximate position of the resonance band within the PSB and black dotted arrow lines indicate the blue shift of the resonance bands with $t_{pw}$). a) $t_{an} = 5$, b) $t_{an} = 10$, c) $t_{an} = 15$, d) $t_{an} = 20$, and e) $t_{an} = 25$ h. Insets in a-e display digital pictures of these photonic crystal structures showing vivid interferometric colors when the resonance band is located within the visible region and transparent when the band is within the UV or NIR spectral regions.

The quality factor ($Q_C$), defined as the ratio of the resonance band wavelength ($\lambda_R$) to its full width at half maximum ($FWHM_R$) (Equation 5), is an important criteria in assessing the strength of photon confinement within optical microcavities.\textsuperscript{64,65} The $Q_C$ of these NAA-µCVs was estimated by fitting the resonance bands shown in Figures 5 and 7 to Gaussian envelopes, using as a baseline the lower love of the PSB as indicated by the horizontal dotted black lines showed in these graphs.
Figure 7. Combinational effect of anodization time ($t_{an}$) and pore widening time ($t_{pw}$) on the resonance band of NAA-$\mu$CVs produced by ASPA at $T_p = 1200$ s (note: horizontal dotted black lines denote the baseline ($y_0$) used for the Gaussian fittings, which correspond to the lower lobe of the PSB, and vertical dotted red lines indicate the central wavelength of the resonance band ($\lambda_R$) and the symmetry of the Gaussian fitting). a) $t_{an} = 5$, b) $t_{an} = 10$, c) $t_{an} = 15$, d) $t_{an} = 20$, and e) $t_{an} = 25$ h.
A summary of the estimated values of $y_0$, $\lambda_R$, FWHM$_R$ and $Q_C$ are compiled in Tables S1-S3 (Supporting Information) along with the quality ($R^2$) of these Gaussian fittings. Figure 8 shows contour maps summarizing the dependency of $Q_C$ and $\lambda_R$ with $t_{An}$ and $t_{pw}$ for NAA-$\mu$CVs produced with $T_P = 1200$ and 1300 s, $J_{offset} = 0.280$ mA cm$^{-2}$, and $\Delta A_J = 0.210$ mA cm$^2$.

Figure 8a shows the dependency of $Q_C$ on $t_{An}$ and $t_{pw}$ for NAA-$\mu$CVs fabricated with $T_P = 1300$ s. It is apparent that $Q_C$ becomes more dependent on these fabrication parameters at short pore widening times (i.e. from $t_{pw} = 0$ to 2 min) and longer anodization times (i.e. from $t_{An} = 15$ to 25 h). This trend is denoted by a closer and denser concentration of color fields around the $Q_C$ maximum (i.e. $Q_C = 63.1 \pm 1.2$), which is located at $t_{pw} = 2$ min and $t_{An} = 20$ h. In general, an increase in $t_{an}$ leads to an enhancement of the $Q_C$ of NAA-$\mu$CVs, while longer pore widening times worsen the quality factor of the NAA-$\mu$CVs. The relationship between $\lambda_R$ with $t_{An}$ and $t_{pw}$ for NAA-$\mu$CVs produced with $T_P = 1300$ s is displayed in Figure 8b, where it can be clearly observed that the distance between color fields is closer as $t_{An}$ is reduced from 10 to 5 h. This indicates a strong dependency of $\lambda_R$ with $t_{An}$ at shorter anodization times. Furthermore, it is observed that $\lambda_R$ is blue-shifted with $t_{pw}$ across the UV-visible spectrum from $t_{An} = 5$ to 25 h. This analysis also reveals that the effect of $t_{An}$ on the position of the resonance band is not as significant as that of $t_{pw}$, since only a slight red shift is observed as $t_{An}$ increases from 5 to 20 h, and a slight blue shift from 20 to 25 h, achieving its maximum value (i.e. $725 \pm 1$ nm) at $t_{An} = 5$ h and $t_{pw} = 0$ min.

