TiO₂ Nanotube Arrays for Photocatalysis: Effects of Crystallinity, Local Order and Electronic Structure

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To furnish insight into correlations of electronic and local structure and photoactivity, arrays of short and long TiO₂ nanotubes were synthesized by electrochemical anodization of Ti foil, followed by thermal treatment in O₂ (oxidizing), Ar (inert) and H₂ (reducing) environments. The physical and electronic structure of these nanotubes were probed with X-ray diffraction (XRD), scanning electron microscopy and synchrotron-based X-ray absorption spectroscopy, and

correlated with their photocatalytic properties. The photocatalytic activity of the nanotubes was evaluated by monitoring the degradation of methyl orange under UV-VIS light irradiation. Results show that upon annealing at 350 °C all as-anodized amorphous TiO₂ nanotube samples partially transform to the anatase structure, with variations in the degree of crystallinity and in the concentration of local defects near the nanotubes' surface (~ 5 nm) depending on the annealing conditions. Degradation of methyl orange was not detectable for the as-anodized TiO₂ nanotubes regardless of their length. However, the annealed long nanotubes demonstrated detectable catalytic activity, which was more significant with the H₂-annealed nanotubes than with the Ar- and O₂-annealed nanotube samples. This enhanced photocatalytic response of the H₂-annealed long nanotubes relative to the other samples is positively correlated with the presence of a larger concentration of lattice defects (such as Ti³⁺ and anticipated oxygen vacancies) and a slightly lower degree of crystallinity near the nanotube surface. These physical and electronic structural attributes impact the efficacy of visible light absorption; moreover, the increased concentration of surface defects is postulated to promote the generation of hydroxyl radicals and thus accelerate the photodegradation of the methyl orange. The information obtained from this study provides unique insight into the role of the near-surface electronic and defect structure, crystal structure and the local chemical environment on the photocatalytic activity and may be employed for tailoring the materials' properties for photocatalysis and other energy-related applications.

I. INTRODUCTION

Titanium dioxide (TiO₂) nanotubes have attracted significant attention due to their potential application in photocatalysis¹⁻³, gas sensing⁴⁻⁶ and dye-sensitized solar cells⁷⁻¹⁰. In

particular, electrochemically-synthesized ordered arrays of TiO₂ nanotubes with a large surface area are promising photocatalysts for degradation of selected organic compounds in wastewater and for hydrogen generation via water splitting^{1-3, 10-15}. The photoreactivity of TiO₂ nanotube arrays is influenced by their morphology (*e.g.* tube length and diameter), electronic structure (such as band gap or local bonding environment) and their crystallinity, all of which may be modified via control of the synthesis parameters (*e.g.* electrolyte components and the applied voltage)¹³⁻¹⁶ and post-synthesis annealing conditions (such as nature of the annealing gas, annealing rate and temperature range)^{12, 17-23}. The enhanced photocatalytic capacity of TiO₂ nanotube arrays as compared to that of thin films and nanoparticles is attributed to the nanotubes' geometrically-ordered porous architecture, larger surface area and longer charge carrier lifetime^{1, 2, 24-26}. A thorough understanding of the fundamental property-functionality relationships of TiO₂ nanotubes is critical for engineering the structure and optimizing the photocatalytic activity of TiO₂ nanotubes and similar nanostructures²⁴⁻²⁸. Effects of temperature, gas pressure and impurities on the concentration of bulk defects in the TiO₂ structures are reported elsewhere,²⁹ and the approaches to alter the defect structure, such as high-pressure hydrogen treatment³⁰ and annealing in CO at elevated temperatures up to 600 °C³¹, to advance the biosensing capability of TiO₂ nanostructures. However, the relationships between the electronic structure, local order, surface defects and crystallinity, specifically in the near-surface region (~ 5 nm), and their effect on the catalytic activity of ordered TiO₂ nanotubes have not been well studied nor clarified to date.

