

Review

Recent Progress in the Fabrication of Photonic Crystals Based on Porous Anodic Materials

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Abstract: Photonic crystals (PCs) based on porous anodic materials have been proven to be a potent and versatile instrument for the emergence of new technologies with a wide range of applications. Their lower production costs are one of the key advantages, making PC-based systems more widely available and appropriate for industrial manufacturing. The ability to produce well-defined pores on metal oxide and semiconductor surfaces has experienced a major renaissance due to the striking differences in characteristics between porous surfaces and dense oxide layers. In this review, we give a general overview of the progress of PC fabrication based on porous surfaces of anodized aluminum (Al), silicon (Si), and titanium (Ti) using various anodization techniques, and their optical characteristics and applications are discussed. The anodizing conditions have a large influence on the pore geometry of the produced porous surfaces. The review fully focuses on the advancements made in manufacturing anodic aluminum oxide (AAO), porous silicon (pSi), and titanium-dioxide nanotube (TNT) PCs manufactured using self-ordered anodization under varied conditions. Additionally, a critical assessment of the upcoming developments in PC manufacturing and their optical characteristics suitable for various photonic devices is provided.

Keywords: anodic aluminum oxide (AAO); anodic porous silicon (pSi); titanium nanotubes (TNTs); photonic crystal; optical sensor; refractive index



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1. Introduction

PCs are specialized periodic light-capturing optical structures and hence can be used for the diffraction-grating phenomenon, which takes place at the bandgap of PCs where a certain wavelength/frequency of light is trapped [1–6]. Based on the dimensionality of their periodic arrangement, PCs are classified into one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D). One-dimensional PCs are made up of alternating layers of materials with various dielectric properties. The structure forbids light of a specific wavelength/frequency to pass through the stack layers, and therefore, the material functions as a Bragg mirror [7–11]. Two-dimensional PCs are those with a variable refractive index (RI) in two normal directions and can be synthesized using etching, spin-coating, or constrained convective-assembly processes [7,8,12]. Opal and inverse opal are two prominent cases of 3D PCs. Generally, PCs can alter photon mobility similar to how semiconductor crystals impact electron motion. According to the structural and optical properties of the multi-layer, the change in RI results in optical-interference effects that block specific wavelength bands. These periodic dielectrics are applied in a diverse range of technical domains as passive and active optical components. Rigorous regulation of the photon mode density at certain spectrum regions can be achieved via thoughtful design of the RI. The periodic arrangement of arrays in dielectric materials such as metal oxide results in a photonic bandgap (PBG). Only certain frequencies/wavelengths of light can propagate through this bandgap, and the rest of the light cannot pass freely. PCs are the ideal optics elements

because of their excellent light-controlling characteristics [13–16]. In addition, PCs are incredibly significant compounds due to the variety of uses they have in all areas of life. PCs have a high surface area and promising optical and structural features, making them one of the most promising elements for different applications. PCs have many benefits over conventional sensing tools, including sensitivity, mobility, consistency, and online result monitoring [17–19]. The diffraction mechanism of PCs, as postulated by Yablonovitch and John [20–22], can be described by Bragg's law: $2nd\sin\theta = m\lambda$, where n presents the RI, d is the lattice-plate spacing, m is the diffraction order, λ is the incoming light wavelength, and θ is the material glancing angle [23,24]. PCs are the most complex sensors for many sensing applications because they improve sensitivity, selectivity, and fluorescence owing to a PBG at a certain wavelength.

Designing 1D PCs based on porous, transparent, and insulator materials is gaining increasing interest in broad research and development areas. In these materials, modulation of the RI is carried out by periodically changing porosity in a monolithic material. The presence of pores with diverse dimensions and architectural configurations has provided new opportunities for the use of porous optical materials such as PCs, amongst other applications, including biological and chemical sensing [25–29], recognition and detection [30], photovoltaics [31], conducting [32], photoconductive coating [33], radiation shielding [34,35], and light emission [36]. PC-based pSi served as the first and most flexible platform for exploring the potential interactions between controlled mass movement, made possible by the presence of accessible and interconnected porosity.

In reality, great progress has been made in the field of optical sensing of numerous species that may be hazardous to the surroundings and environment, based on pSi PCs with functionalized inner walls [37]. The sensing idea has been expanded to include other materials in recent years, greatly expanding the range of possible applications for these kinds of structures. Conventional microfabrication techniques from the microelectronics sector have been used to generate porous structures (e.g., photolithography and electron-beam lithography). Although these techniques offer the necessary structural accuracy, obtaining nanometric structures necessitates an expensive, intricate approach that can only be applied to a tiny area of materials [38]. In addition, inverse opal templating [39], glancing-angle deposition (GLAD) [40], layer-by-layer (LBL) assembly [41,42], and sol–gel methods [43,44] are potential alternative approaches that suffer from their flaws. For example, the GLAD approach necessitates expensive hardware and labor-intensive software, the LBL method entails numerous wet steps that are prone to attack and mix more composites, and the sol–gel method lacks the accuracy of nanostructure engineering. Structure abnormalities can occur while using the inverted-opal-template approach.

Although there are alternative techniques to construct PCs [45–48], electrochemical methods such as the anodizing method are a fantastic way to produce regular porous materials or PCs precisely and affordably [49]. The electrochemistry approach opens a brand-new book on the mass manufacture of self-organized nanoporous materials [50–52]. Over the past ten years, a significant amount of literature has been published about electrochemical approaches. Consequently, there has been a lot of interest in the anodization technique because of its short response times and low cost. The ability to adjust the anodization conditions fully programmatically at nanoscale enables precise adjustments of the interpore distance, pore size, and length, which results in low manufacturing costs. A collection of PCs that have recently undergone anodizing are made of silicon (Si) [53,54], titanium (Ti) [55,56], and aluminum (Al) [57–60]. Anodic pSi, with clearly defined periodic structures, stands out among them as an optical material with tremendous advantages [51,61–63]. Anodic aluminum-oxide (AAO) membrane acts as a model system for particle separation and molecule adsorption as well as a template for functional nanomaterials [64–66]. Anodic titanium-dioxide (TiO₂) nanotubes (TNTs) with unique topologies have multiple uses for cleaning the environment and regenerating energy [67–69]. It has been shown that PCs can modify light in the spectra areas of UV (10–400 nm) [70–72], visible (400–700 nm), near-infrared (700–2500 nm) [70–73], and mid-infrared (8–28 μ m) [74]. The capacity to accurately

design mono- or multi-ordered morphology along the channel remains a challenge, even though their dimensional characteristics, such as wall thickness, channel length, and pore diameter, have been thoroughly defined [50–52,67]. For material systems, the impacts of electrochemical factors on the fabrication of hollow nanostructures are empirical due to the limited fundamental research of the growth mechanisms behind morphological complexity. Many outstanding review papers and books [50–52,75] have focused on the applications of porous nanostructures. In an ongoing attempt to take advantage of the special properties of porous nanostructures, the mechanisms and technologies of anodization are examined, with an emphasis on fundamental anodic parameters [50–52].

In this review, we provide an overview of the progress of PC fabrication based on anodization, under different anodization conditions, of the surface of some metals (e.g., Al and Ti) and semiconductors (e.g., Si) and their optical properties and applications. PCs with a self-ordered porous structure of AAO, pSi, and TNTs were examined, and key optical and electrochemical features were displayed. The morphology of synthesized materials is presented and the effects of the anodizing conditions are discussed. In addition, the appropriate status of engineering nanoporous materials is discussed and mechanisms behind the morphological complexities are explained. Finally, we provide insight into future trends in this field of study as well as future advances in porous PCs for various applications.

2. Fabrication of PCs by Anodization Method

Usually, the electrochemical etching or anodization method changes the valve metal surface to a long-lasting, attractive, and corrosion-resistant anodic-oxide finish. For example, AAO is integrated with the underlying metal substrate rather than being applied to the surface like paint or plating; thus, it will not chip or peel. The anodization process is achieved by dipping Al in an acid bath and applying voltage/current through the cell electrodes. Al serves as the anode in the anodizing tank, which has a cathode positioned inside of it. The applied electric field causes oxygen ions to be released from the electrolyte and interact with Al atoms, and hence the Al is oxidized.

pSi, which is commonly fabricated by anodization of Si in hydrofluoric acid, is an excellent example of a nanoporous PC-platform material [76–78]. The anodization of the Si substrate transforms the Si surfaces into pSi surfaces, and their porosity depends on the Si type, anodizing voltage, current, temperature, etc. Even though pSi offers excellent optoelectronic properties for the development of optical sensing, it is constrained by its weak mechanical strength and poor chemical stability, and its fabrication method includes some risks, such as the use of dangerous HF-based electrolytes [37,79]. In contrast, PCs based on AAO have been developed to be an alternative material to develop optical-sensing systems amongst other optoelectronic applications [80]. AAO PCs are usually made by an anodization Al element due to their low-cost, industrially scalable nanofabrication method that has been used in industry for decades. Different anodization techniques can be used to tailor the nanoporous structure of AAO to form PC structures with precisely tuned optical characteristics throughout the spectrum ranges. AAO offers chemical and thermal stability, programmable and adaptable nanopore shape, steady and tunable optical signals, and mechanical strength. Additionally, a variety of functional compounds could be applied to change the surface chemistry of AAO to obtain chemical selectivity for desired analytes [81]. This process is based on the selective removal of well-defined parts of a metal wafer via oxidation and subsequent dissolving in high-pH conditions. Through this process, tuning of the current density (or voltage) applied to the substrate is necessary, as it is employed to determine the overall void volume and pore-size distribution of the generated pore networks. The resulting morphology is characterized by interconnected pores and is typically a tubular shape. The applied current density is utilized to control the thickness of the pore walls that influence the RI of a specific layer of the structure. In order to achieve a clear Bragg peak in the optical-reflectance patterns, multiple periods must be built up because the change in porosity, and hence the refractive index, of the surrounding layers obtained by this approach is often modest.

PCs made of TNTs have recently drawn a lot of interest due to their periodic top nanoring layer being able to trap visible light and improve photoelectrochemical (PEC) performance [82–85]. TNTs are exceptional because of their high aspect ratio, surface-to-volume ratio, and size-dependent properties. In addition, TNTs can be considered effective gas sensors because they are 1D and have a large surface area [86]. Unfortunately, the UV and visible-light spectrums of TNTs exhibit multi-absorption peaks. Strong light absorption over a wider visible-light spectrum is recommended to maximize light trapping. The main disadvantage of anodization technology is that it can only be used on materials that can be obtained in the form of conducting wafers. One of the many advantages of this procedure is the excellent reproducibility and accuracy of the resulting pore modification.

2.1. Mechanism of the Anodization Process

In the electrochemical-fabrication process of porous materials, two or three electrodes are usually used. Anodized materials such as Al, Si, and Ti serve as the anode; platinum or any other conductor that is insoluble in the electrolyte is used as the cathode; and the third electrode is the reference electrode, such as an Ag/AgCl reference. The counter electrodes are partially submerged in a moderately acid electrolyte, as shown in Figure 1a. The anodization process of Al or Ti is accomplished by applying current/voltage between two electrodes that establish two simultaneous oxidation and dissolution processes at the barrier layer (dense oxide layer) located at the bottom of the nanopore, as illustrated in Figure 1b. The oxidation process is defined by the formation of an oxide-thin layer at the metal/oxide interface, whereas the dissolution process describes the dissolution of oxide at the oxide/electrolyte interface. An electric field generated during the anodization helps to drive the flow of ionic species (such as Al^{3+} , O^{2-} , OH^- , and H^+ in the case of Al) involved in the production and dissolution of a given oxide [87]. pSi is prepared by electrochemical etching of an Si substrate in fluorine media. Several ideas and methods have been offered to explain pore generation when porous brown oxides were discovered on crystalline Si substrates after anodization in hydrofluoric acid (HF) [87–90]. The chemical processes at the Si/electrolyte interface, like oxide production and dissolution, compete with one another, which theoretically leads to the creation of pores. Beale et al. supposed that the imperfections at the Si/electrolyte interface caused localized current flow at the start of anodization and the beginning of pore formation [91]. Between the pores, the semiconductor Si is stripped of its carriers and achieves a resistance that is significantly higher than that of the electrolyte or bulk Si. It is preferable for the current to pass through the electrolyte in the pores, and dissolution takes place at the tips of the pores. According to Smith et al., the chemical interaction of the pores on the Si surface that have diffused from the bulk is what starts the dissolution process [92]. The anodic voltage and dopant concentration control the pore morphologies, and the pore tips serve as locations for the reaction for the hole-migration process. Small pore sizes cause charge carriers to be quantum-confined and bandgap energy to increase, which forms a barrier for holes to travel toward the Si skeleton [75]. Quantum effects passivate the porous structure, making the pore tips places where the holes collect, and the pore expansion continues. The so-called current-burst concept (CBM), which is still under development [87–90], is a recently acknowledged and novel model. The direct dissolving of the Si surface that has been hydrogen passivated is defined as the basic process, which is followed by fast silicon-oxide production, terribly low dissolution of the produced oxide, and then another round of hydrogen passivation. The dissolving process at the Si/electrolyte interface is defined by the period of the current burst. Consequently, the dynamics of pore formation and propagation are affected by the electrolyte composition. The CBM is effective at describing several facets of pSi production. However, it is not yet possible to, for instance, forecast the final shape or homogeneity of the pSi layer [75,88].

