The Effects of Pt Doping on the Structure and Visible Light Photoactivity of Titania Nanotubes

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Platinum-doped titania nanotubes were prepared by a hydrothermal technique to produce visible light activated catalysts. Pt loading, however, also affected the morphology of the titania nanotubes. Scanning electron microscopy and scanning transmission electron microscopy (STEM) results reveal that up to 1 mol % loading Pt-doped titania retains its nanotubular structure, but at 2 and 4 mol % Pt the nanotubes collapse to a nanopowder. High-angle annular dark field STEM images show that the Pt nanoparticles have diameters of ∼2−5 nm and are uniformly distributed on the nanotube surface. Pt doping enhances the photoactivity of titania nanotubes in visible light for the photooxidation of acetaldehyde. Titania nanotubes doped with 0.5 mol % Pt show the maximum visible light photoactivity with a decay rate constant nearly 7 order of magnitude higher than commercially available P25 titania (0.0005 min⁻¹). Electron paramagnetic resonance (EPR) spectroscopy was used to probe the mechanism by which Pt-doping alters the structure and function of the titania nanotubes. EPR spectra revealed that undercoordinated sites and oxygen deficiency on the surface of the titania nanotube are created in synthesis (calcination in hydrogen atmosphere). These surface features interact with the Pt centers to alter the optical, electronic, and chemical behavior of the titania nanotube. These results also suggest the potential for practical applications such as incorporating Pt-doped titania nanotubes with commercially available light sources for indoor air purification.

Introduction

Semiconductor-mediated photocatalytic decomposition of aqueous and gas-phase pollutants has received considerable attention.¹ Titania is well suited for the photoassisted degradation of pollutants due to its high activity, wide availability, chemical inertness, and photostability. One of the major disadvantages of titania, however, is its selective activity in the UVA region (band gap 3.2 eV), which is only about 3−5% of the solar spectrum reaching the Earth’s surface. In order to effectively utilize solar energy or indoor lighting, it is necessary to develop a photocatalyst having a visible photosresponse, as well as high surface area and photocactivity.² Consequently, significant efforts have been made to develop modified forms of TiO₂ that are active under visible radiation and have distinct morphologies.³−⁵

Titania in the form of tubular nanostructure is a novel material developed in the past decade that is promising due to its high surface area and reduced charge recombination.⁶ Among the many methods to prepare titania nanotubes,⁷−⁹ the hydrothermal method is more practical because it can be more easily scaled up. There are a variety of approaches to shift the photosresponse of titania into the visible region, ranging from cation and anion doping³,¹⁰−¹⁴ and creating oxygen vacancies¹⁵ to dye sensitizing.¹⁶

Noble metals, e.g. (Pt, Ag, Au), are effective dopants for visible light activation¹⁷−²¹ by photoexciting surface plasmons in the metal atom.²⁰ Moreover, the metal clusters act as sinks for the photogenerated conduction band electrons and reduce charge recombination. The presence of a metal at the surface of TiO₂ results in the formation of a Schottky barrier at the metal—semiconductor interface, which facilitates the interfacial electron transfer and subsequently encourages charge carrier separation.²²

Platinum is one of the more favorable noble metal dopants to enhance the photocatalytic activity of the titania.²³ Pt-doped titania nanotube arrays prepared by anodization are used for photocatalytic water splitting and carbon dioxide reduction reactions by several research groups.⁵,²⁴,²⁵ Kim et al. reported the visible light photocactivity of Pt-doped titania powder. Ishibai et al. reported a higher visible light activity of Pt-modified titania by the formation of Ti−O−Pt bonds.²⁶ Hydrothermally synthesized hydrogen titanate nanotubes modified by Pt and Au using photodeposition techniques were found to have high catalytic activity for the hydrogenation of CO₂.²⁷ Yu et al. reported a similar observation on Pt-doped titania nanotubes.²⁸ Titinate nanotubes modified with Pt show efficacy in formaldehyde degradation.²⁹,³⁰ Hydrothermally hot pressed Pt-doped titinate nanotubes and their photoactivity were studied by Kubo et al. who demonstrated an alternative fabrication method that eliminated the H₂ reduction step.³⁰ The effects of dopant concentration on the morphological stability and photoactivity...
of titania nanotubes are not reported in the literature. Therefore, in the present study Pt-modified titania nanotubes were prepared at varying dopant concentrations. The structural and electronic properties of the photocatalysts were studied using specific surface area and electron paramagnetic resonance spectroscopic techniques. Further, the Pt-doped titania nanotubes were tested for visible light photoactivity by studying the photodegradation of acetaldehyde. Finally, the mechanism of enhanced reactivity was probed by investigating the interactive effects caused by the conditions of synthesis and the Pt centers.