In this study, arrays of short (0.2 μm) and long (25 μm) TiO₂ nanotubes are electrochemically synthesized in aqueous and non-aqueous electrolytes, respectively, and are then subjected to thermal treatment in O₂ (oxidizing), Ar (inert) and H₂ (reducing) flowing gas

atmospheres at 350 °C to induce crystallization. The morphology and crystal structure of these nanotubes are investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. Synchrotron-based X-ray absorption spectroscopy (XAS) is carried out at the Ti $L_{3,2}$ -edge and the O K -edge to probe the local chemical environment, local defect state and elemental electronic structure of the nanotubes in their near-surface region (~ 5 nm), as a complementary technique to the XRD bulk measurements^{32, 33}. The photocatalytic activity of the nanotubes is evaluated by monitoring the degradation of methyl orange in an aqueous solution under UV-VIS light irradiation. In this work, the effects of synthesis and processing conditions on the morphology, crystallinity, local and electronic structure of both short (0.2 μm) and long (25 μm) TiO₂ nanotubes are presented and correlated with their photoactivity, with the objective to further understand and optimize the functionality of this nanostructured material.

II. EXPERIMENTAL SET UP AND METHODOLOGY

A. Synthesis and processing of nanotubes

Ordered arrays of TiO₂ nanotubes were synthesized by electrochemical anodization of titanium foil (99.97% pure, 127 μm -thick, Sigma-Aldrich) located at 4 cm distance from the cathode (platinum mesh) in 120 mL of anodization electrolyte. Short nanotubes were produced in an aqueous electrolyte consisting of 0.25 M hydrogen fluoride under an applied voltage of 15 V_{DC} for duration of 45 min, and long nanotubes were synthesized in a non-aqueous solution of ethylene glycol (98 vol%), 0.05 M potassium fluoride and 1 vol% deionized water under 60 V_{DC} for duration of 4 hours. After anodization, TiO₂ nanotube arrays, still attached to the titanium substrate, were ultrasonicated for 30 minutes in isopropanol (99.95%) and dried in a gentle airflow. Arrays of short and long substrate-supported as-anodized TiO₂ nanotubes were placed in ceramic boats in a quartz tube furnace and annealed at 350 °C for one hour with heating/cooling

rate of 1 °C/min under flowing O₂ (99.8%), Ar (>99.995%) and H₂ (>99.995%) at a fixed flow rate of 30 cm³/min. One set of nanotube samples (short and long) was annealed in the similar conditions but at 300 °C to examine the effect of annealing temperature on the nanotube physical properties.

B. Characterization of nanotubes

The nanotube morphology in the as-anodized and annealed states was examined with field-emission scanning electron microscopy (FESEM, Hitachi S4800). The crystal structure of nanotube samples was probed by laboratory-based XRD (Philips X'Pert Pro PANalytical) with Cu K_α as the X-ray source. The Ti *L*_{3,2}-edge and O *K*-edge XAS for the supported TiO₂ nanotubes were acquired at the U4B beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. The XAS spectra of the supported nanotubes were collected with the linearly polarized incident beam, parallel to the surface normal of the Ti substrate, in total electron yield mode. The data were normalized to the incident beam intensity with an energy resolution of ~ 0.2 – 0.3 eV. Under these conditions, XAS probes the near-surface region of the material (approximately 5 nm probe depth). The collected spectra were compared with those of the reference titanium oxide-based powders, 99.6% pure anatase, 99.8% pure rutile and 99.8% pure Ti₂O₃, all examined under the same conditions as indicated above. The peak positions and intensities for each Ti *L*_{3,2}-edge absorption spectrum were quantitatively determined by deconvolution of the absorption peaks into eight Voigt-function peaks after subtracting two step functions as the background. The centroid of each Voigt peak was designated as the peak position and the peak intensity, *I*, were used to define the area of each peak. The split peaks ascribed to *e_g* symmetry were denoted as *e_{g(a)}* (with lower energy) and *e_{g(b)}* (with higher energy). The position of the *L*₃-*e_g* peak was determined as the average value between

the $e_{g(a)}$ and $e_{g(b)}$ positions.