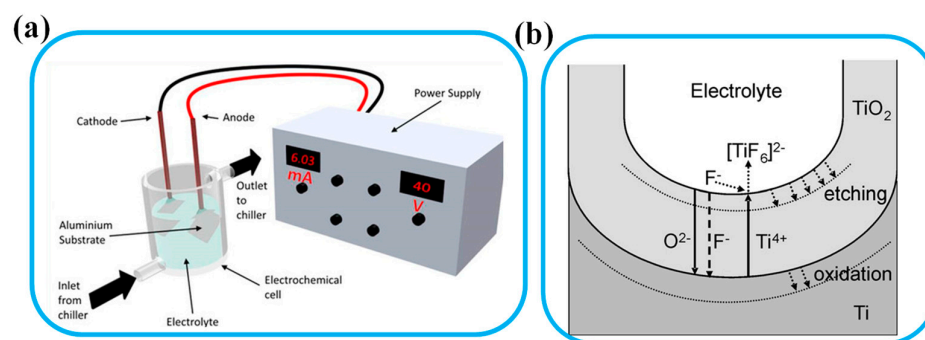


Figure 1. (a) Schematic for the electrochemical cell for the anodization process (reprinted with permission from Ref. [93]). (b) Electrochemical mechanism, including the development of an oxide film in an electrolyte containing F^- (reprinted with permission from Ref. [94]).

Anodic metal oxides of anodized valve metals such as Al and Ti have a variety of morphologies, including compact (dense) layers, ordered or random nanochannels, nanotubes, nanopores, and sponge-like morphologies [50,52,95,96]. According to fundamental electrochemistry concepts, the production of a dense oxide layer is accomplished by the anodization inside natural electrolytes and a straightforward scenario. It has not yet been fully determined how pore oxides form [52,96–98]. As stated below [52,97,99], two widely accepted theories for the pore's generation are the theory of the plastic deformation flow of oxide and the electrical-field-assisted oxide-dissolution theory. According to the electrical-field-assisted dissolution/oxidation theory, a continuous compact oxide layer forms first, followed by pitting beneath it. The growth of porous structures is a result of the oxide dissolving, assisted by an applied electrical field. According to Figure 1b, the chemical processes that lead to the production of metal oxides (MO_x) and the dissolution of oxides happens simultaneously [100–102]. The chemical dissolution of the oxide formed at the pore tip and the pace at which the barrier advances compete to identify the thickness of the porous layer. Temperature, anion (F^- in the case of Ti anodization) concentration, pH level, and anodizing voltage are the main processing variables that affect the oxide-growth rate [50,52]. According to the plastic-flow model [103–105], pore formation is caused by a stress-driven creep of oxide from the pore bottom toward the cell walls. The mass migration of metal ions within the barrier oxide is the most possible reason for stress generation and distribution. The elastic tension caused by volume expansion in the case of the AAO self-assembly approach controls the degree of homogeneity and propels the perfect cylinder and hexagonal pore layout [99,105]. Although the empirical theories can accurately predict the qualitative characteristics of pore formation, no quantitative form has yet been developed that would produce numerical values linking, for instance, porosity and distinctive structure sizes with electrochemical parameters applied during synthesis.

2.2. Different Anodization Methods

Anodized materials were employed in the past for industrial applications. The surface-finishing industry's principal goal was to form a cost-effective anodization method with enhanced end products. Therefore, the traditional method employed at the time to manufacture porous PCs did not provide an ordered pore morphology (nano/microstructure) free of cracks. As a result, that procedure could not be exploited for nanotechnology applications. Therefore, efforts were made to modify a procedure for anodizing metals so that the geometrical elements could be engineered. Due to the ease of production and control over geometric characteristics, self-coordinated nanopores known as porous PC structures have attracted a lot of attention. The next section provides a brief explanation of each type of anodization strategy used to synthesize porous PC structures.

2.2.1. Mild Anodization

The condition of anodization at a range of potentials below the breakdown potential/electric field of the developing oxide layer is known as mild anodization (MA). Above this breakdown potential, the formed oxide often burns and cracks with an expanding number of developing flaws. As the MA occurs at a lower voltage, the formation of the oxide is modest. The transient curve of MA is illustrated in Figure 2a, which consists of various distinct stages. The rapid decrease of current density is connected to the formation of the oxide-barrier layer via stage I. Electrical resistance is raised as a result of that process's formation of a thick oxide layer, which has the properties of an insulator. The current density then starts to increase with early pore nucleation until it reaches its maximum, which is a defining feature of stage II. The highest point of current density is associated with the real formation of early disordered pore arrays. As the density of pores increases, a steady state is reached through stages III and IV. From that moment, the thickness of the barrier layer remains more or less stable. In stage IV, the disorganized pores begin to combine, and pores that are normal to the surface but parallel to each other begin to expand. The current density starts to decrease and eventually stabilizes as the final steady state is established. Figure 2a depicts a schematic illustration of steady-state oxide development and the associated chemical processes. In this steady state, the barrier layer's thickness is kept fixed while the thickness of the porous structure is enhanced by increasing the anodizing period as a result of the balancing. Masuda et al. invented a two-step anodization procedure in 1996, which involves anodizing in two separated steps, as described in Figure 2b. Etching was applied to eliminate the deformed area of AAO in between these two procedures. Except for the time interval between each stage, the anodization conditions during both anodization steps should have been the same. Researchers conducted several additional investigations to better understand the factors and how they relate to anodization conditions as a result of the creation of this technology. For a variety of applications, the anodization method has to be tailored [106,107].

2.2.2. Hard Anodization

In the early 1920s, companies used a standard hard-anodization (HA) procedure that was performed at a potential greater than the breakdown value, leading to cracks in the formed anodic oxide with poor mechanical stability. As a result, the formed morphology was useless for actual nanotechnology applications. There have been several attempts to solve the issue with the standard HA method because it was difficult to manage the membrane's properties using it. Lee et al. [108] applied the HA technique for the anodization of Al. In the HA approach, Al foil was pre-anodized under MA conditions to form a homogeneous and sufficiently thick barrier layer. After the relatively short MA, the voltage was increased to high target values. The MA step is important to prevent breakdown phenomena and to allow for stable oxide formation without undesired cracks. Using target voltages of 110–150 V and oxalic acid ($C_2H_2O_4$) as an electrolyte, a high aspect ratio of AAO membrane that was completely organized and had a very high oxide-growth rate ($70 \mu m/h$) was obtained [109]. The main advantage of this form of anodization is that it allows for the rapid synthesizing of high-quality nanoporous oxide structures.

2.2.3. Pulse Anodization

During the pulsed-anodization procedure, low and high potential pulses are performed in both MA and HA conditions, respectively, to get the appropriate membrane properties. Tu and Huang first described pulsed-AC and -DC anodization in 1987 [110]. Despite flaws and a rough surface, the findings revealed that the formed oxide had adequate corrosion resistance. For the synthesizing of AAO with regular and periodically modulated porosity, Lee et al. employed pulses of HA and MA voltage in the presence of sulfuric acid (H_2SO_4) at a low temperature ($1^\circ C$) [111]. The duration of both MA and HA pulses was adjusted to the oxide-growth rate, which was an order of magnitude greater in the case of HA. In addition, it was observed that repeating a similar experiment in the

$\text{H}_2\text{C}_2\text{O}_4$ electrolyte resulted in a lack of current recovery after applying the MA pulse immediately after the HA pulse. This was ascribed to the thick barrier layer formed by the HA, which slowed down the ion migration through the barrier layer under MA conditions, reducing the current flow to almost zero [109]. Anodization with HA/MA pulses is a continuous structural-engineering method that was used to periodically modulate nanoporous structures under potentiostatic conditions in 0.3 M H_2SO_4 , $\text{H}_2\text{C}_2\text{O}_4$, or H_3PO_4 electrolytes [108,111]. Figure 2c shows the current–time curves and a structural schematic resulting from the pulse anodization [111,112]. These porous materials with properly controlled pores can serve as distributed Bragg reflectors (DBR), which are made up of layers that are periodically stacked and have various refractive indices. A pulse current that causes periodic structures along the growth direction takes the shape of periodic waves or pulses with a low anodizing voltage (MA) followed by a high anodizing voltage (HA).

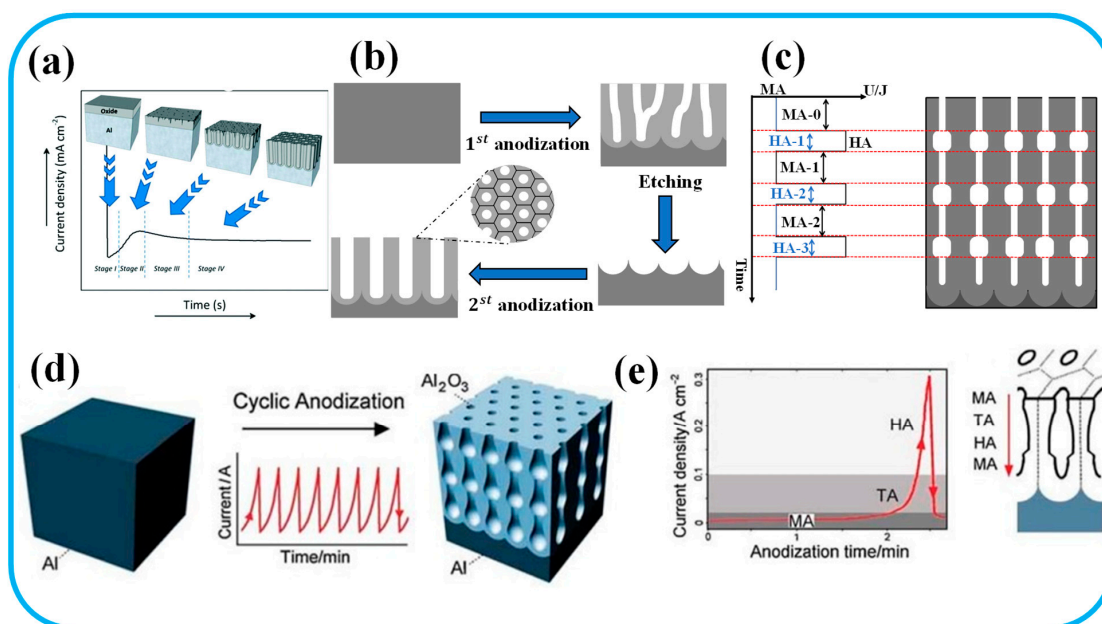


Figure 2. (a) Current density–time curve recorded during potentiostatic anodization (reprinted with permission from Ref. [113]); (b) a schematic sketch illustrating the two-anodization process developed by Masuda et al. [106,107]; (c) The pore-diameter modulation is accomplished by pulse anodization (reprinted with permission from Ref. [114]); (d) the principles of cyclic-anodization processes; and (e) the current-density signal applied in a single anodization cycle shows different anodization conditions and corresponding pore geometry (reprinted with permission from Ref. [115]).

2.2.4. Cyclic Anodization

Figure 2d shows the cyclic-anodization technique that employs a periodic oscillating signal that is either galvanostatic or potentiostatic. The periodic signal is used for a gradual change between the MA and HA conditions, forming the porous structure. This kind of anodization procedure was performed by Losic et al. [115] to prepare the modulated membrane. Cyclic anodization is not a novel concept, but it was used in the past to anodize alloys that were deposited via sputtering. The shape of the anodized membrane varies depending on the cyclic-anodization parameters [108,115]. Figure 2e illustrates the fluctuation in the potential changes for pulse anodization and cyclic anodization during the HA and MA methods. In general, when the periodic-modulation period of the pore diameters is on the order of the wavelength of visible light, the generated porous structure may exhibit AAO with various colors. Such structures can reflect a variety of wavelengths known as photonic stop bands (PSBs) that travel perpendicular to the stacked layers. The RI and layer thickness both affect the PSB's center wavelength. Fei's group has conducted extensive research on the optical characteristics of structurally designed

porous materials [116–118]. They discovered that periodic variations in potential during anodizing and subsequent wet-chemical etching of the obtained porous oxide could be used to form a periodic nanomorphology with the main and branched pores made of “air” [116]. Recent research by Fei et al. has shown that the designed porous structure of AAO is efficiently functionalized as sensors [119,120]. The ultra-narrow PSB of porous structures, whose entire width at half maximum is ~30 nm, demonstrates a significant shift and good reproducibility towards the detection of ethanol (C_2H_6O) vapor.

