Nanoscience and nanotechnology have attracted much interest in recent years because materials exhibit novel properties when structured at nanometer dimensions. In particular, titania (TiO$_2$) nanotubes, a unique functional material combined with directionality and dimension, have been regarded as having unlimited potential. Although many successes have already been achieved, for instance, as solar-energy materials$^{{[1–5]}}$ for use in batteries$^{{[6–8]}}$ and as a tool for sensing$^{{[9–11]}}$, significantly less research has focused on the potential of such structures for manipulating photons in terms of an optical material—“photonic crystals” (PCs)—which can open a new range of possibilities for flexible materials synthesis and new phenomena generation.

Three-dimensional (3D) PCs, which have enormous omnidirectional bandgaps, became an emerging field in the 1990s since when various synthesis approaches have been proposed and demonstrated, such as self-assembly$^{{[12–16]}}$ lithography$^{{[17–19]}}$ and direct laser writing$^{{[20–22]}}$. However, most of these methods bear inherent limitations that may hinder their practical deployment, for instance, complicated and costly micromanipulation techniques, the limited tunability of the stop band, and the difficulty of integration. Herein, we present a material assembly route that can bridge the gap between TiO$_2$ nanotubes and photonics. The main benefit of this method for 3D PC manufacture is its high efficiency, good quality, and continuous production, thereby promoting a new application of TiO$_2$ nanotubes for photon manipulation.

To fabricate nanostructured TiO$_2$ arrays, anodization is a simple, straightforward, and self-driven approach among several synthesis strategies$^{{[23–25]}}$ both on Ti foils and Ti thin films$^{{[26,27]}}$. For years, scientists in the realm of anodization predominantly focused on the investigation of tube synthesis under potentiostatic conditions. Anodization at a certain voltage predominantly focused on the investigation of tube synthesis under potentiostatic conditions. Anodization at a certain voltage leads to an ordered oxide layer consisting of smooth or irregular corrugated tubes in different electrolytes$^{{[28]}}$, and such corrugated stacks show defined interference patterns. Proposals of the potential application of nanopores and nanotubes in 2D PCs firstly emerged due to their periodically aligned nature in two dimensions$^{{[29–33]}}$. Recently, 3D structural TiO$_2$ nanotubes were made available under specific alternating-voltage conditions, with the attempt to create bamboo-type or multilayer nanotubes$^{{[34,35]}}$, for example, for optimizing solar-cell efficiencies. However, the complex architectures fabricated with the aid of periodic voltages are erratic, and lack the quality that PCs demand. Ordered 3D pore structures were only developed in alumina (Al$_2$O$_3$) in combined mild and hard anodization processes with periodic changes in diameters in specific electrolyte solutions$^{{[36–38]}}$. Cyclic anodizing voltages$^{{[39,40]}}$ have also been utilized to create periodically and partially branched Al$_2$O$_3$ pore structures for PC applications, but the regularity and precise control of the structures along the nanotubes are far from satisfactory. Also, the refractive index of Al$_2$O$_3$ (n = 1.7) is too small to perform a complete bandgap of PCs, which is the principal requirement for a material used for PCs and desirably should be higher than 2$^{{[41,42]}}$. Herein, we introduce a well-defined periodic structure in the tube direction of TiO$_2$ for the synthesis of 3D PCs. In addition to its greater chemical stability, outstanding functional properties, and fundamental applications, TiO$_2$ possesses a larger index of refraction (n = 2.7) than Al$_2$O$_3$ or other oxides$^{{[43]}}$ thus making it suitable for the preparation of high-quality and functional structural color materials$^{{[44–48]}}$

Instead of the spontaneous random current oscillation found when anodized in certain electrolytes leading to tubes with irregular ripples$^{{[9,28,32,49,50]}}$, the strictly controlled periodic modulations should be ensured for their use as PCs. Modulated-voltage anodization, also known as “pulse anodization”, was previously exploited to improve the surface morphology$^{{[51,52]}}$ and can also be expected to introduce structural variation along the tubes. The key point of the different oxide morphologies across the tube length is the interruption of the established tube growth state between the voltage steps. However, the potentiostatic current flow usually exhibits an exponential decrease as a function of time, and the growth rate of oxide films in such processes decreases with time$^{{[53,54]}}$. Therefore, a periodic voltage will lead to gradually decreased period lengths, and precise control of the tube length for structural engineering can hardly be achieved. The details of the tube length deviation from top to bottom are also included below. To ensure the uniformity of tube length during each pulse cycle, current pulses were employed to attain a constant growth rate of TiO$_2$ nanotubes, which are developed from the galvanostatic anodization$^{{[55–56]}}$ recently used in TiO$_2$ nanotube formation, and have also been utilized in the structural engineering of Al$_2$O$_3$ nanopores$^{{[36]}}$. The State Key Laboratory on Fiber Optic Local Area Communication Networks and Advanced Optical Communication Systems, Shanghai Jiao Tong University, 800 Dongchuan Rd., Shanghai 200240, China. E-mail: xzhchen@sjtu.edu.cn