C. Evaluation of the nanotube photocatalytic activity

The photocatalytic activity of the TiO₂ nanotubes was investigated via monitoring the photodegradation of methyl orange (MO) in an aqueous solution (10 mL) in the presence of 0.6 cm² exposed surface area of titanium-supported nanotube arrays. Prior to exposure to UV-VIS light irradiation, the nanotubes were immersed in the MO solution in a dark environment for 1 h to reach equilibrium in the adsorption-desorption processes of MO molecules on the nanotube surface. The supported nanotubes were mounted in the reaction cell facing the UV-VIS light source at a distance of 19 cm; efficient mass transport in the system was ensured by constantly stirring the solution. The UV-VIS light source was a 147 W mercury lamp with 0.5 M copper sulfate solution as the light filter. The experimental set-up was water-cooled to maintain a constant temperature of 25 °C during the irradiation process. The absorption spectrum of MO was obtained with a UV-VIS spectrometer (8452A Diode Array Spectrophotometer, Hewlett Packard) at specified irradiation time intervals of 30 min. The absorption peak at 463.8 nm wavelength in the MO UV-VIS absorption spectrum was used to monitor the concentration profile of MO in the solution. The change in MO concentration was evaluated by its fractional conversion, $f_{MO} = (1 - C_t/C_0)$, where C_t is the absorption at a given reaction time and C_0 is the absorption at time $t = 0$, after reaching equilibrium in dark environment. A blank control experiment was carried out with Ti foil under the same conditions, the results of which were subtracted from those obtained from the nanotube samples. The rate constant of the catalytic MO degradation reaction, k , was calculated assuming a first order reaction given by $\ln(1/(1-f_{MO})) = kt$.

III. RESULTS

A. Microstructure and crystal structure

Cross-sectional and pore-side SEM images of the as-anodized and annealed TiO₂ nanotube arrays are shown in Figure 1(a-h). The short nanotubes feature an average diameter of 60 nm and an average length of 0.2 μm (Figures 1a, c, e, g) and the long nanotubes are $\sim 25 \mu\text{m}$ long with an average diameter of 90 nm and a wall thickness of ~ 10 nm. Both short and long nanotubes exist in closely-packed arrays and their morphology remained intact upon annealing, regardless of the annealing atmosphere or temperature.

FIG. 1. SEM images of the short (left-hand side) and long (right-hand side) TiO_2 nanotubes. Side-view of nanotubes: (a-b) as-anodized. Top view of nanotubes: (c-d) as-anodized; (e-f) O_2 -annealed; and (g-h) Ar-annealed.

XRD confirmed that the short and long TiO_2 nanotubes are amorphous in their as-anodized states (figure not shown), consistent with previous reports^{19, 20, 22, 34}. The anatase structure develops upon annealing at 350 °C as evident by the XRD patterns in Figure 2. The

Bragg peaks associated with metallic titanium in these XRD patterns are due to the Ti substrate. The highest intensity (101) Bragg peak of anatase is present for all the annealed nanotube samples regardless of the nanotube morphology or the annealing atmosphere.

reveal information on the structure, including the local (angstrom-level) structure^{35, 36}, the medium-range (~ 1 nm) structure and the long-range crystallographic order⁴⁰⁻⁴³ in the near-surface region of the nanotubes. Quantitative information is extracted from the Ti $L_{3,2}$ -edge of the annealed TiO₂ nanotubes based on the peak positions and intensities summarized in Table 1.

Table 1. The peak fitting parameters of Ti $L_{3,2}$ -edge XAS spectra of the as-anodized and annealed TiO₂ nanotubes (NTs), and anatase, rutile and Ti₂O₃ reference oxides. The error for the peak fitting is < 0.1 eV and the beam resolution is approximately 0.2-0.3 eV.