3. PCs Based on AAO

Al can be anodized in an oscillating voltage/current to produce PCs with PSBs in the visible and near-infrared portion in a repeatable, scalable, and affordable manner. To produce AAO PCs with pore sizes < 100 nm, the anodization process should be performed at lower anodization voltages, and consequently, H_2SO_4 , $H_2C_2O_4$, and selenic (H_2SeO_4) acid-based electrolytes were employed [121,122]. Anodizing at higher voltages in phosphoric acid (H_3PO_4) resulted in AAO films with bigger pores [123]. The first porous 1D PCs built of this material were made possible by the invention of the HA method, which enables tailoring the oxide layers with significantly different porosity [109]. As the first electrochemical step, anodizing an Al substrate with mirror polish in an acidic solution produces a grid of uniformly spaced pores. After the dissolution of the first oxide layer, the current is periodically regulated in the second anodization step to modulate a pore structure throughout the whole AAO thickness. As seen in Figure 2e, the linked tubular-shaped porous architecture of the AAO is visible. The size of the pores is dependent on both the type of acid and the applied voltage. $H_2C_2O_4$, H_3PO_4 , and H_2SO_4 are the most common utilized acids for pulse (or cyclic) anodization of Al. During the anodizing process, the various properties and structures of porous PCs are impacted by the characteristics of acid solutions. The following sections introduce the AAO PCs synthesized by the anodization of Al in various common electrolytes that have been reported.

3.1. Sulfuric Acid

The fabrication characteristics of the AAO produced by the anodization of Al in H_2SO_4 acid allow it to pass and reflect some particular wavelengths; for this reason, it is typically employed in optical fields such as PCs [124,125]. Birner et al. [126] reported that the hexagonal pore arrays in AAO were successfully synthesized by the anodizing procedure in 0.3 M (1.7 wt%) H_2SO_4 at 10 °C to form AAO with an interpore distance of 60 nm. It was found that during the anodizing process, the voltage rise caused a linear increase in the interpore distance of the AAO. The mechanism of the ordered pore arrays is that the nearby pores' repulsive forces at the metal/oxide interface stimulate the development of a hexagonally ordered array of pores [126,127]. A novel method for AAO fabrication with highly organized hexagonal pore arrays was disclosed by Chu et al. [128], in which high-field anodizing is applied in H_2SO_4 solutions. This method is subject to intense field anodizing, where the anodization is carried out at 70 V and a current density of 200 mA. Instead of being measured in days, the production pace is measured in h, or the anodization rate becomes higher. In recent studies, Bruera et al. [129] produced AAO using a low-cost approach by varying H_2SO_4 concentration, temperature, and anodization voltage for the duration of the two anodization stages. It was demonstrated that the optimal conditions to produce regular pore arrays are 10 °C, 20 V, and 0.3 M H_2SO_4 . The pore width was roughly 34 nm, the interpore distance was approximately 56 nm, the pore density was close to 4.4×10^{10} pores/cm², and the porosity was approximately 29.8% when the anodization technique was performed under the optimum conditions. Additionally, measurements and analyses were performed on the pore diameter, interpore distance, thickness, porosity, and pore density. It was demonstrated that the anodization voltage affected the pore diameter and interpore distance, the pore density was significantly dependent on the H_2SO_4 concentration and anodization voltage, and the thickness of AAO was affected by the H_2SO_4 concentration, temperature, and anodization voltage. Dobosz [130] used

the two-step anodization method to synthesize AAO in 0.3 M H_2SO_4 at 25 V. The results demonstrated that the pore width, interpore distance, porosity, and pore density were completely under the control of the anodizing conditions. Pore width and density can be tailored and varied through chemical treatment such as pore-opening and -widening processes. The manipulation of the RI in 1D can be accomplished by controlling these parameters under anodization conditions. Additionally, measurements were carried out to determine the relationship between anodization voltage, Al-substrate purity, and the growth rate of AAO. It has been shown that the anodic film's performance can be improved when ethanol is added to the H_2SO_4 solution [131–133]. Resende et al. [134] used the anodization process in 1.1 M H_2SO_4 at 0.13 mA/cm² and 3 V to obtain AAO with pore sizes < 10 nm and an interpore distance of 17 nm. The controlled anodization in 1.1 M H_2SO_4 revealed evidence that pore size decreased with decreasing current density. The standard preparation conditions are represented by low voltages and moderate production rates. Consequently, consume preparation costs are a benefit of employing H_2SO_4 in the manufacture of AAO. In future advances, the utilization of higher voltages for the H_2SO_4 -based AAO-synthesis process could be improved.

The periodic RI in the AAO can be obtained by altering the anodization conditions, as discussed earlier, to produce the PCs. Kushnir et al. [135] anodized Al with a square-wave-current profile in H_2SO_4 to produce 1D AAO PCs with striking colors. It has been shown that increasing the number of anodizing cycles while keeping the anodizing conditions constant results in wider stop bands, less intense background illumination, and more saturated sample colors. Therefore, the number of anodizing cycles is a key factor to be considered while synthesizing PC materials based on AAO. Its modification enables the manufacture of an array of functional materials, ranging from transparent PCs with intense, narrow stop bands to decorative coatings on the surface of valve metals. The periodic structure can be engineered as layers with differences in pore width, pore density, and porosity. Typically, porosities are kept within a few tens of a percent. Similar to Si, these 1D PCs have a homogenous composition, and the controlled adjustment of the anodic current is used to achieve the 1D modulation of the RI [28,117,136]. To detect clear Bragg-reflector features, a large number of layers must be produced because the difference between the RI of the layers is low and can only be achieved by altering the porosity of AAO.

3.2. Oxalic Acid

Masuda et al. produced AAO with a honeycomb morphology by two-step anodizing in 0.3 M $\text{C}_2\text{H}_2\text{O}_4$ at 40 V with a pore size of 70 nm [137]. Li et al. [138] investigated anodizing conditions of 0.3 M $\text{C}_2\text{H}_2\text{O}_4$ at 40 V and 0–15 °C to fabricate AAO with an interpore distance of 100 nm. Recent research has reported on the synthesis of AAO using high-field anodizing in 0.75 M $\text{C}_2\text{H}_2\text{O}_4$, which provides a faster growth rate of AAO [139]. The effect of the $\text{C}_2\text{H}_2\text{O}_4$ temperature, anodization time, grain orientation, and purity of the Al substrate on AAO growth was demonstrated. AAO with a thickness of 57 nm, an interpore spacing of 120 nm, and a pore width of 75 nm was obtained at anodization of Al at 50 V at 30 °C with 50 min of anodizing in 0.75 M $\text{C}_2\text{H}_2\text{O}_4$. $\text{C}_2\text{H}_2\text{O}_4$ temperature can affect how regular the AAO structure is; however, high temperatures (40 °C) can cause pore collapse [66]. Additionally, the production of AAO at a constant voltage and 8 °C with varying $\text{C}_2\text{H}_2\text{O}_4$ concentrations from 0.1 M to 0.9 M was investigated. The maximum regularity ratio for the anodization in 0.3 M $\text{C}_2\text{H}_2\text{O}_4$ was discovered to be 6.46. Research by Leontiev et al. [140] looked at the impact of temperature change throughout the anodization process. The resulting interpore distance was roughly 101 nm at 40 V, 0 °C in 0.3 M $\text{C}_2\text{H}_2\text{O}_4$. It was found that when the temperature is high, kinetically regulated anodization to the mixed regime results from the destruction of the hexagonal pore ordering due to the increasing diffusion current. According to their findings, the two-step anodization procedure is quick and can produce AAO at a temperature range of 10–20 °C at a rate that is comparable to that of anodization at 0 °C.

Szwachta et al. [141] investigated the impact of annealing temperature on geometrical stability and optical properties of PCs produced in 0.3 M $C_2H_2O_4$ using two-step anodization. The second step was carried out under the same settings as the first one, and the pulse anodization was completed by utilizing the triangular- and trapezoidal-profiled modalities at 5 and 30 °C, respectively, as shown in Figure 3a. The four stages that made up the pulse sequence were as follows: (1) progressive voltage increase from U_{min} to U_{max} , (2) anodization at a specific time with maximum voltage ($U_{max} = 50$ V), (3) a slow descent from U_{max} to U_{min} , and (4) anodization at a specific moment with a low voltage ($U_{min} = 20$ V). For triangular modalities, the sequence was repeated 150 times, and for trapezoidal modalities, 20 times. They tested the two AAO PC products over 24 h at annealing temperatures of 450, 750, 950, and 1100 °C. Cross-sectional views of two different structures, one including bilayers with a non-linear transition between n_H and n_L and the other containing layer pairs with an abrupt change in n_H and n_L , are shown in Figure 3b,c, respectively, where n_H and n_L are the RI of the low and high regions, respectively. The thickness of the various porosity segments was determined for both samples. In the AAO PCs produced using the triangular profile, only one layer with thickness d could be distinguished due to the ongoing transition between n_H and n_L . On the contrary, the high (d_H)- and low (d_L)-porosity segments in the AAO PCs fabricated based on the trapezoidal profile were resolved as a result of the rapid change in U_{low} . It was shown that modified pore structure is unaffected by phase transformation brought on by annealing. From the perspective of two AAO PCs' optical qualities, changes in thickness of a few nanometers are insignificant. The ability to prepare nanopores with higher regularity at higher anodization temperatures in $C_2H_2O_4$ and a faster growth rate of AAO are benefits of employing $C_2H_2O_4$ for the manufacture of AAO. On the other hand, the possibility of pore collapse as a result of higher-temperature annealing can be a disadvantage of this production process. $C_2H_2O_4$ solutions can be used to prepare AAO-based PCs with a specific range of pore diameters and other AAO features, which are utilized to engineer humidity sensors and biosensors [142,143].

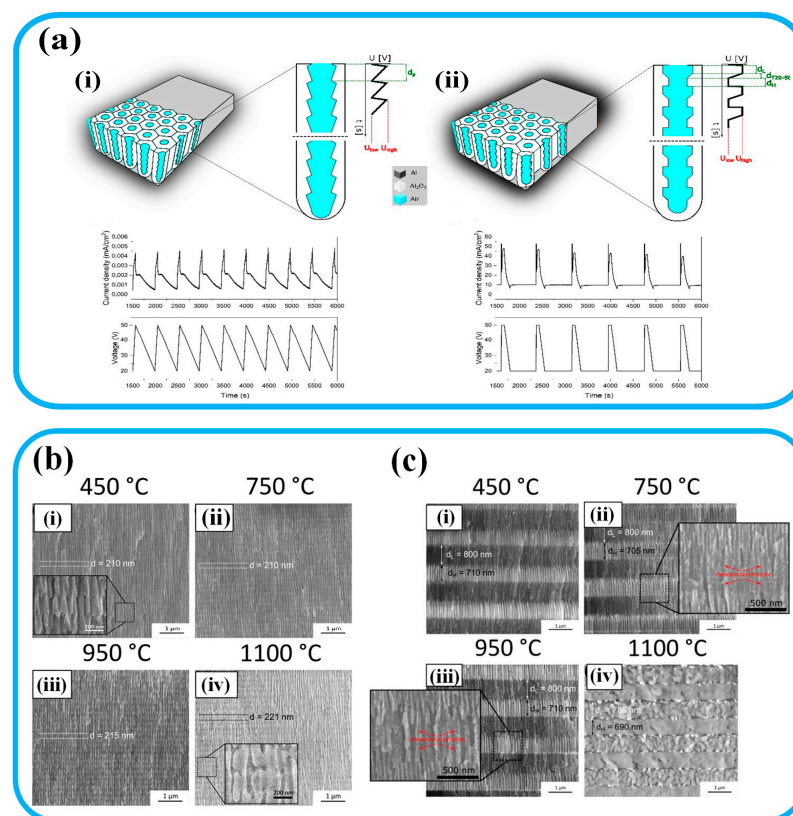


Figure 3. (a) A scheme of the applied pulse sequence and the resulting pore structure for (i) triangular- and (ii) trapezoidal-profiled pulse sequence, (b) cross-sectional SEM images of Vis-GIFs annealed at

450 °C (i), 750 °C (ii), 950 °C (iii), and 1100 °C (iv); the insets in (i,iii) present a higher magnification of the well-resolved arrow-shaped pores and the cluster pores, respectively, and (c) cross-sectional SEM image of IR-DBRs annealed at 450 °C (i), 750 °C (ii), 950 °C (iii), and 1100 °C (iv) (the insets in (ii,iii) present the mesoporous structure of AAO cell walls consisting of the crystalline particles of low-temperature alumina polymorph) (reprinted with permission Ref. [141]).