The distribution of $Q_C$ and $\lambda_R$ for NAA-$\mu$CVs produced at $T_P = 1200$ s with $t_{An}$ and $t_{pw}$ is presented in Figures 8c and d, respectively. The contour map shown in Figure 8c reveals a concentration of color fields at the region of longer $t_{An}$ and shorter $t_{pw}$, achieving a local maximum of $Q_C$ (i.e. $112.6 \pm 5.2$) at $t_{An} = 20$ h and $t_{pw} = 2$ min, which is the highest quality factor reported for a NAA-based optical microcavity to date.
Figure 8. Combinational effect of anodization time ($t_{\text{An}}$) and pore widening time ($t_{\text{pw}}$) on the optical properties of NAA-$\mu$CVs (i.e. quality factor – $Q_C$, position of resonance band – $\lambda_R$, and interferometric color) produced by ASPA. a) Contour map showing the dependency of $Q_C$ with $t_{\text{An}}$ and $t_{\text{pw}}$ for NAA-$\mu$CVs produced with $T_P = 1300$ s. b) Contour map showing the dependency of $\lambda_R$ with $t_{\text{An}}$ and $t_{\text{pw}}$ for NAA-$\mu$CVs produced with $T_P = 1300$ s. c) Contour map showing the dependency of $Q_C$ with $t_{\text{An}}$ and $t_{\text{pw}}$ for NAA-$\mu$CVs produced with $T_P = 1200$ s. d) Contour map showing the dependency of $\lambda_R$ with $t_{\text{An}}$ and $t_{\text{pw}}$ for NAA-$\mu$CVs produced with $T_P = 1200$ s. e) Digital images showing the interferometric color displayed by NAA-$\mu$CVs produced with $T_P = 1200$ s as a function of $t_{\text{An}}$ and $t_{\text{pw}}$. f) Digital images showing the interferometric color displayed by NAA-$\mu$CVs produced with $T_P = 1300$ s as a function of $t_{\text{An}}$ and $t_{\text{pw}}$. 
The distance between field lines around the local maximum is shorter, indicating a stronger dependency of $Q_C$ on $t_{An}$ and $t_{pw}$ around that set of fabrication conditions. In contrast, the combination of shorter $t_{An}$ (i.e. 5 to 15 h) and longer $t_{pw}$ (i.e. 4 to 6 min) worsens $Q_C$ as the distance between field lines and color fields is relatively broad at these areas. Figure 8d shows how $t_{An}$ and $t_{pw}$ affect $\lambda_R$ of NAA-µCVs produced at $T_P = 1200$ s. This graph denotes a homogenous but broad distribution of color fields with equidistant field lines throughout, from $t_{An} = 5$ to 25 h and from $t_{pw} = 0$ to 4 min, which indicates a weak dependency of $\lambda_R$ on $t_{An}$ and $t_{pw}$ at these combinations of fabrication parameters. As $t_{pw}$ increases from 4 to 6 min and $t_{An}$ decreases from 10 to 5 h, $\lambda_R$ shows a stronger dependency with these parameters, as suggested by the closer field lines and high density of color fields. $\lambda_R$ is red-shifted as $t_{An}$ increases from 5 to 20 h and slightly blue-shifted when $t_{An}$ increases from 20 to 25 h. The maximum value of $\lambda_R$ (i.e. 665 ± 1 nm) is achieved at $t_{An} = 20$ h and $t_{pw} = 2$ min. Furthermore, this analysis also reveals that $t_{pw}$ blue-shifts the resonance band of NAA-µCVs produced at $T_P = 1200$ s as $t_{pw}$ increases. The comparative analysis of Figures 8a and c reveals that a combination of long $t_{An}$ (i.e. from 15 to 25 h) and short $t_{pw}$ (i.e. from 0 to 2 min) results in high quality NAA-µCVs with narrow and well-resolved resonance bands. The average $Q_C$ estimated for NAA-µCVs produced with $T_P = 1200$ and 1300 s were $46.4 \pm 24.8$ and $33.7 \pm 13.8$, respectively. It is worthwhile noting that only one of the NAA-µCVs produced at 1300 s showed superior light-confining performance than those reported in previous studies (i.e. $Q_C = 63.1 \pm 1.2$ for NAA-µCV produced with $T_P = 1300$ s, $t_{pw} = 2$ min and $t_{An} = 20$ h – Wang et al. (24), Lee et al. (55) and Yan et al. (41)). However, up to six NAA-µCVs produced with $T_P = 1200$ s showed superior properties to confine light than previously NAA-based optical microcavities (i.e. $Q_C = 64.0 \pm 1.0$ at $t_{pw} = 2$ min and $t_{An} = 10$ h, $Q_C = 70.5 \pm 2.1$ at $t_{pw} = 4$ min and $t_{An} = 10$ h, $Q_C = 66.0 \pm 1.3$ at $t_{pw} = 6$ min and $t_{An} = 15$ h, $Q_C = 75.2 \pm 3.1$ at $t_{pw} = 0$ min and $t_{An} = 20$ h, $Q_C = 112.6 \pm 5.2$ at $t_{pw} = 2$ min and $t_{An} = 20$ h, and $Q_C = 73.5 \pm 2.6$ at $t_{pw} = 0$ min and $t_{An} = 20$ h).
at $t_{pw} = 4$ min and $t_{An} = 20$ h). Although both types of NAA-µCVs have a weak correlation between the shift in $\lambda_R$ with $t_{An}$, Figures 8b and d show that the $\lambda_R$ of NAA-µCVs produced at $T_p = 1300$ s evolves in a slightly different manner with $t_{An}$ as compared to NAA-µCVs fabricated at $T_p = 1200$ s. This graph also indicates that, as observed in the transmission spectra (Figures 4 and 6) the position of the PSB and resonance bands of NAA-µCVs produced at $T_p = 1200$ s is blue-shifted as compared to their equivalent NAA-µCVs fabricated at $T_p = 1300$ s. It is also observed that both sets of NAA-µCVs show a stronger dependency of $\lambda_R$ with $t_{pw}$ than that shown for $t_{An}$. A pore widening treatment blue-shifts the position of the respective resonance bands, and the longer $t_{pw}$ is, the shorter the wavelength where the resonance band is positioned at. It is worthwhile to note that, for a given $t_{pw}$, the position of the resonance band of NAA-µCVs at $T_p = 1300$ s is located at longer wavelengths than that of NAA-µCVs produced with $T_p = 1200$ s due to the red shift associated with the longer anodization period and longer period length. Another interesting optical property of NAA-µCVs is their vivid interferometric colors, which correspond to the wavelength of their respective PSB and $\lambda_R$ when these are positioned within the visible range of the spectrum.