		Ti $L_{3,2}$ -edge					
		Peak position/separation (eV)					Intensity ratio
		t_{2g}	$e_{g(a)}$	$e_{g(b)}$	e_g	d [$e_{g(b)}-e_{g(a)}$]	$I(e_{g(a)})/I(e_{g(b)})$
Long TiO ₂ NTs	As-made	458.3	459.7	460.5	460.1	0.8	1.19
	O ₂ -annealed	458.3	459.8	460.7	460.3	0.9	1.00
	Ar-annealed	458.2	459.7	460.7	460.2	1.0	1.07
	H ₂ -annealed	458.2	459.7	460.7	460.2	1.0	1.05
Short TiO ₂ NTs	As-made	458.2	459.6	460.5	460.1	0.8	0.92
	O ₂ -annealed	458.3	459.8	460.7	460.3	0.9	0.82
	Ar-annealed	458.3	459.8	460.7	460.3	0.9	0.87
	H ₂ -annealed	458.3	459.8	460.7	460.3	0.9	0.89
TiO ₂ anatase		458.3	459.9	460.7	460.3	0.9	0.82
TiO ₂ rutile		458.2	459.8	460.9	460.4	1.0	0.73
Ti ₂ O ₃		458.2	459.6	460.6	460.1	1.0	0.79

In the as-anodized state, the Ti $L_{3,2}$ -edge absorption spectra of the short and long TiO₂ nanotubes, Figure 3, are quite similar to those of amorphous TiO₂⁴⁰ featuring: (1) broad peaks centered at both the L_3 and L_2 edges; (2) reduced L_3-t_{2g}/L_3-e_g intensity ratios as compared to those of the reference anatase and rutile structures; and (3) a rather poorly-resolved L_3-e_g doublet structure. The shapes and positions of the pre-edge (456 – 457.8 eV) features for all as-anodized

nanotube samples are more similar to those of anatase than to those of Ti_2O_3 , which strongly suggests that the dominant oxidation state of near-surface Ti in the as-anodized nanotubes is Ti^{4+}

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FIG. 3. (Color Online) XAS spectra of the Ti $L_{3,2}$ -edge of short (red) and long (black) TiO_2 nanotubes: (a) as anodized; annealed at 350 °C in (b) O_2 , (c) Ar, (d) H_2 ; and annealed at 300 °C in (e) Ar. Comparison spectra for: (f) anatase, (g) rutile and (h) Ti_2O_3 reference oxides.

Annealing the nanotubes in Ar or H_2 resulted in a 0.1 eV shift in position of Ti $L_{3,2}$ - t_{2g} absorption peak as compared to those of the as-anodized and O_2 -annealed nanotubes, Figure 3 and Table 1, although the difference in this peak position is within the beamline resolution. The observed differences in the Ti $L_{3,2}$ - t_{2g} peak positions (0.1 eV) in the spectra of standard reference anatase and rutile are in accordance with results from earlier high-resolution XAS studies⁴⁰. The Ti $L_{3,2}$ - t_{2g} and e_g absorption peaks and peaks within the 465 – 480 eV energy range of both short and long nanotubes sharpen upon annealing and resemble those of the anatase structure, as

shown in Figure 3. Further, comparison of the XAS spectra of the long nanotubes annealed in Ar at two different temperatures (300 °C and 350 °C, Figure 3) implies that the annealing temperature is a critical factor in the amorphous-to-anatase transformation.

The Ti- e_g peak exhibits a distinct doublet structure in the spectra of the annealed short nanotubes (for all annealing atmospheres) and of O₂-annealed long nanotubes. The shape of the e_g peak in the Ti $L_{3,2}$ -edge spectrum may be considered as a determining “fingerprint” for various TiO₂ polymorphs: the anatase and rutile spectra feature a doublet structure while amorphous TiO₂ shows only a single broad asymmetric peak^{37, 38, 40, 42}. The separation d between the Ti L_3 - e_g doublet feature in the as-anodized TiO₂ nanotube spectra ($d = 0.8$ eV for both short and long nanotubes) is smaller than those of the annealed nanotubes ($d = 0.9$ to 1.0 eV) and of other reference oxides ($d(\text{anatase}) = 0.9$ eV and $d(\text{Ti}_2\text{O}_3) = d(\text{rutile}) = 1.0$ eV). In addition, as reported elsewhere⁴⁰, the overall intensity of Ti- e_g peak of the amorphous TiO₂ nanotubes is higher than that characterizing the Ti- e_g peaks of reference anatase and rutile; upon annealing the nanotubes, the intensity ratio of Ti- e_g doublet peaks ($I_{eg(a)}/I_{eg(b)}$) decreases and approaches the value of reference anatase. The e_g doublet peak intensity ratios in the Ti L_3 -edge spectra of all annealed nanotubes approach that of the reference anatase, indicating that their local structure, and medium- and long-range order are similar to those of the anatase structure.