3.3. Phosphoric Acid

The third common acid applied in the anodization process to prepare AAO is H_3PO_4 , where the interpore expanses can range from 370 nm to 440 nm, as the suitable applied anodizing-voltage window is 150–180 V [144]. The synthesis of AAO during electrochemical reactions can be influenced by the solution content, temperature, and applied voltage. Masuda et al. [137] found that in the AAO-anodization process by H_3PO_4 , the size of the cell, also known as the interpore distance, is 500 nm when the anodizing voltage approaches 195 V. Anodization conditions for AAO generation are 195 V, 0.3 M H_3PO_4 , 0 °C, and the anodizing time is 16 h. Consequently, the cell size can vary between 370 nm and 500 nm, and the voltage of the H_3PO_4 employed in the anodization process ranges between 150 V and 195 V [137,145]. One-step anodization was utilized to form AAO in 0.53 M H_3PO_4 with a range of 40–120 V, resulting in pores with a diameter of 60–200 nm [146]. Jagminien et al. [147] described a different one-step anodization process using 80 V and 0.4 M H_3PO_4 at 25 °C. This method resulted in pore diameters of 80 nm and interpore distances of 208 nm. Nielsch et al. [148] demonstrated that the maximum value of the voltage of the H_3PO_4 -anodizing process could go above 180 V and reach 195 V. By using 0.1 M H_3PO_4 , the AAO structure's interpore distance and size of the pore were found to be 501 nm and 158 nm, respectively. In recent works, H_3PO_4 was used to produce AAO with pores ranging in size from 185 to 187 nm [149]. Montero-Rama et al. [150] reported that AAO production using the anodizing procedure at 195 V and 1 wt% H_3PO_4 resulted in a 200 nm barrier layer, which was liquefied using 4 wt% H_3PO_4 at a steady current of 17.0 $\mu\text{A}/\text{cm}^2$. They also showed that AAO without a barrier layer can be manufactured at low current densities. Higher current densities cause the anodizing voltage to drop and then climb, shifting the barrier layer's thickness during AAO development to a new equilibrium point.

One-dimensional PCs based on AAO were produced by Kushnir et al. [121] with two steps of Al cyclic anodizing in 1 M H_3PO_4 at 4.5 °C and sine-wave modulation between 135 and 165 V. The resulting PC structure with nonbranched macropores synthesized in H_3PO_4 for the first time is shown in Figure 4a and schematically in Figure 4b. Straight pores produced by the sine-wave profile had a diameter > 100 nm and alternated in size regularly. This was demonstrated by varying the electric-charge density, which governs the periodicity of porosity modulation along the normal to the AAO film, during one cycle of anodizing between 0.33 and 1.04 $\text{C}\cdot\text{cm}^{-2}$. They observed that the pore-diameter modulation's periodic period fluctuated between 135 and 170 nm. The samples S1, S2, S3, S4, S5, and S6 were produced using the anodizing-cycle number (N) and charge-density-per-cycle (q_0) values, where for all samples the total charge was the same: $0.330 \text{ C}\cdot\text{cm}^{-2} \times 130$, $0.418 \text{ C}\cdot\text{cm}^{-2} \times 100$, $0.534 \text{ C}\cdot\text{cm}^{-2} \times 80$, $0.632 \text{ C}\cdot\text{cm}^{-2} \times 65$, $0.832 \text{ C}\cdot\text{cm}^{-2} \times 50$, and $1.043 \text{ C}\cdot\text{cm}^{-2} \times 40$, respectively. Straight nonbranched pores with substitutional widths greater than 100 nm were produced under the applied conditions. The study of SEM images, as displayed in Figure 4a, revealed that the pore diameter fluctuated between 135 and 170 nm. Through Al anodizing in H_2SO_4 , H_2SeO_4 , and $\text{C}_2\text{H}_2\text{O}_4$ electrolytes, this range of pore diameter was not accessible. H_3PO_4 has an advantage over $\text{C}_2\text{H}_2\text{O}_4$ and H_2SO_4 in the production of AAO since it can be produced at greater voltages. By raising the voltage and changing other anodization conditions with the use of H_3PO_4 , it will be possible to investigate more varied AAO structures in the future [149]. H_3PO_4 is used to produce AAO films, which offer several unique attributes. These qualities, such as bigger pore size, are frequently employed in solar-energy applications, such as solar panels [151–154].

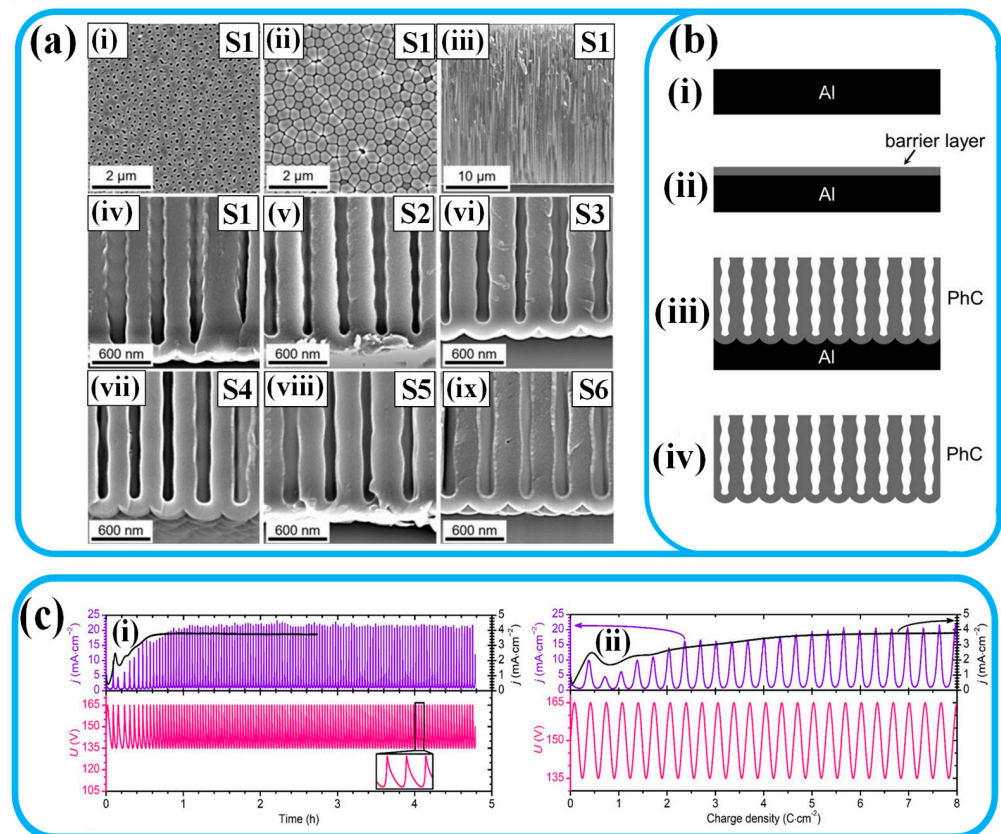


Figure 4. (a) AAO 1D PC morphology developed in 1 M H₃PO₄ at 4.5 C in sine-wave voltage with the modulation of the electric charge in the range of 135–165 V; Scanning electron microscope (SEM) images of the sample fabricated under the $0.330 \text{ C}\cdot\text{cm}^{-2} \times 130$ condition: the top (i) and bottom (ii) surfaces of the AAO film, and cleavage of the sample (iii). Enlarged views of the cleavages of the samples S1–S6 with various charge densities per cycle (q_0) and the number of anodizing cycles (N): $0.330 \text{ C}\cdot\text{cm}^{-2} \times 130$ (iv), $0.418 \text{ C}\cdot\text{cm}^{-2} \times 100$ (v), $0.534 \text{ C}\cdot\text{cm}^{-2} \times 80$ (vi), $0.632 \text{ C}\cdot\text{cm}^{-2} \times 65$ (vii), $0.832 \text{ C}\cdot\text{cm}^{-2} \times 50$ (viii), and $1.043 \text{ C}\cdot\text{cm}^{-2} \times 40$ (ix). (b) synthesis of AAO 1D PCs: Electropolished aluminium foil (i), barrier-type anodic alumina layer grown on the Al foil (ii), 1D PhC prepared by aluminium anodizing in phosphorous acid electrolyte (iii), and free-standing 1D PhC (iv); and (c) the electrochemical responses to sine-wave voltage versus electric-charge modulation in the 135–165 V range were recorded ((i) time dependences of anodizing voltage (U) and current density (j) and (ii) the impact of charge density on U and observed j values) (reprinted with permission from Ref. [121]).

4. PCs Based on pSi

A wafer of crystalline Si is commonly anodized in a fluorhydric-acid solution, releasing Si hexafluoride as a result. An external source can modulate the anodic current over time, resulting in a multi-layer structure with clearly defined slabs with various porosities and, consequently, refractive indices, which is one straight route to pSi PCs [155,156]. This offers a unique foundation for manufacturing adaptable 1D PCs based on porous multilayers produced by electrochemical etching of Si [157]. The porous multilayers can be divided into three types, including microcavities [158], Bragg mirrors [159], and rugate filters [160]. Sailor et al. are credited with studying this type of porous lattice and making important strides in optimizing the photonic properties of these and related structures, such as optical resonators [161]. They have thoroughly investigated various methods of functionalizing Si walls to provide these materials with a specific response to various chemicals.

The pore size can be regulated precisely between 2 nm and a few microns depending on the charge density, ion-fluoride concentration, and Si wafer-doping amount [162,163]. Harraz et al. [154] prepared pSi by anodization of n-type Si in 6 wt% aqueous HF and 1 mM of KMnO₄ with pore diameters in a few nanometers. It was proven that the applied

etching current directly impacted the pore diameter and shape. The pore diameter and morphology were investigated at current-density values of 5, 10, 15, 20, and 25 mA/cm². Figure 5a shows SEM pictures displaying various pore sizes attained at different current densities. Small pores with a few nm scales were produced at five mA/cm². The pore size increased when the current density increased to 10 mA/cm², although it was <50 nm and showed many branched pores. At 15 mA/cm², the pore size was >50 nm and the pore-wall roughness was reasonably low. At 20 and 25 mA/cm², cylindrical, well-defined pore arrays devoid of side pores (branches) were produced. These pores were observed to propagate along the direction and had diameters of 100 and 150 nm, respectively. It was frequently observed that when the etching-current density increased, the average pore width increased and the roughness of the pore wall decreased. It is important to note that applying current densities of more than 25 mA/cm² caused the porous structure to collapse because, in the electropolishing phase, the effective current-density value was disputed. After all, the selective breakdown of the interface is what caused the pore formation. According to Harraz et al. [154], Si was anodized in HF as the electrolyte, and the resultant pores had diameters between 2 and 25 nm. The applied current signal as a sinusoidal function varied from 5 to 25 mA/cm², with a periodicity of 3 s in each cycle. The overall process lasted 5 min, producing a layer with a thickness of about 4.5 µm. As with the multilayer construction seen in Figure 5b, the structure's porosity was determined gravimetrically using single porous layers. For lower and higher current densities, the porosity values were found to equal 14% and 52%, respectively. The side views of the prepared rugate structure, appropriate sinusoidal wave, porosity fluctuation, and structure drawing are shown in an SEM micrograph in Figure 5b. A difference in porosity, or the direction of pore propagation, can be seen. This would result in various RI profiles, and the higher the RI, the lower the porosity. This particular porous structure makes it easy to develop Si-based biosensors. A bigger pore diameter is best suited for large molecules in particular, and thus it is anticipated that this kind of photonic structure will improve the infiltration process during sensing applications.