Figures 8e and f compile digital images of NAA-µCVs produced at $T_p = 1200$ and 1300 s as a function of $t_{An}$ and $t_{pw}$, respectively. The analysis of these images is in good agreement with the results obtained in Figures 8b and d, where the $\lambda_R$ is blue-shifted with $t_{pw}$. It is also apparent that $\lambda_R$ is red-shifted with increasing $t_{An}$ from 5 to 20 h and slightly blue shifted from $t_{An} = 20$ to 25 h.

3.3. Effect of Anodization Period ($T_p$) on the Optical Properties of Nanoporous Anodic Alumina Microcavities. To demonstrate the tuneability of the position of the resonance band across the spectral regions and to further optimize the quality of NAA-µCVs produced by ASPA, we produced a set of NAA-µCVs with different $T_p$, where this fabrication parameter
was systematically modified from 800 to 1300 s with $\Delta T_P = 100$ s, while keeping constant $J_{offset}$ and $\Delta A_J$ at 0.280 mA cm$^{-2}$ and 0.210 mA cm$^{-2}$, respectively. The anodization profiles and transmission spectra of these NAA-$\mu$CVs are shown in Figure S3 (Supporting Information) and Figure 9, respectively. Figures 9a-d show the transmission spectra of these NAA-$\mu$CVs as a function of $T_P$ and $t_{pw}$ (i.e. from 0 to 6 min) and Figure 10 shows magnified views of the resonance bands and Gaussian fittings used to estimate $\lambda_R$, $\text{FWHM}_R$ and $Q_C$. In all these cases it is verified that the PSB and resonance band of theses NAA-$\mu$CVs is red-shifted with $T_P$ and blue shifted with $t_{pw}$. Note that those NAA-$\mu$CVs produced with $T_P > 800$ s also showed second and third order PSBs. NAA-$\mu$CVs fabricated with $T_P = 900$ s have both first and second order PSBs, while NAA-$\mu$CVs produced at $T_P = 1000, 1100, 1200$ and 1300 s show second and third order PSBs. However, the first order PSB plays the primary role in determining the optical properties of NAA-$\mu$CVs since this band is much more intense and well-resolved than their higher order counterparts. At $t_{pw} = 0$ min (Figure 9a), all NAA-$\mu$CVs display a weak resonance band within their first order PSB, which is in the range of 400 to 700 nm and red-shifted with $T_P$. As $T_P$ increases, the intensity of the resonance band increases and shifts its position ($\lambda_R$) toward the NIR spectral region. As the digital pictures shown in Figures 9a-d (insets) indicate, for a given $t_{pw}$ the interferometric color of these NAA-$\mu$CVs is red-shifted with $T_P$. For instance, at $t_{pw} = 0$ min, the interferometric color of NAA-$\mu$CVs changes from transparent (i.e. UV region) ($T_P = 800$ s), blue ($T_P = 900$ s), green ($T_P = 1000$ s), orange ($T_P = 1100$ s) to transparent (i.e. NIR region) ($T_P = 1200$ and 1300 s) as $T_P$ increases. It is also verified that the resonance band increases its intensity and it is blue-shifted with a pore widening treatment (i.e. $t_{pw}$ increases), which is in good agreement with our previous observation.
Figure 9. Combinational effect of anodization period (T_P) and pore widening time (t_{pw}) on the optical properties of NAA-µCVs (i.e. quality factor – Q_C, position of resonance band – λ_R, and interferometric color) produced by ASPA. a-d) Transmission spectra showing the position of the resonance band (colored rectangles) and digital pictures (insets) of NAA-µCVs for each anodization period (T_P = 800–1300 s) at different pore widening times (i.e. a) t_{pw} = 0 min, b) t_{pw} = 2 min, c) t_{pw} = 4 min, and d) t_{pw} = 6 min).