C. O K-edge X-ray absorption spectra

Complementary structural information concerning the TiO₂ nanotubes is obtained from the O K-edge X-ray absorption spectra comprised of two groups of peaks, Figure 4. The first group consists of two major peaks within 530 – 536 eV energy range, which are centered at approximately 531 and 534 eV. This group of peaks signals the transition of O-1s core-level

electrons to the hybridized O-2*p* and Ti-3*d* (*t*_{2*g*} and *e*_g) molecular orbitals^{37, 45} with a detailed structure that is sensitive to the local symmetry and ligand coordination^{33, 37, 39}. The second group of peaks resides in the higher energy region (537 – 550 eV) and is associated with the O-1*s* core-level transitions to the hybridized orbitals of O-2*p* and the Ti-4*sp* states; this group of transitions is quite sensitive to the long-range crystallographic order^{33, 37, 39}. Upon annealing the nanotubes in O₂, H₂ or Ar gas, the O-*t*_{2*g*} and O-*e*_g peaks become sharper and their separation increases from 2.1 eV to 2.4 – 2.5 eV (± 0.1) (Figure 4) confirming the formation of the anatase structure in the annealed nanotubes. Spectra collected for the annealed short TiO₂ nanotubes are essentially identical and differ only slightly from those of the long nanotubes.

FIG. 4. (Color Online) XAS spectra of the O K-edge of short (red) and long (black) TiO₂ nanotubes: (a) as anodized; annealed at 350 °C in (b) O₂, (c) Ar, (d) H₂; and annealed at 300 °C in (e) Ar. Comparison spectra for: (f) anatase and (g) rutile.

D. Photocatalytic activity of TiO₂ nanotubes

The photocatalytic activity of the as-anodized (amorphous) and annealed (crystalline) TiO₂ nanotubes is evaluated by the photodegradation of MO in an aqueous solution. Prior to initiation of the photocatalytic experiment (at time $t = 0$), the initial MO concentration, C_0 , was similar for all the nanotube samples. Over the course of the experiment the amorphous as-anodized nanotubes (short and long) did not detectably degrade the MO; the annealed short nanotubes also did not detectably degrade the MO within the experimental error, despite their good crystallinity, which is attributed to the short length rather than the crystallinity. However, the annealed long nanotubes successfully degraded the MO dye, as depicted in Figure 5 which shows the fractional conversion for photodegradation of MO, $f(\text{MO})$, under UV-VIS illumination in presence of TiO₂ nanotubes annealed in O₂, Ar and H₂. The inset in Figure 5 shows the change in the UV-VIS absorption spectra of the MO as a function of time.

FIG. 5. (Color Online) Photocatalytic activity of annealed TiO₂ nanotubes, showing the fractional conversion for photodegradation of methyl orange, $f(\text{MO})$, under UV-VIS illumination in contact with TiO₂ nanotubes annealed in O₂, Ar and H₂. The inset shows the UV-VIS absorption of the MO in contact with long H₂-annealed nanotubes measured at each time interval, illustrating the time decay of the 463.8 nm absorbance peak.

The concentration of MO in the presence of the annealed nanotubes gradually decreased as a function of UV-VIS exposure time, independent of the annealing gas type. After a 240-min exposure of the long crystalline nanotubes to UV-VIS light, the fractional conversion of MO reached values of $f_{\text{MO}}(\text{H}_2\text{-annealed}) = 86\% \pm 4\%$, $f_{\text{MO}}(\text{Ar-annealed}) = 80\% \pm 4\%$ and $f_{\text{MO}}(\text{O}_2\text{-annealed}) = 62 \pm 3\%$. In addition, assuming a first-order reaction for the degradation of MO, Figure 6(a), the rate constant k of the reaction is plotted in Figure 6(b). The reaction rate in the presence of the H₂-annealed nanotubes is faster compared with the reaction rate in the presence of the Ar- or O₂-annealed NTs.