Experimental Section

Titania nanotubes were prepared by a modified hydrothermal method reported previously. In a typical experiment, 2 g of anatase titania powder (assay 99%, Sigma Aldrich Chemicals, USA) was stirred with 50 mL of 10 M NaOH solution (assay 97%, BDH Chemicals, USA) in a 125 mL Teflon cup. The Teflon cup was kept in an oven for 48 h maintained at 120 °C, and the resultant precipitate was washed with 1 M HCl (assay 38%, EMD Chemicals, USA) followed by several washings using deionized water to attain a pH between 6 and 7. The titania nanotube powder thus formed was dried in an oven at 110 °C overnight. The resultant powder was mixed with an aqueous solution of hexachloroplatinic acid corresponding to 0.1, 0.5, 1, 2, and 4 mol % dopant concentration. Doped and undoped titania samples were then calcined under a hydrogen atmosphere (80 mL min⁻¹) at 400 °C for 1 h. X-ray diffraction (XRD) patterns of the samples were taken in a Rigaku X-ray diffractometer in the diffraction angle 2θ range 5°–80° using Cu Kα radiation. The crystallite size was calculated using the Scherrer equation

\[ \Phi = K\lambda/\beta \cos \theta \]  

where \( K \) is the shape factor taken as 0.9 for the calculations, \( \lambda \) is the wavelength of the X-ray, \( \beta \) is the full width at half-maxima, and \( \theta \) is the diffracting angle.

The morphology of titania nanotubes was observed under a scanning electron microscope (Hitachi S-4800-II) with an accelerating voltage of 5 kV, a transmission electron microscope (Hitachi H-8100) at 200 kV, and a Hitachi HD-2300A dedicated scanning transmission electron microscope with three image detectors (secondary electron detector, bright-field detector, and high-angle dark-field detector) at 200 kV. The surface area measurements and pore size analysis were carried out by nitrogen adsorption using a Micromeritics Gemini 2010 surface area analyzer after degassing the sample at 120 °C for 24 h. Electron paramagnetic resonance (EPR) spectra were collected on a Bruker Elexys E580 spectrometer equipped with a helium cryostat. For the characterization of photogenerated charges, samples dispersed in Milli-Q water were purged with argon and illuminated within the cavity while spectra were acquired. A 300 W xenon lamp (ILC Inc.) was used as the light source for EPR studies. The \( g \) tensor values were calibrated for homogeneity and accuracy by comparing to a coal standard (\( g = 2.00285 \pm 0.00005 \)).

The visible light photoactivity of Pt-doped titania nanotubes was studied by following the photodegradation of acetaldehyde. Ten milligrams of undoped and Pt-doped nanotube powder was placed in a photocatalytic system consisting of a closed square Teflon container having a quartz window. One milliliter of saturated vapor of acetaldehyde was introduced into the closed dark chamber and then allowed to equilibrate for 1 h. Photo-catalytic reactions were carried out with a natural daylight bulb (60 W, Halco Lighting, Pure Lite, neodymium), which operated

![Figure 1. XRD spectrum of titania nanotubes doped with (a) 0, (b) 0.1, (c) 0.5, (d) 1, (e) 2, and (f) 4 mol % Pt calcined at 400 °C.](image-url)
at wavelengths of ∼400–850 nm and an energy density of ∼31 mW/cm² (the emission spectrum of the bulb is shown in Figure S1, Supporting Information). As the photocatalytic reaction proceeded, the degradation of acetaldehyde was monitored at periodic time intervals using an HP 5890 gas chromatograph equipped with a flame ionization detector (GC-FID).