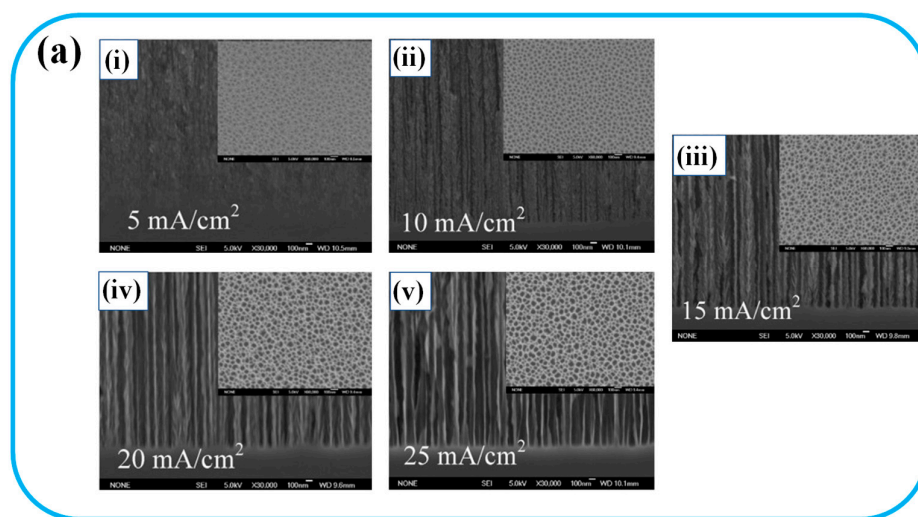


Figure 5. Cont.

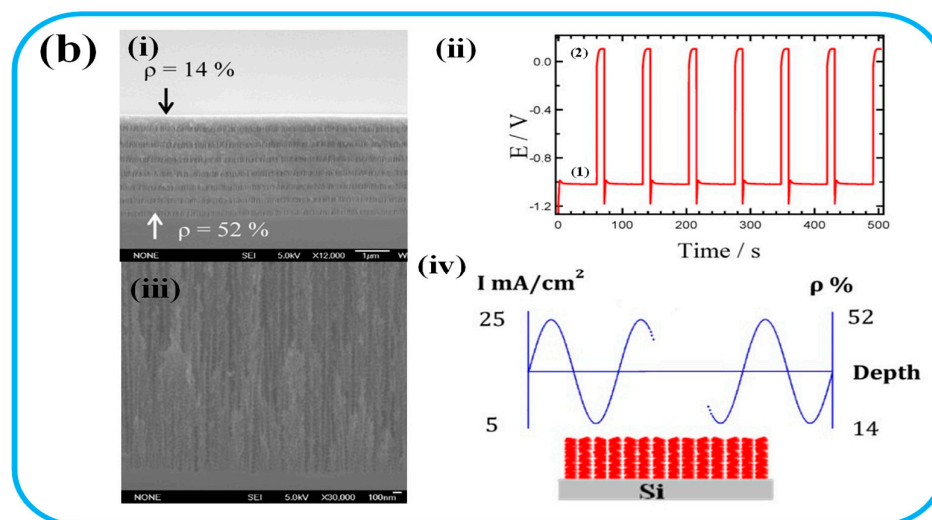


Figure 5. (a) The view of the top and cross-sectional SEM images display the effect of current density ranging from (i) 5 mA/cm^2 to (v) 25 mA/cm^2 on pore size; (b) (i) cross-section SEM image of a multilayer showing meso/macropore structures, (ii) double-step current modulation detailed at two current-density values of 5 and 25 mA/cm^2 , (iii) cross-section SEM image of a rugate structure generated by modulating a sinusoidal wave with periodic variations in current density, (iv) a rugate structure with a sinusoidal wave and porosity variation (adopted and reprinted with permission from Ref. [154]).

5. PC-Based TNTs

TNT arrays are considered viable competitors among 1D semiconductor nanostructures employed in photoelectrochemical (PEC) water splitting due to their exceptional properties, such as their vertically aligned structure and enormous surface area. These characteristics are beneficial for improving PEC performance [37,155,156,162,164]. Unfortunately, TNTs have drawbacks, such as strong surface reflection, wide band-gap energy, and ineffective harvesting of visible light [25,26]. Numerous viable solutions have been suggested to address this issue, including band engineering [37], element doping [29], and the introduction of oxygen deficits [27,164], among others. The emerging solution to this problem may be provided by engineering PCs based on TNTs.

Wang et al. [165] used one-step periodic-pulse anodization in a mixture of 0.5 wt% NH_4F and 3 vol% deionized water to produce PCs with multilayers. In contrast to the morphology under constant-anodization processes, a periodic layered structure with varying porosity was found along the longitudinal direction of the tubes under the multi-pulsed-anodization voltage conditions, outside of the TNTs (indicated by a simple drawing in Figure 6a). The tube's thickness and the pit's size may therefore be modified and controlled by varying the duration of the high and low voltages. Moreover, the process of forming the periodic structure was addressed. It was shown that the homogeneous pore disperses itself across the sample surface in an organized manner. Small voids were present around each stack interface in these structurally engineered tubes under the multi-pulse-anodization voltage conditions, as opposed to the bamboo-like tubes' representative morphologies through hardened embedded parts at the edge regions and tube walls with the constant-anodization process. In addition, the periodic structure was preserved from top to bottom. A similar cyclic characteristic in the current transient appeared as the cyclic voltage was applied. Figure 6a depicts the multilayer production scheme caused by the periodic multi-pulsed-oxidation voltage wave.

Successful fabrication of TNT PCs was accomplished by Liu et al. [166] using a straightforward two-step anodization method. The TNTs demonstrated bright-light absorption throughout a broad spectrum of visible light. For the first anodization stage, TNT arrays were produced at 60 V for 1 h in 0.3 wt% NH_4F . The oxide layer could be removed by

an ultrasonic process, producing a Ti substrate with a nano-concave texture. Then, the roughened Ti substrate was subjected to the second anodization step for 30 min at 30 V, 35 min at 35 V, and 30 min at 40 V. After the two-step anodization, the TNT PCs were annealed at 450 °C for 3 h.

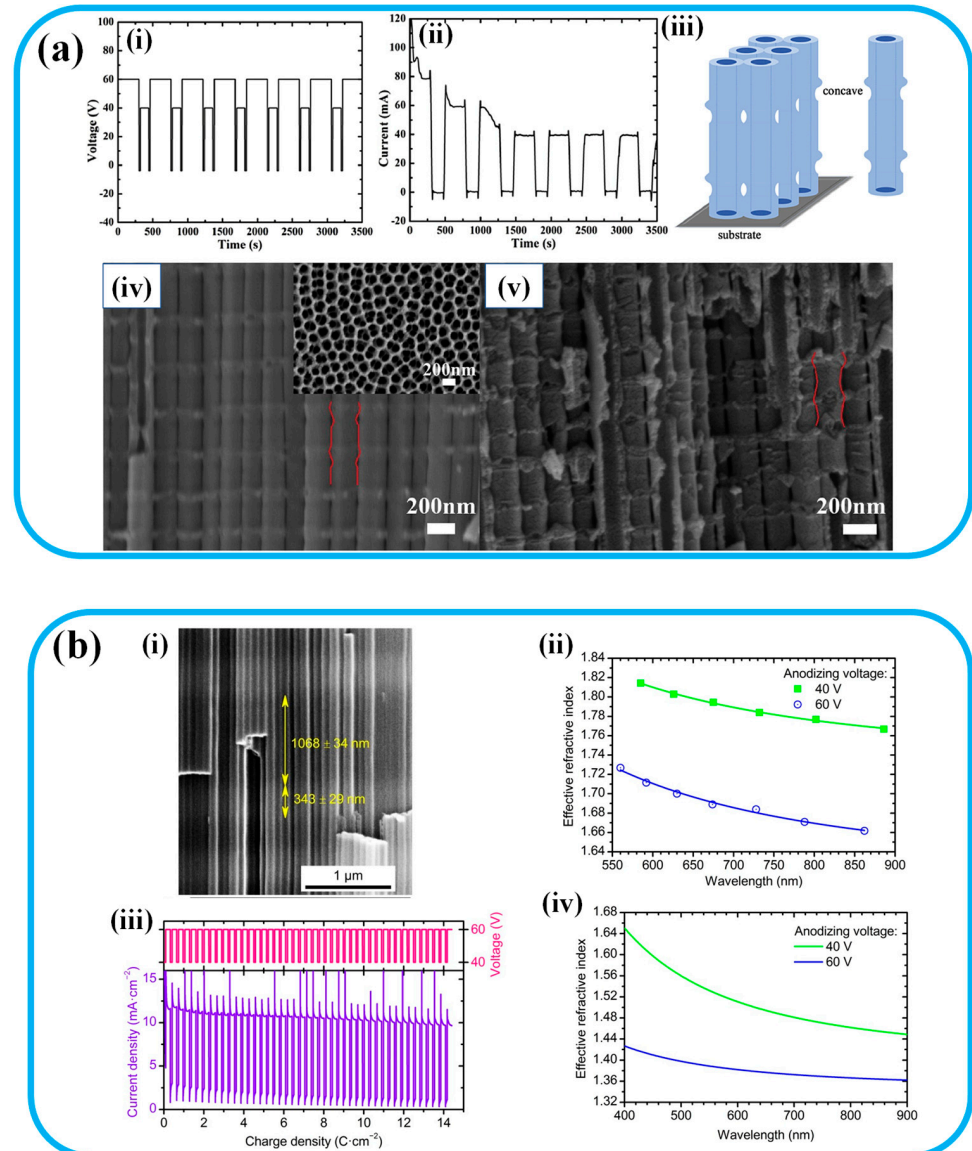


Figure 6. (a) (i) The periodic-voltage wave, (ii) the recorded anodization-current time, (iii) the scheme of TiO₂ PCs with concave tube walls, (iv) FE-SEM showing that the periodic TNTs have a concave structure, as seen in the inset, and (v) the morphology of TNT films after annealing in the air (reprinted with permission from Ref. [165]). (b) (i) SEM image of cleavage of the sample obtained at 60 V, (ii) the effective refractive indices of TNT coatings obtained at 40 V and 60 V, (iii) effects of charge density on anodizing voltage and current density, (iv) the PC layers' effective RI at various anodizing voltages (reprinted with permission from Ref. [167]).

The construction of TNT PCs with exact PSB positions was achieved for the first time by Ermolaev et al. [167] using anodizing with voltage and optical-path-length (OPL) modulation. High-quality PC fabrication demands precise periodicity of the effective refractive index (n_{eff}) as a function of the OPL (OPL is the result of multiplying together the layer thickness (d) and the n_{eff} of the medium of the traveling light). It was revealed that the n_{eff} of oxide films made at constant voltages of 40 or 60 V (1.66–1.77 at $\lambda = 800$ nm) is higher than the n_{eff} of TNT PCs made with a periodic square-wave modulation of

anodizing voltage between 40 and 60 V (1.37–1.46 at $\lambda = 800$ nm) in an electrolyte with high concentrations of NH_4F . Both times, TNT layers produced at 40 V had higher n_{eff} than those produced at 60 V. This shows that the n_{eff} of TNTs depends on the anodizing regime (modulating voltage). Moreover, the proposed model considers a partial dissolution of TNTs in an electrolyte, usually consequential in a broader pore diameter at the top part of the oxide film compared to the bottom [96,135,168]. SEM images and wavelength dispersions of the n_{eff} of TNT-PC layers formed at constant voltages of 40 and 60 V are shown in Figure 6b. The variation in porosity is caused by a variation in the diameter of the pores, which is empirically observed as a modulation of Z-contrast along the axis of the pores in the SEM images. It is therefore evident that the lesser porosity of TNTs is correlated with the higher brightness in the SEM image. Based on this, it was concluded that the porosity of TNTs produced at 60 V was higher than that of the layers formed at 40 V since the thick layer generated at 60 V appeared darker than nearby layers. Accordingly, TNT PCs hold promise for application as RI sensors because the PSB location is extremely sensitive to the RI of filled pores.

Despite these efforts, reaching the efficiency of hydrogen conversion for solar TNTs has remained alarmingly low, and an efficient strategy to increase visible-light absorption is still urgently needed. TNTs and hierarchical TNTs with a top layer acting as PCs have recently garnered a great deal of interest due to the periodic top nanoring layer's ability to trap visible light and enhance PEC performance [25,155,156,169]. Unfortunately, the UV and visible-light spectrums of the TNTs exhibit multi-absorption peaks. Bright-light absorption throughout a wider visible-light spectrum is preferred to enhance light trapping.