FIG. 6. (Color Online) Photocatalytic activity of annealed TiO₂ nanotubes: (a) Plot of $\ln(1/(1-f_{MO}))$ of the photodegradation of methyl orange (MO) under UV-VIS illumination in contact with TiO₂ nanotubes annealed in O₂, Ar and H₂, showing that the degradation of MO follows a first-order reaction. The solid lines are linear fits to the data points, leading to evaluation of the reaction rate constant, k , as plotted in (b) for the different annealing gases.

IV. DISCUSSION

This study has two main outcomes: (I) clarification of the influence of the annealing gas on the local structure, degrees of medium- and long-range order, and the density of the structural defects in the near-surface region of the TiO₂ nanotubes; and (II) correlation between these annealing-induced changes and the near-surface electronic structure of the nanotubes. The latter

feature is critical in determination of the catalytic functionality of long nanotubes for the degradation of MO dye, with H₂-annealed nanotubes confirmed to be more effective in catalytic degradation of MO, as compared to the Ar- and O₂-annealed nanotube samples. The short nanotubes (200 nm long) did not show a noticeable catalytic activity within the detection limits of the experimental set up.

Correlation of the both near-surface crystal and the electronic structure of the TiO₂ nanotubes with their catalytic functionality may be accomplished by comparison of their Ti *L*₃-edge and O *K*-edge XAS spectra. The Ti *L*₃-edge *e_g* peak features of the annealed long nanotubes resemble those of the anatase structure and confirm the bulk measurement results indicating that anatase crystal structure forms upon annealing; the crystallinity is more prominent in the O₂-annealed nanotubes than in the nanotubes annealed in Ar- or H₂, as supported by a comparison of the intensity ratio of Ti-*e_g* doublet peaks (*I_{eg(a)}*/*I_{eg(b)}*). In addition, the larger value of the *e_g* peak separation, *d*, in the nanotubes annealed in reducing (H₂) and inert (Ar) gas atmospheres indicates a higher concentration of surface defects (Ti³⁺ species or O vacancies) as compared to those annealed in the oxidizing environment (O₂). Reduction of Ti⁴⁺ to lower oxidation states such as Ti³⁺ is concurrent with the loss of lattice oxygen, as reported elsewhere for TiO₂ annealed in oxygen-deficient or reducing atmospheres, although for higher annealing temperatures such as 400 °C to 650 °C^{1, 22, 29, 30, 46}. During such thermal treatment, two Ti⁴⁺ ions transform into two Ti³⁺ ions for charge compensation by receiving electrons freed from the removal of one lattice oxygen atom in stoichiometric TiO₂ lattice to create a doubly-charged oxygen vacancy, $\dot{V}_O$.

The presence of structural defects in the H₂- and Ar-annealed nanotubes, *viz.* Ti³⁺ species associated with $\dot{V}_O$, is further evidenced by the observation of a smaller separation between their

O K -edge t_{2g} and e_g peaks when compared with that measured from the O₂-annealed nanotubes^{37, 39, 40, 47-52}. These changes in the defect state of the nanotubes are anticipated to affect the electronic band gap of TiO₂ and thereby influence the visible light absorption capability⁵³.

Annealing the nanotubes in oxygen promotes the surface oxidation of TiO₂ and thus maintains the Ti : O stoichiometric ratio. In this manner, intrinsic oxygen vacancies, which are reported to migrate towards the surface of nanotubes during the nanotube annealing process⁵⁴, can be annihilated by the oxidizing annealing gas, which decreases the number of near-surface local defects (Ti³⁺ associated with $\ddot{V}_O$) in the O₂-annealed nanotubes. On the contrary, annealing nanotubes in H₂ or Ar gas retards the near-surface defect annihilation progress and further facilitates the defect formation by reducing the Ti⁴⁺ to lower oxidation states. A higher concentration of local defects near the nanotube surface generated by annealing in a reducing gas can facilitate charge separation and may enhance the production of hydroxyl radicals. These hydroxyl radicals can contribute to catalytic activity of TiO₂ nanotubes by serving as reactive sites for degradation of organic compounds^{25, 55, 56}.