**Synthesis of Periodically Structured Titania Nanotube Films and Their Potential for Photonic Applications**

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After current-pulse anodizations of different durations of the higher current limit, lower current limit, or total reaction process, tubes with periodic structures in the tube direction were obtained. Schematic illustration of the fabrication strategy and the representative scanning electron microscopy images of the resulting samples are shown in Figure 1.

**Figure 1.** From the top, middle, and bottom view images, the detached film reveals a conventional regular nanoporous structure on the surface and a tube structure underneath. The well-defined segment interfaces can be clearly distinguished in the cross-sectional image. Note that the concave morphology of the tube walls at the interfaces is quite different from the bamboo-type structure grown under alternating-voltage conditions. These results confirm the successful assembly of films with periodic structure along the tubes.

During the anodization process, there is a set of factors that influences the morphology and growth of TiO₂ nanotubes. By varying the water content in the electrolyte, tubes with smooth or corrugated walls can be obtained (Figure 2a,b). Unlike the typical morphologies of tube walls under conventional anodization processes, and also bamboolike tubes with the reinforced compact parts at the interface regions (Figure 2c), these structurally engineered tubes under the current-pulse conditions feature small voids around each stack interface (Figures 1c and 2d). As mentioned above, decreased current densities are observed under the voltage-pulse conditions shown in Figure 2e. The profile of the current curve is quite similar with a typical current–time relation during constant-voltage anodization (shown in the inset of Figure 2e), with a sharp drop at the initial stage of the process. The current density gradually decreased during the process, from 10.37 to 3.52 mA cm⁻², which indicates a quite nonuniform tube growth rate. However, the performance of the voltage variation during current pulses is quite different (Figure 2f). Apart from the initial stage of several periods, the voltage only varied from 60 to 68 V during a 35-period process lasting ≈100 min, which is quite a small deviation and does not have any significant influence on period regularity (demonstrated from the results below).

From the representative voltage–time relations shown in the inset of Figure 2f, a decrease in the voltage during the higher-current process can be clearly seen after a voltage peak within a period. After careful examination of the voltage variations during the pulse sequences, we find that the difference between the lower voltage at the end of the previous pulse and higher voltage at the forepart of the subsequent pulse is about 5 V, which leads to sufficient diameter variation with an estimated value of about 9.5 nm during a voltage contrast, in accord with previously reported results of the proportionality between pore diameter and anodization voltage in the high-field condition. This important characteristic of the voltage curve enables the formation of periodic structures with concaves. Note that although the field-assisted reaction stopped at the lower level of the pulse sequence, the optimal holding time existed for sufficient local diffusion. A longer total reaction time will create more periods along the tube, but too thick a film will lead to the collapse of the tube surfaces, which is also a common phenomenon after the extended normal anodization, and might be further avoided by proper treatments.

After extended period of time, the interfaces of the segments near the surface are etched off and the layers separate. The interfaces of modulated tube structures formed at the lower voltage correspond.
to the thinnest parts of the tube walls\cite{62} and will be etched out first due to permanent chemical dissolution in fluoride-containing electrolyte.

As mentioned above, the pulse duration of the higher current limit determines the length of the periods, and the spacing between interfaces is almost unchanged from top to bottom (see Figure 3b,c, with interfaces indicated by arrows), with different average period lengths of 292 and 352 nm. The detailed data of the length of each period are also shown in Figure 3d. In the range of ≈20 periods for both the samples, which is enough to reveal bright colors, periodic structures formed under current-pulse conditions reveal excellent regularities, and reach the long-range order required for PCs. As shown in Figure 3e, the growth speed is about 0.26 μm min\(^{-1}\), which is consistent with our previous data under the same anodization conditions. This leads to the simple and precise modulation of the length of the periods. However, for the sample fabricated under voltage-pulse conditions with the bamboo-type morphology (shown in Figure 3a), the period length changed greatly from about 470−260 nm during 20 periods, which is also consistent with the largely decreased current density shown in Figure 2e.

