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Multiple bands light trapping in ultraviolet, visible, and near infrared regions with TiO$_2$ based photonic materials†

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The TiO$_2$ based photonic materials (TiO$_2$ PMs) with hierarchical top-nanonet/bottom-nanotube structures were fabricated by a facile two-step electrochemical anodization method. The TiO$_2$ PMs demonstrated multiple bands light trapping activity not only in ultraviolet and visible regions, but also in near infrared region.

Photonic materials (PMs) are periodically structured electromagnetic mediums, with light trapping property by light scatter and diffract, which express great significance in controlling light for display, sensor, telecommunication, and solar energy conversion. Physicists fabricated the PMs by lithographic method, which required complex and expensive instruments and clean-room facilities, while the chemists implemented that in much easier ways by biological templates, polymerized crystalline colloidal arrays, opal hydrogel, and inverse opal hydrogel methods. The most popular chemical method today was the self-assembly of low refractive index PMs, such as silica or polystyrene microspheres, in the form of colloidal crystals to form opals structure, and then replicated the opal template with functional materials, followed by removing the template, then the inverse opal PMs with high reflective index were prepared. However, the inverse opal high reflective index PMs suffer from disadvantages of (1) single band or narrow light trapping region, most of them suppressed in visible light region; (2) existence of cracks, significantly detrimental to the optical properties of the materials.

Titanium dioxide (TiO$_2$), one of the vital materials for fabrication of solar energy conversion devices, distinguished itself due to its favorable band-edge positions, superior chemical and optical stability, and low lost. The TiO$_2$ materials with photonic structure would be advantageous for enhancing solar energy conversion efficiency due to its unique light trapping properties, which assured its potential and promising applications in this field. Nowadays, the TiO$_2$ based PMs have been fabricated by bio- or opal-templates methods, but as well as suffered shortcomings originated from these methods as aforementioned. The preparation of TiO$_2$ based PMs with multiple bands light trapping property in broad spectrum region, crack-free surface in large scale area by a facile and effective chemical method is still a big challenge.

Very recently, Huang et al reported the fabrication of TiO$_2$ nanotube based PMs by modulate the multi-layered thickness along the axial direction of the nanotubes, and implemented the enhancement of light trapping in visible region, thus improved the performance of dye sensitized solar cells based on this material. However, to the best of our knowledge, there has no report for TiO$_2$ based PMs with significantly light trapping properties in near infrared region. In the present study, we report a facile two-step electrochemical anodization approach to prepare a new class of TiO$_2$ based PMs with broad light trapping activity, which harvest the light not only in ultraviolet and visible regions, but also in near infrared region. The superior optical quality and property guaranteed its potential wide applications in many fields.

Scheme 1. Two-step electrochemical anodization process for TiO$_2$ PMs preparation.
removed in an ultrasonic bath. The high voltage resulted in fast grow rate and high TiO₂ NTs thickness, which was favourable for its removal form the Ti substrate with ultrasonic treatment. The same Ti foil with surface textured nanoconcares (Fig. S1, ESI†) underwent the second-step anodization with progressive increasing voltages from 10 V to 30 V, thus the hierarchical TiO₂ PMs with top-nanonet/bottom-nanotube structures were fabricated. The successive increasing voltage was vital in the second anodization step for the formation of uniform and periodic nanostructures. The as-anodized TiO₂ PMs were annealed in air at 450 °C for crystallization (XRD pattern in Fig. S2, ESI†). For comparison, one step anodized TiO₂ NTs and two-step anodized TiO₂ NTs at constant voltages in the second step anodization were also prepared.

The morphology of the TiO₂ PMs was determined by field-emission scanning electron microscope (FESEM, FEI Quanta 600). Fig. 1a shows the large scale SEM image of the TiO₂ PMs, as expected, a uniform and clean top surface is observed, no any cracks and debris can be found. The high magnification SEM image is presented in Fig. 1b, which indicates clear hexagon nanonets on the top, and vertical nanotubes underneath. The top nanonet shows an average diameter of 160 nm, and frame thickness of ~50 nm. The diameter of nanonet is equal to the diameter of nanoconcaves on the textured Ti surface, and the network frame thickness is similar with the ridge thickness on nanoconcaves (Fig. S1, ESI†), which implies that the top-nanonet structure is formed with textured nanoconcave as template. The high magnification cross-sectional view SEM image (Fig. 1c) confirms the hierarchical top-net/bottom-tube nanostructure with the top layer thickness being ~50 nm and the bottom-tube diameter in the range of 60-70 nm. The bottom of nanotubes is closed and hexagonally packed as shown in Fig. 1d, which is helpful for the formation of nanoconcaves underneath the nanotubes.