Figure 10. Combinational effect of anodization period ($T_p$) and pore widening time ($t_{pw}$) on the resonance band of NAA-$\mu$CVs produced by ASPA (note: horizontal dotted black lines denote the baseline ($y_0$) used for the Gaussian fittings, which correspond to the lower lobe of the PSB, and vertical dotted red lines indicate the central wavelength of the resonance band ($\lambda_R$) and the symmetry of the Gaussian fitting). a) $t_{pw} = 0$ min. b) $t_{pw} = 2$ min. c) $t_{pw} = 4$ min. d) $t_{pw} = 6$ min. e) Contour map showing the dependency of $Q_c$ with $T_p$ and $t_{pw}$ for NAA-$\mu$CVs produced with $T_p = 800$–1300 s. f) Contour map showing the dependency of $\lambda_R$ with $T_p$ and $t_{pw}$ for NAA-$\mu$CVs produced with $T_p = 800$–1300 s.
Figures 10e and f show contour maps depicting the graphical correlation of $Q_C$ and $\lambda_R$ of NAA-µCVs with $T_p$ and $t_{pw}$ (Table S2). Figure 10e reveals that the color fields in the region of shorter $T_p$ (i.e. from 800 to 1000 s) are relatively broad across $t_{pw}$, from 0 to 6 min, which is a visual indication of the weak correlation of $Q_C$ with the fabrication parameters for NAA-µCVs produced at shorter $T_p$. Therefore, NAA-µCVs produced at $T_p = 800, 900$ and $1000$ s have low $Q_C$. In contrast, the color fields become denser with closer field lines when $T_p$ increases from 1100 to 1300 s. This suggests that $Q_C$ has a stronger dependency with longer $T_p$, where the maximum of $Q_C$ (i.e. $112.6 \pm 5.2$) is achieved at $T_p = 1200$ s and $t_{pw} = 2$ min. The average $Q_C$ estimated for NAA-µCVs as a function of $T_p$, excluding those PCs without resonance band, was $44.5 \pm 23.1$. However, seven of these NAA-µCVs showed superior light-confining performance than those reported in previous studies (i.e. $Q_C = 56.8 \pm 3.2$ at $T_p = 900$ s and $t_{pw} = 4$ min, $Q_C = 60.2 \pm 2.1$ at $T_p = 1000$ s and $t_{pw} = 0$ min, $Q_C = 56.5 \pm 1.5$ at at $T_p = 1100$ s and $t_{pw} = 2$ min, $Q_C = 75.2 \pm 3.3$ at $T_p = 1200$ s and $t_{pw} = 0$ min, $Q_C = 112.6 \pm 5.2$ at $T_p = 1200$ s and $t_{pw} = 2$ min, $Q_C = 73.5 \pm 4.1$ at $T_p = 1200$ s and $t_{pw} = 4$ min, and $Q_C = 63.1 \pm 1.2$ at $T_p = 1300$ s and $t_{pw} = 2$ min). The distribution of $\lambda_R$ as a function of $T_p$ and $t_{pw}$ is depicted in Figure 10f. This graph shows two local minima in the contour plot due to the absence of resonance bands within the PSB of these NAA-µCVs, which are located at $t_{pw} = 0$ min for $T_p = 1100$ s as well as at $t_{pw} = 6$ min for $T_p = 800$ s. At $t_{pw} = 2$ and $4$ min, the color distribution reveals a red shift in $\lambda_R$ resulting from the manipulation of $T_p$ from 800 to 1300 s, where the longest resonance wavelength is achieved at $T_p = 1300$ s and $t_{pw} = 0$ min (i.e. $709 \pm 1$ nm). In general, the longer the anodization period, the longer the wavelength at which NAA-µCVs confine light. This analysis also indicates that an increase in $t_{pw}$ results in a blue shift of $\lambda_R$, thus NAA-µCVs confine light of shorter wavelengths although in a less efficient manner as indicated by the $Q_C$ analysis shown in Figure 10e due to light scattering effect.
3.4. Effect of Current Density Offset ($J_{\text{offset}}$) on the Optical Properties of Nanoporous Anodic Alumina Microcavities. To further understand the effect of the different fabrication parameters on the photonic features of NAA-µCVs produced by ASPA, we investigated the how the current density offset ($J_{\text{offset}}$) affects the quality factor and the tuning of resonance bands of NAA-µCVs. To this end, $J_{\text{offset}}$ was systematically modified from 0.140 to 0.560 mA cm$^{-2}$ with an interval of 0.140 mA cm$^{-2}$ while keeping constant the rest of fabrication parameters (i.e. $T_P = 1300$ s, $J_{\text{offset}} = 0.280$ mA cm$^{-2}$, and $\Delta A_J = 0.210$ mA cm$^{-2}$). The anodization profiles of NAA-µCVs produced at different $J_{\text{offset}}$ are compiled in Figure S4 (Supporting Information). The transmission spectra of these NAA-µCVs shown in Figures 11a-d were analyzed to establish the effect of this fabrication parameter on $Q_C$ and $\lambda_R$.