6. Optical Properties and Applications of PCs

Periodic changes in the formation parameters will cause the porosity and RI to change periodically over the depth of anodized materials. The resulting porous multilayer allows for control of the light traveling within the photonic structure [157]. Due to repeated reflections at the interferences resulting from the variation of the RI, the reflectance of such multilayers can be as high as about 99.5% [158]. As mentioned above, the four primary types of photonic multilayers that can be engineered by varying the porosity in depth during electrochemical anodization in an appropriate electrolyte are Bragg mirrors [159], rugate filters [160], and microcavities [158]. Repeated double layers with lower and higher RI values make up DBR. The optical thickness of each layer is $\lambda/4$, where λ is the resonance wavelength of the structure. A crisp photonic band can be obtained by increasing the layer count and the index contrast (high RI–low RI). On the contrary, rugate filters exhibit a sinusoidal fluctuation of the RI with depth. Whereas the porosity of filters gradually changes, the porosity of DBR changes drastically layer by layer. Whereas rugate filters do not have this criterion and are, therefore, easier to manufacture, the individual layers of a Bragg stack must be built so they are phase matched. The third category, microcavities, is the most effective technique to alter the optical characteristics of porous materials. The reflectance/transmission qualities can be significantly enhanced by sandwiching an active layer between two Bragg mirrors with an optical thickness of $\sim\lambda$ or $\lambda/2$. The Fabry–Perot interference filter is the name of the resulting structure.

6.1. Distributed Bragg Reflectors

The opening of a PSB is caused by the periodic modification of the RI in one spatial dimension, which is accomplished through the pulse anodization of materials with distinct natures or porosities. Light beams can interact positively or negatively at the interfaces of layers with a varying RI. As a result, electromagnetic-wave transmission through the photonic structure is prohibited for photons of a particular energy. Constructive interference in the opposing direction causes the maximum to occur in the reflectance spectrum that characterizes these structures [145,170]. Thus, the PSB and wavelength ranges are connected where the material exhibits strong light reflection and low light transmittance. The thickness, RI, and the number of stacked layers that make up the crystal influence

the reflectance spectra from PCs. The reflectance peak becomes more intense and larger because the difference in the RI of adjacent layers grows. Increasing the number of layers in the stack has a similar impact.

Conversely, the PSBs move to lower energies when the layer's optical thickness, which is determined by multiplying the real thickness by its RI, increases. The porosity of a layer is strictly correlated with its RI, which falls as porosity increases [112]. The careful regulation of the porosity of the alternate and following layers is thus one of the key design considerations for this form of PC. The intensity of the PSB at a particular wavelength can be increased by increasing the amount of light reflected from the layer boundary and the RI contrast (the difference between the low and high RI of alternating layers). This feature serves as the foundation for the design of a wide variety of optical sensors since the spectral location of PSB is extremely sensitive to even a little change in the RI of a medium [171–174]. Pulse anodization, which depends on periodic alteration of anodization parameters such as voltage or current density, is used to produce 1D PCs with regularly variable porosity of alternative layers [175,176]. To design the desired pore architecture and to shape strong and narrow resonances at a given spectral range, the pulse sequence can be altered in the appropriate ways (controlling the anodization modes, current/voltage values of the generated cycles, pulse shapes such as saw-like or pseudo-stepwise anodization waves, ramp rates between high (U_H) and low potential (U_L), pulse durations, numbers of pulses, etc.).

Bialek et al. [177] examined the impact of anodization temperatures in the range of 5 °C to 30 °C on the photonic optical characteristics of DBRs produced based on AAO. The location and shape of the PSBs were determined by recording transmission $T(\lambda)$ spectra. The PSB characteristics significantly deteriorated above 10 °C up to 25 °C, as evidenced by a progressive reduction and splitting of transmission peaks, as seen in Figure 7a. At 30 °C, however, the PSBs returned with several small, low-intensity peaks between 1000 and 2500 nm and a symmetric resonance peak in the mid-infrared (MIR) spectra, located at 4386 nm with $T = 0.2$. A slight adjustment of the pulse sequence sharpened at the interface of d_H and d_L segments that enhance the AAO-30 °C DBR photonic characteristics. Additionally, it was demonstrated that a greater porosity difference between consecutive low- and high-RI layers increased the intensity of the respective PSBs. Despite having the same U_H-U_L contrast, the structural and optical characteristics of the DBR anodized under 40–20 V at 10 °C were significantly superior to those of the DBR synthesized under 50–30 V. On the other hand, the characteristics were equivalent to those of the DBR synthesized at a lower temperature of 5 °C under 50–20 V (U_H-U_L contrast = 30 V). This also implies that a crucial element in designing high-quality PCs is temperature. The $T(\lambda)$ spectra of the AAO-10 °C DBRs produced at 10 °C were contrasted, as shown in Figure 7a. First, the PSBs were pushed into the blue region of the spectrum as U_H decreased, mostly due to the thinned d_H layer. The strength of the resonance peaks gradually diminished, but in contrast to the sample anodized at 50–20 V, the DBRs anodized at 45–20 V and 40–20 V became more symmetrical and thinner. The absence of PSBs in the $T(\lambda)$ spectra of the AAO-10 °C anodized at 50–30 V indicates that virtually no DBR structure was formed under these conditions. Additionally, this work demonstrated that anodization at high temperatures offers new opportunities for developing and customizing AAO-based photonic devices with favorable optical properties in the MIR region (according to a frequently utilized subdivision scheme, the MIR region falls into 3–8 μm [178]).

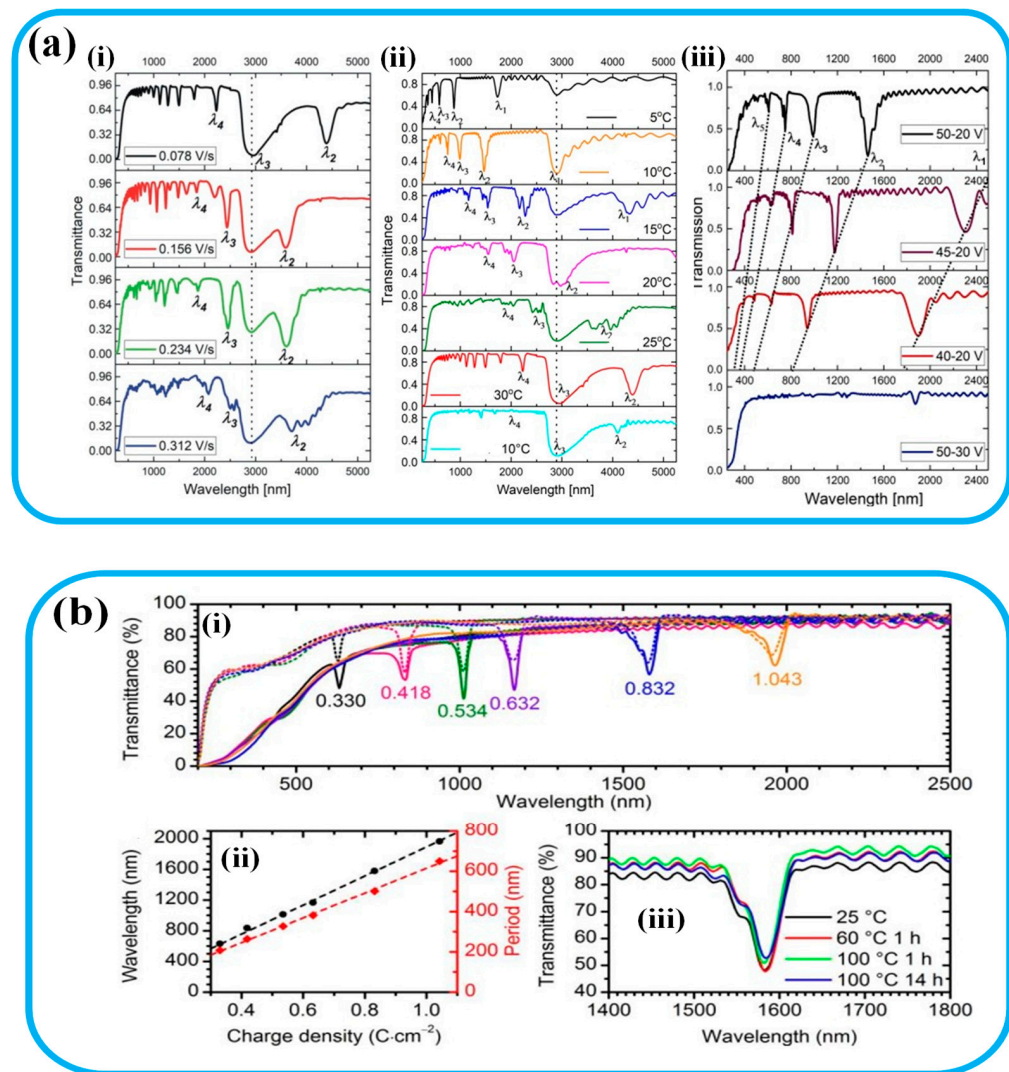


Figure 7. (a) Transmission spectra with decreasing $U_H \rightarrow U_L$ drop rate from 0.078 V/s to 0.312 V/s (i), transmittance spectra of AAO-based (ii) PCs anodized at 5–30 °C, and (iii) DBR fabricated at 10 °C under various U_H and U_L values (reprinted with permission from Ref. [177]). (b) Optical properties of AAO 1D PCs prepared by Al anodizing in 1 M H_3PO_4 (i) specular (solid lines) and total (dotted lines) transmittance spectra of the samples with various $q_0 \times N$, where transmittance minima are labeled with the values of q_0 ; (ii) the charge density and wavelength position of the photonic band gap and the period of AAO 1D PCs; and (iii) transmittance spectra of the sample with $q_0 = 0.832$ after 2 months of successive aging at 25 °C (black), 60 °C (red), 100 °C (green), and 14 °C (blue) (reprinted with permission from Ref. [121]).

One-dimensional PCs based on AAO of nonbranched macropores in the range of 135 nm to 170 nm were prepared in two steps of Al cyclic anodizing with periodic modulation for the first time by Kushnir et al. [121]. It was shown that adjusting the density of the electric charge of one cycle (q_0) of anodizing between 0.33 and 1.04 $C \cdot cm^{-2}$ is what causes the periodicity of such a structure. The PSBs are visible as transmittance minima in Figure 7b, and their positions migrated to higher wavelengths with the increase in q_0 . The transmittance peak out of the PSBs increased with wavelength as the ratio of wavelength to pore diameter increased, possibly due to less light scattering [179,180]. All the samples' specular and total transmittance outside the PSBs exceeded 73 and 87%, respectively, in the near-IR range as a function of wavelength. The Bragg–Snell law [69] states that the first PSB is in the following position: $\lambda = 2d\sqrt{n_{eff}^2 + \sin^2 \theta}$, where θ is the incident angel, d is the

structure period, and λ is the wavelength of the first PSB. When the incidence is normal (i.e., $\theta = 0^\circ$), $n_{\text{eff}} = \lambda/(2d)$. The n_{eff} value for the prepared PCs was 1.58 ± 0.05 . As a result, the near-IR absorbance inside the AAO PCs was $<4\%$. In addition, interference between the beams reflected at the top and bottom sides of the multilayer led to the formation of secondary maxima via Fabry–Perot oscillations.

6.2. Fabry–Perot Interferometers

Fabry–Perot interferometers, which have a constant n_{eff} throughout their construction, are the most basic optical structures. The n_{eff} of these thin films, which can have thicknesses of up to $2\ \mu\text{m}$ to demonstrate this effect, can be modulated through careful control of their thickness and porosity [181]. Due to variations in the material's RI when it fills the straight pores, these structures can serve as sensing platforms (from solids to liquids and gases). Ferro et al. [182] evaluated the resulting Fabry–Perot interference spectra of AAO films as a function of glucose concentration and tested their effectiveness as chemical-sensing platforms. This method has been reported to determine glucose levels with good analytical performance. The range of structural parameters that can be employed to construct AAO membranes, such as interpore distance, porosity, pore diameter, and thickness, is geometrically constrained by these ideas based on straight pore channels. As a result, their versatility is insufficient for the majority of practical applications. Due to the generated Fabry–Perot interference, Kushnir et al. [135] produced 1D AAO PCs with striking colors. The resulting interference of porous film at different angles was utilized to determine the wavelength dispersion of AAO with an effective RI. In addition, the effect of the number of layers in the resulting AAO PCs on the PSB intensity and color of the oxide coating was examined.