The one-step anodized TiO₂ NTs were also prepared, which show severe cracking and fragile bundling debris on the surface (Fig. S3, ESI†). The TiO₂ NTs, prepared by two-step anodization method with constant anodized voltages (30 V and 60 V) in the second-step anodization process, fail to show uniform and periodic nanonet structures. The 30 V anodized sample presents random nanoring structure on the top layer (Fig. S4, ESI†), and the 60 V anodized sample presents uniform nanopore structures (Fig. S5, ESI†), however, the pore size is too small to interact with long wavelength light.

The crystalline structure of TiO₂ PMs was analyzed by X-ray diffraction (XRD, Bruker D8 Discover diffractometer, using Cu Kα radiation, λ = 1.540598 Å). The strong XRD diffraction peak at 25.3° indicates highly crystallized and dominant anatase phase with preferential orientation of (101) (TiO₂: JCPDS No. 21-1272, Ti: JCPDS No. 44-1294) (Fig. S2, ESI†). The chemical components and surface chemical state of TiO₂ PMs were characterized by photoelectron Spectroscopy (XPS) with an Axis Ultra instrument (Kratos Analytical) under ultrahigh vacuum (<10⁻⁸ torr) (Fig. S6, ESI†). The survey spectra of the TiO₂ PMs confirm its pure TiO₂ constituent. The high resolution spectra of Ti 2p present dominant peaks centered at 458.6 eV (Ti 2p 3/2) and 464.3 eV (Ti 2p 1/2), which associate with Ti ions with a formal valence of four (Ti⁴⁺). The core-level XPS of O 1s show a two-band structure, with dominant peak at 529.8 eV for the oxygen in TiO₂ lattice, and an additional peak at 532.0 eV for the oxygen in hydroxyl.

The diffuse reflectance UV-vis-NIR (ultraviolet-visible-near infrared) absorption spectra of TiO₂ PMs were recorded on spectrophotometer (Shimadzu, UV 3600) with fine BaSO₄ powder as reference. As presented in Fig. 2, multiple absorption peaks around 320, 428, 482, 542, 620, 725, 879, 1128, 1585, and 2430 nm were clearly observed in U/V, visible, and near infrared light regions due to its featured photonic structure. The strong UV absorption below 380 nm can be ascribed to its excitation through band gap. The absorption reached maximum at 320 nm, which can be explained by strong light diffraction induced by the well matching of half wavelength with the top-nanonet’s diameter (160 nm). The other moderate absorption peaks in visible and infrared regions can be ascribed to two concurrent processes: first, the light possesses slower transport velocity in high refractive index medium than in air, which results in higher reflectivity, and prolongs the interact time between light and the surrounding sample, enhancing the efficiency of scattering processes, leading to further improvement of light trapping. Second, the unique hierarchical top-nanonet/bottom-nanotube structure acted like a Fabry-Pérot resonator, induced strong finite-size effects, and presented characteristic oscillations and resonances. The top inset in Fig. 2 shows an actual photo of a TiO₂ PMs, in which presents a visual colour patterns on the surface, provides a macroscopic evidence of the formation of a unique photonic structure. It is worth mentioning that the one-step TiO₂ NTs sample did not show any photonic property (Fig. S7, ESI†), due to...
its rough and dis-uniform surface. The two-step samples prepared with voltages presented strong peak in UV region and broad absorption in visible region, but failed to show multiple peaks characterization (Fig. 5, and Fig. 6, ESII).

The formation of TiO\textsubscript{2} PMs in anodization processes is an outcome of competition between electric field driven oxidation of metal to form oxide and chemical and field-assisted dissolution of the metal oxide layer.\textsuperscript{19} The overall reactions of the two processes can be presented as:

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{OH}^- + \text{H}^+ \\
\text{OH}^- & \rightarrow \text{O}^2^- + \text{H}^+ \\
\text{Ti} + 2\text{O}^2^- & \rightarrow \text{TiO}_2 + 4\text{e}^- \\
\text{TiO}_2 + 6\text{F}^- + \text{H}^+ & \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O}
\end{align*}
\]

The dissolution in the form of [TiF\textsubscript{6}]\textsuperscript{2-} is highly affected by the applied electric field. In the second anodization step, electric field existed in the bottom of concave possessed higher intensity than that at the top surface, which induced the faster dissolution rate in the middle of the nanoconcave, thus preferred for the formation of TiO\textsubscript{2} NTs into depth, but remained the edge of concave to form network NTs into depth, but remained the edge of concave to form network.

In summary, we successfully fabricated TiO\textsubscript{2} PMs by a facile two-step electrochemical anodization method. The prepared TiO\textsubscript{2} PMs not only showed strong light trapping activity in UV and visible region, but also possessed infrared light harvesting activity, implemented multiple bands light trapping activity in broad spectrum.

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