Figure 11a shows the transmission spectra of NAA-µCVs produced at $J_{\text{offset}} = 0.140$ mA cm$^{-2}$ as a function of $t_{\text{pw}}$ (i.e. 0 to 6 min). The PSB of this set of NAA-µCVs is located within the visible region, with a very weak resonance band that is almost vanished at long pore widening times (i.e. $t_{\text{pw}} > 2$ min). The pore widening treatment blue-shifts the position of the PSB and leads the NAA-µCV to lose its light-confining characteristics. The transmission spectra shown in Figure 11b reveals that the position of the PSB of NAA-µCVs produced at $J_{\text{offset}} = 0.280$ mA cm$^{-2}$ are located within the upper range of visible spectrum (i.e. 600–800 nm). Unlike NAA-µCVs produced at $J_{\text{offset}} = 0.140$ mA cm$^{-2}$, the resonance band of these NAA-µCVs ($J_{\text{offset}} = 0.280$ mA cm$^{-2}$) remains well-resolved and sharp after pore widening from 0 to 6 min. On the other hand, both sets of NAA-µCVs produced at $J_{\text{offset}} = 0.420$ and 0.560 mA cm$^{-2}$ have their PSBs located in the NIR range (i.e. 900–1100 nm) (Figures 11c and d). These NAA-µCVs also show the presence of an intense resonance band within their PSB, which is slightly widen and blue-shifted with the pore widening treatment, from 0 to 6 min.
Figure 11. Combinational effect of anodization offset \( (J_{\text{offset}}) \) and pore widening time \( (t_{\text{pw}}) \) on the optical properties of NAA-µCVs (i.e. quality factor – \( Q_C \), position of resonance band – \( \lambda_R \), and interferometric color) produced by ASPA. a-d) Transmission spectra showing the position of the resonance band, digital pictures (insets) of NAA-µCVs for each anodization offset \( (J_{\text{offset}}) = 0.140–0.560 \text{ mA cm}^{-2} \) at different pore widening times (from 0 to 6 min) (i.e. a) \( J_{\text{offset}} = 0.140 \text{ mA cm}^{-2} \), b) \( J_{\text{offset}} = 0.280 \text{ mA cm}^{-2} \), c) \( J_{\text{offset}} = 0.420 \text{ mA cm}^{-2} \), and d) \( J_{\text{offset}} = 0.560 \text{ mA cm}^{-2} \) (note: color rectangles denote the approximate position of the resonance band within the PSB and black dotted arrow lines indicate the blue shift of the resonance bands with \( t_{\text{pw}} \)).
By comparing the transmission spectra at different $J_{\text{offset}}$, it is apparent that an increase in $J_{\text{offset}}$ causes a red shift in the position of resonance band. As the digital images shown in the insets in Figures 11a-d demonstrate, these NAA-µCVs display vivid interferometric colors, which are affected by the fabrication parameters: $J_{\text{offset}}$ and $t_{\text{pw}}$. Although these NAA-µCVs show second and third order PSBs, the color displayed by these PCs corresponds to the wavelength at which the first order PSB is located, denoting a more efficient reflection of light within these spectral regions. In this case, NAA-µCVs produced at lower $J_{\text{offset}}$ (i.e. 0.140 and 0.280 mA cm$^{-2}$) display vivid colors corresponding to the position of their PSB in the visible spectral range. In contrast, the PSBs of NAA-µCVs produced with high $J_{\text{offset}}$ (i.e. 0.420 and 0.560 mA cm$^{-2}$) are within the NIR range, thus no color is observed (i.e. transparent – black). Figures 12a-d show magnified views of the resonance bands and Gaussian fittings used to estimate $\lambda_R$, $FWHM_R$ and $Q_C$ for these NAA-µCVs and Figures 12e and f compile a summary of the estimated values for $Q_C$ and $\lambda_R$ in the form of contour maps.