TNT PCs made by two-step periodic-pulse anodization of Ti were studied by Wang et al. [165] for their chemical-sensing capabilities. Researchers have discovered that the periodicity of this structure replicated as a change in porosity along the longitudinal axes of tubes was created as a result of various applied-pulse durations. The $T(\lambda)$ spectra of TNT PCs synthesized with various high- and low-voltage pulse durations are shown in Figure 8. By increasing the time of the higher-level pulse from 2 min to 4 min, the red shift occurred for all PSBs. Inversely, the blue shift of PSBs occurred with the increase in the time of the lower-level pulse, as displayed in Figure 8. According to the Bragg law, the n_{eff} and periodic-layer thickness both influence the center wavelength of PSBs. The thickness of the dielectric layers grows as the high-level pulse length increases, causing the redshift of the PC's PSBs. In their prepared state, the PCs can act as a sensor to detect analytes. The transmission spectra of PCs submerged in water ($n = 1.333$), acetone ($n = 1.3588$), ethyl alcohol ($n = 1.3618$), and ethylene glycol ($n = 1.4318$) are shown in Figure 8iii. The air in the pores of the PCs was replaced by liquids with a greater RI when they were submerged in the analytes, raising the n_{eff} of both the higher and lower dielectric layers. The PSB for the analyte-soaked PCs moved to a longer wavelength as a result. The transmission spectra of the PCs, when it was submerged in glucose solutions with concentrations of 0.05, 0.1, 0.2, and 0.4 mol/L, are shown in Figure 8iv. With the increase in glucose concentration, the center wavelength of the PBGs underwent a red shift; this dependence must be attributable to the various glucose solutions' refractive indices.

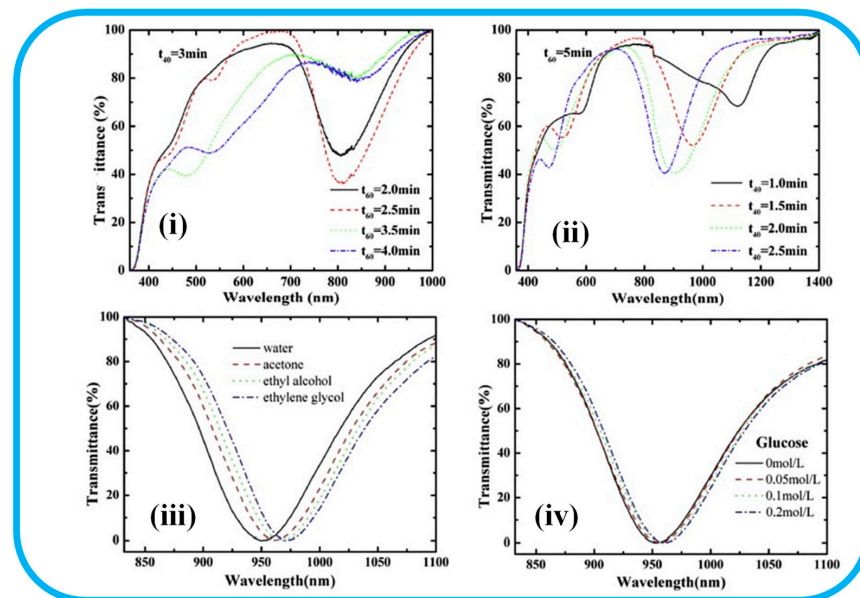


Figure 8. The transmittance spectra of PCs formed with different durations of higher (i) and lower (ii) voltage pulses, (iii) transmission spectra of PCs soaked in different liquids, and (iv) the soaked PCs for different NaCl concentrations (reprinted with permission from Ref. [165]).

6.3. Optical Microcavities

A development in the manufacturing of the cavity sections between two Bragg-stacked reflectors for light confinement is the use of optical microcavities. A microcavity structure with two PCs that have varying porosities depending on the applied anodized current density is used. For instant, Ouyang et al. [183] synthesized photonic pSi. As illustrated in Figure 9, two DBRs were prepared in their work at various applied current densities. It was shown that the two DBRs interfered destructively with one another in two places, producing the highest reflectance, as shown in the $T(\lambda)$ spectra in Figure 9.

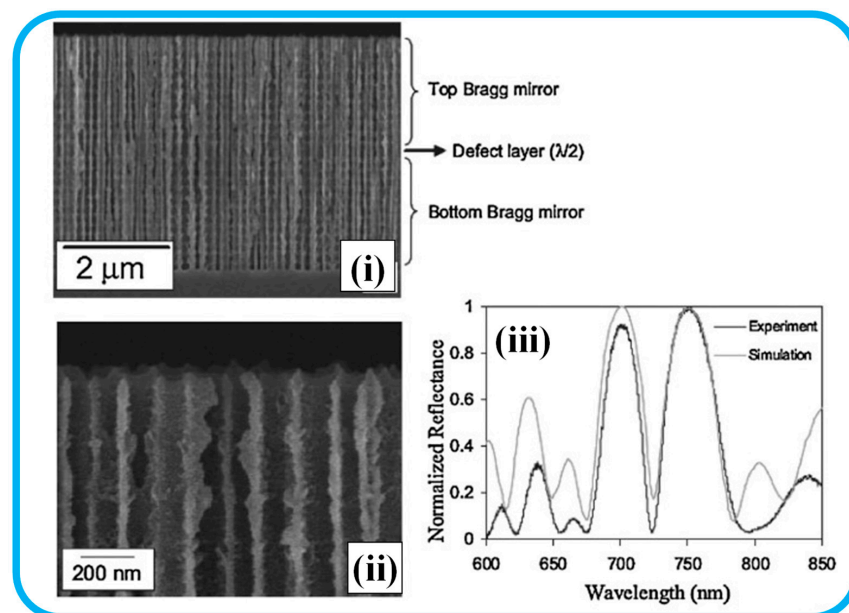


Figure 9. SEM images of a pSi microcavity (high-porosity layers created at (i) 40 mA/cm², low-porosity layers formed at (ii) 34 mA/cm², and (iii) microcavity spectra were measured in black (black) and simulated in grey (grey) (reprinted with permission from Ref. [183]).

By adjusting the period, for which high voltage (V_H) is continued over time, the cavities' length can be changed. Consequently, by using a center high-voltage pulse with a specific duration, an essential microcavity can be synthesized between the Bragg reflectors in the structure. As a result, Wang et al. [184] prepared two types of optical microcavities, I and II, which can be seen in Figure 10a. Constructive or destructive interference was induced at certain wavelengths depending on whether the two N cycles of pulsed anodization required to make the AAO Bragg reflectors were applied in phase or whether a phase shift was imposed between them without the usage of a central microcavity. According to the Bragg condition for constructive interference, $n_H d_H = \lambda/4 = n_L d_L$, where n_H , d_H and n_L , d_L , are the refractive indices and thicknesses of the formed layers under high and low voltage, respectively. The resonance peaks were located in type I at each side of a central-cavity layer with a constant RI. Resonant peaks appeared in locations corresponding to the various-order resonant peaks connected to the Bragg-reflector structure by maximizing the length of the resonant cavity. To generate destructive interference and create type II, a phase shift from $\frac{1}{2}\pi$ to $7/4\pi$ was added between the two Bragg reflectors, as shown in Figure 10 [184]. This led to a change in the bottom DBR structure's RI. Nevertheless, resonant first-order peaks were only visible for phase shifts $\geq 7/4\pi$. Substantial structural varies were not seen at the interface at lower phase shifts; in other words, the pore shape was not modulated. The authors postulated that these small phase shifts correspond to a period in which a steady current condition has not yet been attained, as the voltage is being decreased from V_H to V_L . As a result, there were no modifications to the pore shape and hence no changes to the RI.

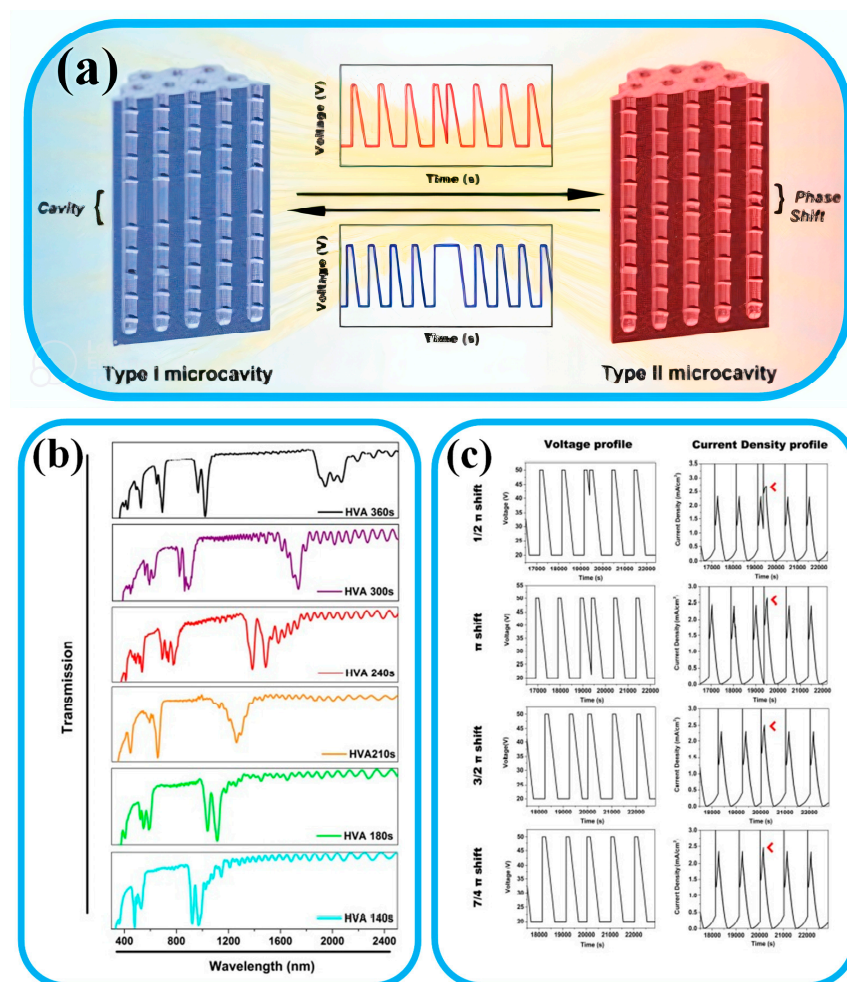


Figure 10. Cont.

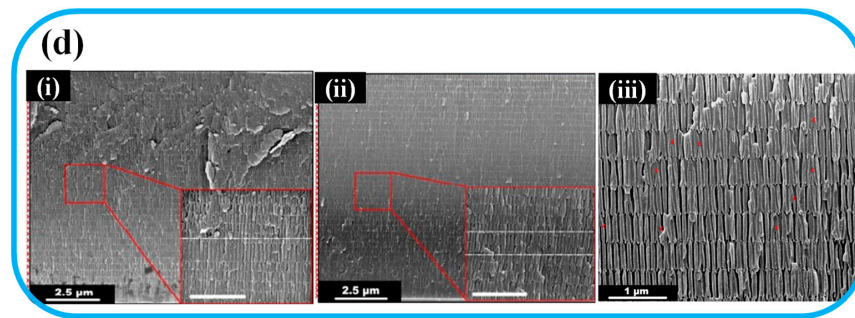


Figure 10. (a) Illustration of the fabrication process of type I and II AAO microcavities by pulse anodization, (b) transmission spectra of AAO microcavities (type I), (c) voltage and current-density profile of pulse anodization with programmed phase change after 20 cycles of pulses. Red arrowheads denote the transition of current density corresponding to the phase change of the voltage profile. (d) Cross-section SEM images of AAO microcavities (type II) produced by a phase shift of the RI profile at (i) $1/2\pi$ and (ii) $7/4\pi$, (iii) SEM cross-section image of AAO-DBR structure. Red arrowheads denote the end of a branching nanopore (reprinted with permission from Ref. [184]).

This is one of the key drawbacks of this technology, since it necessitates very long recovery times before the new steady state is reached, slowing the pore production due to the voltage reduction that takes place during the generation of branched pores. Once the steady state is reached, that is, when the barrier layer has been thinned down to the equivalent value of the low anodization potential V_L , changes in the pore structure can be seen. Additionally, compared to the DBR's genuine photonic stop bands, the resonant peaks that were intentionally inserted were narrower and transmitted more energy, improving these photonic structures' performance [184,185]. The authors synthesized a humidity sensor [184] by fusing the enhanced photonic response of the aforementioned type II microcavities with the inherent reliance of Bragg reflectors on the effective medium. The UV, visible, and near-infrared spectra can be tuned using either type of microcavity to produce resonant peaks and stop bands.