Thin films with periodic structures along the tube can be designed in a variety of different colors and transparencies, simply by adjusting the length and number of the periods. Figure 4a shows photographs of the structured films. Visually, the crystalline films display uniform and monochrome colors in reflected light. Since TiO\(_2\) responds only in the UV, these 3D structured films are optically transparent in the visible region. Note that the complementary colors of the reflected light can be seen in the transmitted light. The anatase TiO\(_2\) is naturally white in color and the film coloration must originate from the periodic microstructures, which is attributed to the diffraction of light and interference effects. Unlike the smooth-walled tubes, modulated air pillars exist in the hollow tubes and the voids among the tubes, which leads to the required refractive index modulations in three dimensions. Figure 4b shows the typical optical reflection spectra of the colorful films for samples with different period lengths. The distinct reflection peaks over the entire visible spectrum correspond to the Bragg peaks of the samples. The gap positions are located at about 441, 500, and 660 nm, which reveal the three primary colors of blue, green, and red, respectively. The average period lengths of the three samples are about 115, 257, and 339 nm, and by careful examination of other colorful samples a correlation with the gap position of about 0.25 is obtained, which awaits further verification possibly by theoretical modeling.

Structural color is not static and the color appearance changes when the incident angle of the illuminating white beam varies with respect to the film plane. Figure 5 shows the colorful nanostructured film kept attached to the substrate (for convenient observation) with a series of various incident and viewing angles. Since the periodic structure is three dimensional, the bandgap for light propagation changes in different directions. Moreover, due to the flexible nature of the nanotube films, application of a certain mechanical force can also induce changes in the observing angles of the films, consequently leading to different colors in various parts of the films, as can be seen in Figure 5c.
Furthermore, as the structural colors originate from modulation of the refractive indices of the microstructures, tunable colors can be obtained by filling the tubes with materials with variable refractive indices.\(^44\) We have already noted that the colors of the films for different stages of the fabrication processes are also different in the electrolyte and after drying in air. By introducing the 3D PCs directly into TiO\(_2\) nanotubes, the solar-cell efficiencies are also expected to be greatly improved via photon localization.\(^63\) Other architectures, such as periodic structures with specific patterns, the introduction of controlled defects,\(^64\) and quasi-periodic tube structures, can also easily be realized in the 3D PCs developed here. Taking into account the photocatalytic and photoinduced superhydrophilicity properties of TiO\(_2\) nanotubes, new functional materials can be achieved by combining this optical element.

In summary, we have reported the simple preparation of colorful 3D PC films made of anodic TiO\(_2\) nanotubes. The optically active three-dimensionally periodic TiO\(_2\) nanotube arrays were obtained under current-pulse anodization. These films display structural colors and corresponding photonic bandgaps in the entire visible spectrum, and their photonic characterization is under way. Significantly, the structures can be precisely controlled by reaction parameters, and large-area, transparent, and flexible 3D PCs can be synthesized conveniently, ready for on-chip integration. Finally, since TiO\(_2\) is electronically active and biologically adaptive, the integrated optical properties will open new prospects for future application of TiO\(_2\) nanotubes.
Experimental Section

Highly ordered TiO₂ nanotube arrays revealing different structural colors were prepared by current-pulse anodization in a two-electrode electrochemical cell with the working electrode Ti foil and the counter electrode Pt foil. The component of the electrolyte used in the Ti anodization was ethylene glycol solution containing NH₄F (0.5 wt%) and H₂O (3 vol%). The Ti foil (0.2 mm in thickness) was firstly cleaned ultrasonically in deionized water, acetone, and ethanol and then pretreated by anodization at 60 V for 10 min. The patterned Ti surface was exposed by a subsequent ultrasonic treatment in deionized water for 3–5 min. The pretreated foil was then used for the fabrication of a periodic structure at room temperature using current-pulse waveforms in the as-prepared electrolyte without any pretreatment of the solution. The currents were pulsed between 7 and 0 mA cm⁻², and the durations at the higher and lower limits of the pulse were controlled from 20 to 100 s and 0.5 to 3 min to tailor the length of period and the interface morphology, respectively. The period number was varied from 20 to 50 for different samples, corresponding to various total reaction times and film thicknesses. The resulting oxide layers containing NH₄F (0.5 wt%) and H₂O (3 vol%) were obtained after the process.

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