The visual analysis of the magnified resonance bands shown in Figures 12a-d reveals that, in general, the intensity of the resonance band increases with $J_{\text{offset}}$ and decreases with $t_{\text{pw}}$. A closer analysis of the values of $Q_C$, visually shown in Figure 12e and compiled in Table S3 (Supporting Information), reveals that the combination of low values of $J_{\text{offset}}$ (e.g. 0.140-0.280 mA cm$^{-2}$) and moderate pore widening times (i.e. 2-4 min) are favorable in the production of NAA-µCVs with high quality resonance bands. The $Q_C$ maximum is achieved by NAA-µCVs produced with $J_{\text{offset}} = 0.140$ mA cm$^{-2}$ and $t_{\text{pw}} = 4$ min (i.e. 65.5 ± 2.3), although these PC structure show considerably weaker resonance bands as compared to their counterparts produced at higher $J_{\text{offset}}$ (i.e. > 0.140 mA cm$^{-2}$). The dependency of $Q_C$ on $J_{\text{offset}}$ increases within the range 0.140-0.420 mA cm$^{-2}$, as denoted by the denser color fields with short distance between adjacent field lines.
Figure 12. Combinational effect of current density offset ($J_{\text{Offset}}$) and pore widening time ($t_{\text{pw}}$) on the resonance band of NAA-µCVs produced by ASPA (note: horizontal dotted black lines denote the baseline ($y_0$) used for the Gaussian fittings, which correspond to the lower lobe of the PSB, and vertical dotted red lines indicate the central wavelength of the resonance band ($\lambda_R$) and the symmetry of the Gaussian fitting). a) $J_{\text{Offset}} = 0.140$ mA cm$^{-2}$, b) $J_{\text{Offset}} = 0.280$ mA cm$^{-2}$, c) $J_{\text{Offset}} = 0.420$ mA cm$^{-2}$, and d) $J_{\text{Offset}} = 0.560$ mA cm$^{-2}$. e) Contour map showing the dependency of $Q_C$ with $J_{\text{Offset}}$ and $t_{\text{pw}}$ for NAA-µCVs produced with $J_{\text{Offset}} = 0.140–0.560$ mA cm$^{-2}$. f) Contour map showing the dependency of $\lambda_R$ with $J_{\text{Offset}}$ and $t_{\text{pw}}$ for NAA-µCVs produced with $J_{\text{Offset}} = 0.140–0.560$ mA cm$^{-2}$.