Overall, the better catalytic performance of the H₂- or Ar- annealed long nanotubes relative to the O₂-annealed long nanotubes in the degradation of MO is attributed to the higher concentration of local surface defects (Ti³⁺ or oxygen vacancies) that developed upon annealing at temperatures as low as 350 °C, and the anticipated decrease in the electronic band gap, along with the presence of the anatase structure^{22, 46, 52, 57}.

V. SUMMARY AND CONCLUSIONS

The photocatalytic activity of the TiO₂ nanotubes was monitored by the degradation of methyl orange in contact with the nanotubes. The photocatalytic activity of crystalline nanotubes

was the highest in H₂-annealed nanotube sample, somewhat lower for the Ar-annealed nanotubes, and significantly lower for the nanotubes annealed in O₂. XAS characterization of the e_g peak in Ti L_3 -edge and the O K -edge reveals a distortion in the local symmetry and confirms long-range order in the near-surface region of the nanotubes. Compared with H₂ or Ar annealing atmospheres, O₂ provides a more effective annealing environment to reduce local surface defects (Ti³⁺ and O vacancies), which enhances the local structure and long-range crystallinity in both short and long nanotubes. In addition to the correlation between nanotube crystallinity and photoactivity, the presence of these local defects is also decisive in the enhancement of the photocatalytic activity. The relatively higher concentration of local defects near the H₂-annealed long TiO₂ nanotube surface is hypothesized to contribute to an enhanced visible light absorption and conversion. In addition, these effects are thought to increase the production of hydroxyl radicals and lead to an increased photocatalytic activity. Clarification of these structure/property/functionality correlations demonstrates that the photocatalytic activity of TiO₂ nanotubes may be controlled by tailoring the crystallinity, the concentration of surface local defects, and the electronic structure of TiO₂ nanotubes via post-synthesis processing.

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Figure Captions:

Fig. 1. SEM images of the short (left-hand side) and long (right-hand side) TiO₂ nanotubes. Side-view of nanotubes: (a-b) as-anodized. Top view of nanotubes: (c-d) as-anodized; (e-f) O₂-annealed; and (g-h) Ar-annealed.

Fig. 2. (Color Online) XRD patterns of the short and long TiO₂ nanotubes annealed in O₂, Ar and H₂ in comparison with standard anatase and titanium powder diffraction patterns. Note the presence of anatase structure in all annealed nanotubes, regardless of nanotube's length. The Ti peaks are from the titanium substrate from which the TiO₂ nanotubes are formed.

Fig. 3. (Color Online) XAS spectra of the Ti $L_{3,2}$ -edge of short (red) and long (black) TiO₂ nanotubes: (a) as anodized; annealed at 350 °C in (b) O₂, (c) Ar, (d) H₂; and annealed at 300 °C in (e) Ar. Comparison spectra for: (f) anatase, (g) rutile and (h) Ti₂O₃ reference oxides.

Fig. 4. (Color Online) XAS spectra of the O K-edge of short (red) and long (black) TiO₂ nanotubes: (a) as anodized; annealed at 350 °C in (b) O₂, (c) Ar, (d) H₂; and annealed at 300 °C in (e) Ar. Comparison spectra for: (f) anatase and (g) rutile.

Fig. 5. (Color Online) Photocatalytic activity of annealed TiO₂ nanotubes, showing the fractional conversion for photodegradation of methyl orange, $f(\text{MO})$, under UV-VIS illumination in contact with TiO₂ nanotubes annealed in O₂, Ar and H₂. The inset shows the UV-VIS absorption of the MO in contact with long H₂-annealed nanotubes measured at each time interval, illustrating the time decay of the 463.8 nm absorbance peak.

Fig. 6. (Color Online) Photocatalytic activity of annealed TiO₂ nanotubes. (a) Plot of $\ln(1/(1-f_{\text{MO}}))$ of the photodegradation of methyl orange (MO) under UV-VIS illumination in contact with TiO₂ nanotubes annealed in O₂, Ar and H₂, showing that the degradation of MO follows a first-order reaction. The solid lines are linear fits to the data points, leading to evaluation of the reaction rate constant, k , as plotted in (b) for the different annealing gases.