6.4. Gradient-Index Filter

The geometry of the pores in these anodized materials is determined by the sinusoidal pulses used in the manufacture of gradient-index filters (GIF) or apodized gradient-index filters. Both techniques include the addition of a mathematical function, but the latter modifies the initial sinusoidal profile to improve the structure of the PC properties. As a result, photonic stop bands that are more intense and narrower are obtained [186]. However, in both situations, tuning the placement of the allowed and prohibited bands across the UV-visible to near-infrared spectra is possible thanks to the applied pulse's time (T_p) [81,185–187]. Figure 11 shows how PAA with a $PSB_{\lambda 1}$ was generated in the 800–2500 nm range using the conventional sinusoidal-pulse-anodization technique. According to measurements of transmittance, as shown in Figure 11, it was found that an increase in the anodization period (t_p) and amplitude (A) led to a considerable change in the optical characteristics of the PAAs. A and T_p were increased from the lowest values (5 V and 100 s, respectively) to the highest (15 V and 300 s, respectively), and the gradient index was changed to a step-index filter.

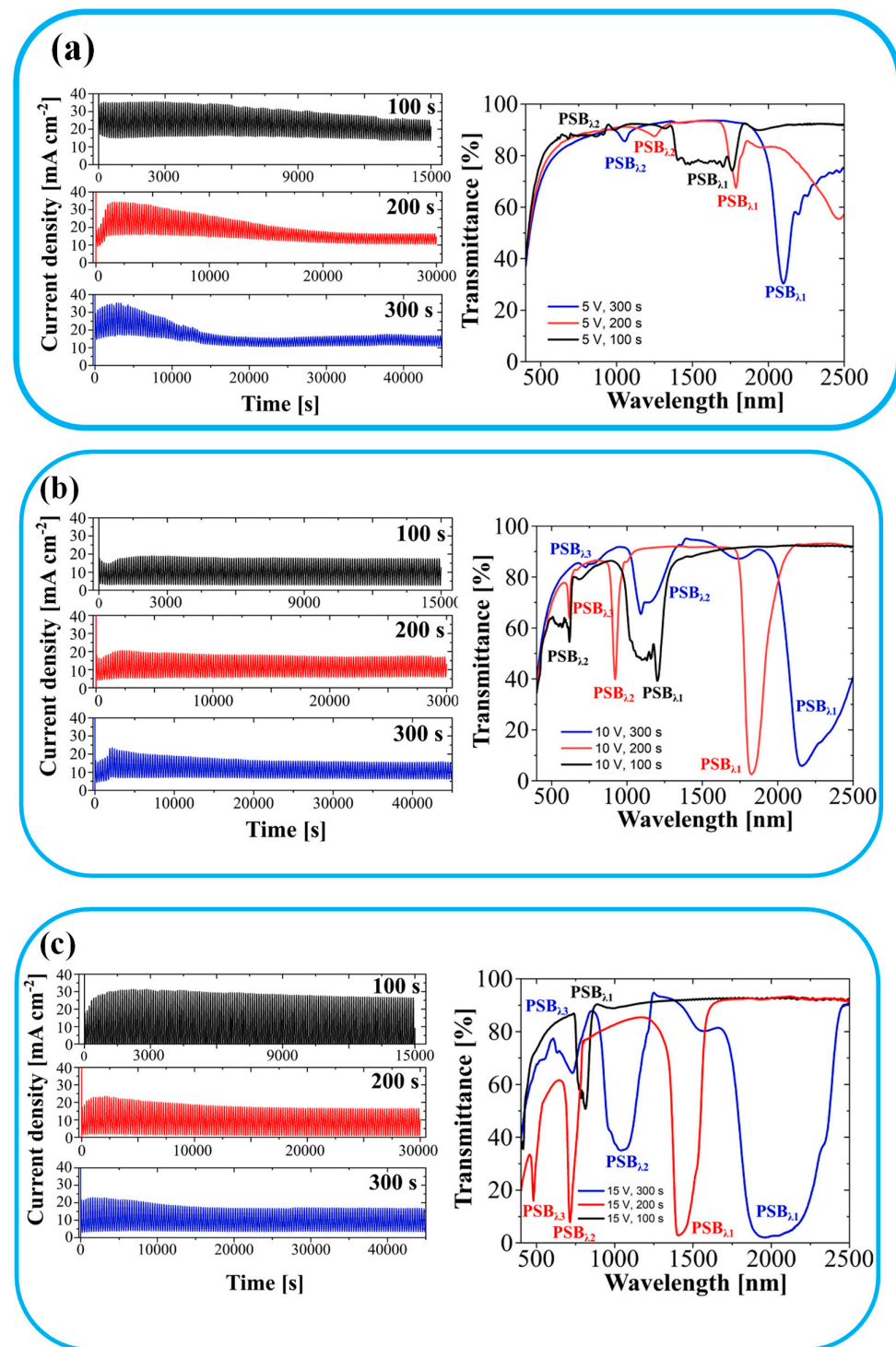


Figure 11. The current-density time curve obtained during a sinusoidal pulse, with colors denoting 100 s (black), 200 s (red), and 300 s (blue), and the resulting optical characterization depicted in the central wavelength position (PSB_{λ}) of sin-PAA samples anodized at (a) 5 V, (b) 10 V, and (c) 15 V (reprinted with permission from Ref. [188]).

Santos et al. investigated the correlation between the anodization parameters and pore geometry to produce AAO optical-bandpass filters using a typical current-pulsed anodization. In addition, when the time between pulses was systematically altered to suit a variety of stop and permitted bands in the spectra or temporal alterations were added in tiny time increments, the bands remained centered but their amplitude increased [189].

For sensing applications, these gradient-index filters have proven beneficial [185,190,191]. More complicated drug- and vitamin-detection methods [192,193] have been developed using more complex functionalizing agents, such as amino acids and proteins. Table 1 displays a few of the previously reported applications of PCs made of porous materials prepared by the anodizing method.

Table 1. Some applications of PCs based on synthesized AAO, pSi, and TNTs.

Preparation Method	Electrolyte	Formed Structure	Descriptions	Ref.
Periodic-pulse anodization	0.5 wt% NH_4	TNT PCs	Acted as a sensor where the air in the pores of the PCs was replaced by liquids with a greater RI. The photonic band gap for the PCs that were analyte soaked moved to a longer wavelength as a result.	[165]
Two-step periodic-pulse anodization	0.3 M H_2SO_4	AAO-DBR	Acted as a chemical sensor where the analyte's infiltration and RI were detected by the wavelength and intensity of the reflected light.	[28]
Two-step periodic-pseudo-sinusoidal anodization	An aqueous solution of $\text{C}_2\text{H}_2\text{O}_4$	AAO-GIF	The obtained results demonstrated that the AAO-GIF structure was sensitive towards changes in the effective RI, which offered a low limit of detection of 0.01 M (i.e., RI of 1.333) and a sensitivity of 4.93 nm M^{-1} (i.e., 164 nm per RI units).	[190]
Multi-sinusoidal pulse anodization	1.1 M H_2SO_4	AAO-GIF	The results show that the AAO-GIF is durable, chemically stable, adaptable, and has several special data-storage features, creating new prospects for the development of powerful nanophotonic instruments for a variety of applications, including sensing and photonic tagging.	[187]
Pulse anodization	0.5 wt% NH_4	TNT PCs	The coupling of TNT PCs into the photoanode of a dye-sensitized solar cell could achieve nearly full-visible-spectra light harvesting, which could lead to more fruitful practical applications of TNT PCs in high-efficiency photovoltaics, sensors, and optoelectronic devices.	[194]
Two-step anodization	0.5 wt% NH_4F	TNT PCs	It is suggested to use defect TNT PCs as the photoelectrode and dopamine as the target molecule for the near-infrared light-responsive PEC-analysis platform.	[195]
Two-step sinusoidal anodization	Aqueous 48% HF	pSi	The resulting structure (pSi film) was oxidized to produce a transparent spectrum filter that could be used with a digital camera (from a smartphone) to construct a tiny spectrometer.	[196]
Multistep anodization	HF/ethanol electrolyte	pSi-DBR	These investigations focus on the use of pSi films as the sensing element in bolometers, which have the potential to solve the performance and material compatibility concerns associated with current technologies such as amorphous Si and vanadium oxide in the long-wave infrared range.	[197]
Sinusoidal-pulse anodization	0.3 M oxalic acid	AAO-GIF	The impact of the applied-pulse amplitude and anodization period on the optical characteristics of the resulting gradient-index PAA was investigated.	[188]
Periodic anodization	HF/ethanol electrolyte	pSi-microcavity	A pSi microcavity structure was proposed as a sensor for real-time flow-sensing applications.	[198]

Santos et al. investigated the optical encoding of information within the porous AAO structure based on a color-barcode system [187]. As another intriguing application, they used multiple-sinusoidal anodization to fabricate more complex AAO-GIF systems

with adjusted localized narrow peaks [187]. They prepared an 8-bit encoding scheme with ON(1) and OFF(0) states by modulating the depth of the pore channels to enable or suppress particular transmission peaks. Additionally, a particular interferometric color was connected to each of the several possible ON/OFF-state combinations.

7. Conclusions and Outlook

Significant advances have been achieved in structural engineering over the past few years and in the surface modification of nanoporous materials. Applications have mostly driven this development. In this review, we compiled cutting-edge methods for fabricating and regulating structural PCs with various pore sizes, configurations, topologies, geometries, and pore architectures based on anodizing the surfaces of materials such as Al, Si, and Ti. It is feasible to access these structures by changing the anodization parameters such as current, voltage, and electrolyte type during the electrochemical self-ordering of PC nanostructures. In addition to their effects on the properties of the materials produced and the applications they enable, examples of innovative surface-modification techniques have been highlighted. By analyzing the outcomes and circumstances surrounding these anodization conditions, it was found that the type of voltage, current density, concentration, anodizing time, anodizing acid, and temperature all affect the diameter of the pore, interpore distance, and other structural characteristics of PCs. In the future, the focus should be on scaling up technologies to build integrated photovoltaics, which allows the integration of these materials on large surfaces. In addition, studies on the activation of internal pore walls with radical groups to anchor specific chemical and biological species must continue to be discovered. It is anticipated that the production of PC nanostructures in conjunction with even more control over surface functionality will result in one-of-a-kind nanostructures and nanodevices with previously-unheard-of functional properties for the next generation of devices. This will include an examination of their potential applications, with a focus on various research fields from electronics to material science and medicine. As a result, PC membranes will be crucial in a variety of new nanodevices.

Although all three 1D porous PCs discussed in this review show great promise to be applied as active or passive optical components in photonics or photovoltaics, their development is at a different stage of advancement. The preparation of periodic TNTs is perhaps the least explored research topic, which requires much more basic research on the formation mechanism and the relationship between the photonic structure and the pulse-anodization parameters. The optical signals are still of low intensity and must be strongly amplified to fulfill the demands for practical applications. On the other hand, pSi PCs have been widely tested as sensing platforms for detecting molecules in complex media such as biological systems or hazardous chemicals in the environment. Yet, the problem of the low sensitivity of pSi PCs to achieve the required detection limit still exists. Therefore, new strategies to better tailor the intrinsic structure and surface chemistry of pSi-based PCs are urgently needed. Despite the obvious advantages of pSi-based photonic structures (e.g., high RI, RI = 3.48), pSi oxidizes in air or aqueous solutions and degrades under acidic or basic media conditions. This leads to unstable optical signals. Therefore, strict surface-passivation protocols have to be worked out via chemical functionalization to make using this material in optical sensing possible. Porous AAO can overcome the drawbacks of pSi photonic-crystal structures because of its excellent mechanical, thermal, and chemical resistance. AAO has a controllable and versatile pore geometry and is produced by a cost-effective and fully scalable fabrication process. However, the low RI of Al₂O₃ (RI = 1.77) will probably hinder the synthesis of the full range of photonic materials (e.g., optical cavity with sufficiently large Q-factor or good-quality Bragg reflectors) with the desired optical properties. The inherent limitation of AAO can perhaps be circumvented by employing other techniques or materials, such as plasmonic metals, with the ability to reinforce the signal by resonance coupling. However, this research is still in the conceptual stage. Most of the porous PCs developed so far were designed for ultraviolet and visible (UV/visible) spectral domains. Yet, the prospective research has to progress beyond the

visible spectral to meet the challenges of producing cost-effective optical components with excellent photonic properties in the broad spectral range extending up to mid-infrared. Although initial trials have been carried out in this respect, the field is largely unexplored and awaiting novel approaches and strategies to be developed in the future.

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