The broad color fields and more separated field lines at the region of high $J_{\text{offset}}$ and long $t_{\text{pw}}$ suggest a weak dependency of $Q_C$ with these combinations of fabrication parameters, which worsens the quality of the microcavity structure. The average $Q_C$ estimated for NAA-µCVs as a function of $J_{\text{Offset}}$ was $39.1 \pm 18.4$ and five of these NAA-µCVs showed slightly superior light-confining performance than those reported in previous studies (i.e. $Q_C = 61.7 \pm 2.2$ at $J_{\text{Offset}} = 0.140$ mA cm$^{-2}$ and $t_{\text{pw}} = 0$ min, $Q_C = 62.5 \pm 3.4$ at $J_{\text{Offset}} = 0.140$ mA cm$^{-2}$ and $t_{\text{pw}} = 2$ min, $Q_C = 65.5 \pm 3.6$ at $J_{\text{Offset}} = 0.140$ mA cm$^{-2}$ and $t_{\text{pw}} = 4$ min, $Q_C = 61.9 \pm 2.4$ at $J_{\text{Offset}} = 0.560$ mA cm$^{-2}$ and $t_{\text{pw}} = 6$ min).
0.140 mA cm\(^{-2}\) and \(t_{pw} = 6\) min, and \(Q_C = 63.1 \pm 1.2\) at \(J_{offset} = 0.280\) mA cm\(^{-2}\) and \(t_{pw} = 2\) min. The effect of \(J_{offset}\) and \(t_{pw}\) on the position of the resonance band of NAA-µCVs is summarized in the contour map shown in Figure 12f. This contour map shows that the field line distances at low \(J_{offset}\) (i.e. \(J_{offset} < 0.280\) mA cm\(^{-2}\)) and high \(J_{offset}\) (i.e. \(J_{offset} > 0.420\) mA cm\(^{-2}\)) are relatively wide. However, the color fields become closer with shorter equidistant field lines for \(J_{offset}\) between 0.280 and 0.420 mA cm\(^{-2}\), which indicates a stronger dependency of \(\lambda_R\) with \(J_{offset}\) within that range of fabrication parameters. It is verified that \(\lambda_R\) is red-shifted towards the NIR region by increasing \(J_{offset}\). The higher \(J_{offset}\) is, the longer the wavelength at which light is confined within the structure of NAA-µCVs produced by ASPA. The maximum value of \(\lambda_R\) (i.e. 1096 \pm 1 nm) is located at \(J_{offset} = 0.560\) mA cm\(^{-2}\) and \(t_{pw} = 0\) min. An increase in \(t_{pw}\) has an opposite effect to that of \(J_{offset}\) on the shifting of \(\lambda_R\). However, \(J_{offset}\) has a more significant effect on the position of the resonance band as denoted by the color field distribution.

CONCLUSIONS

In summary, this study has demonstrated that a rational design of the nanoporous structure of NAA-based optical microcavities using apodized stepwise pulse anodization can lead to an enhancement of the light-confining capabilities of these PCs. The structure of these optical microcavities is composed of two apodized NAA-DBRs, which can confine light efficiently (i.e. \(Q_C = 112.6 \pm 5.2\)). Furthermore, this nanofabrication approach enables the fine-tuning of the optical properties of the two highly reflective mirrors so light can be confined within the PC structure more efficiently across the spectral regions. The optical properties of NAA-based optical microcavities were assessed in terms of quality factor, position of resonance band, and interferometric colors. The anodization parameters investigated were anodization period, anodization time, current density offset and pore
widening time. A systematic modification of these parameters allowed to establish optimization paths toward more efficient light-confining NAA-based PC structures.

In general, our study established that a combination of longer anodization time, longer anodization period, short pore widening time, and moderate current density offset generates optical microcavities with high quality factor, where the most optimal NAA-µCV was that produced with 20 h anodization time, 1200 s anodization period, 2 min of pore widening, and 0.280 mA cm$^{-2}$ of current density offset. Our results provide a better understanding and solid foundation to further enhance the light-confining capabilities of NAA-based optical microcavities, opening new opportunities for further fundamental and applied research for these nanoporous PC structures in optical sensing, photonics, and optoelectronics.

**Supporting Information**

The Supporting Information file provides information about the structure of NAA-µCVs at different pore widening times, anodization profiles of NAA-µCVs produced by ASPA at different anodization periods, from 800 to 1300 s, and current density offsets, from 0.140 to 0.560 mA cm$^{-2}$, and a compilation of the values of $y_0$, $\lambda_R$, $FWHM_R$, $Q_C$, and $R^2$.

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REFERENCES


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