Result and Discussion

Since the hydrogen titanate is reported to have very high cation exchange capacity, treating prepared hydrogen titanate with chloroplatinic acid likely results in the replacement of the hydrogen ion in the titanate nanotube by the Pt ion. X-ray diffraction analysis indicates that all the compositions after calcinations at 400 °C are converted to the anatase crystal phase (Figure 1). The average crystallite size of the titania nanoparticles calcined at 400 °C is approximated from the broadening of XRD peaks using Scherrer’s equation (Table 1). The Pt precursor in the titania matrix increases the crystallite size from 9.4 to 12 nm. Up to 1 mol % Pt loading, no peak corresponding to Pt is observed in the X-ray diffraction spectrum, which

<table>
<thead>
<tr>
<th>mol % doping</th>
<th>BET surface area (m² g⁻¹)</th>
<th>total pore volume (cm³ g⁻¹)</th>
<th>micropore volume (cm³ g⁻¹)</th>
<th>mesopore volume (cm³ g⁻¹)</th>
<th>crystallite size of anatase (nm)</th>
<th>band gap (eV)</th>
<th>rate of the reaction (min⁻¹)</th>
</tr>
</thead>
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<tr>
<td>undoped titania nanotube</td>
<td>261.7</td>
<td>0.8612</td>
<td>0.0047</td>
<td>0.8565</td>
<td>9.5</td>
<td>3.16</td>
<td>0.0005</td>
</tr>
<tr>
<td>0.1 mol % Pt-doped titania nanotube</td>
<td>226.7</td>
<td>0.7379</td>
<td>0.0020</td>
<td>0.7359</td>
<td>10.1</td>
<td>3.11</td>
<td>0.0028</td>
</tr>
<tr>
<td>0.5 mol % Pt-doped titania nanotube</td>
<td>203.9</td>
<td>0.6711</td>
<td>0.0033</td>
<td>0.6678</td>
<td>10.3</td>
<td>3.05</td>
<td>0.0034</td>
</tr>
<tr>
<td>1 mol % Pt-doped titania nanotube</td>
<td>163.6</td>
<td>0.6337</td>
<td>0.0056</td>
<td>0.6281</td>
<td>10.6</td>
<td>3.01</td>
<td>0.0012</td>
</tr>
<tr>
<td>2 mol % Pt-doped titania nanotube</td>
<td>141.8</td>
<td>0.6922</td>
<td>0.0053</td>
<td>0.6869</td>
<td>12.1</td>
<td>2.96</td>
<td>0.0009</td>
</tr>
<tr>
<td>4 mol % Pt-doped titania nanotube</td>
<td>139.9</td>
<td>0.5483</td>
<td>0.0045</td>
<td>0.5438</td>
<td>10.8</td>
<td>2.64</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

Figure 2. SEM images of titania nanotubes doped with (A) 0, (B) 0.1, (C) 0.5, (D) 1, (E) 2, and (F) 4 mol % Pt calcined at 400 °C.
indicates that Pt is dispersed uniformly in the titania matrix.\textsuperscript{40} The XRD spectra of 2 and 4 mol % Pt-doped titania show peaks at 2\( \theta \) values of 40, 46, and 68, which are the characteristic peaks corresponding to the (111), (200), and (220) planes of the face-centered cubic (fcc) crystal of metallic platinum nanoparticles (Figure 1e,f).\textsuperscript{41}

The morphology of the undoped and doped titania nanotubes is presented in Figure 2. The tubular morphology of the system is maintained up to a doping concentration of 1 mol % Pt (Figure 2A–D). Above 1 mol % Pt, the tubular morphology of the titania disappears. The 4 mol % Pt-doped sample exists as a titania nanopowder (Figure 2E,F). From SEM studies it is clear that incorporating higher amounts of Pt precursor (>1 mol %) and heating the powder lead to the destruction of the nanotubular structure (Figure 2 E,F) and the transformation to a powder morphology. A similar observation was made by Kim et al. who reported that titania hollow spheres also lose their original morphology at high Pt-doping percentages (20 wt %) using chloroplatinic acid.\textsuperscript{42}

Scanning transmission electron microscopy (STEM) and TEM images of 0.5 and 1 mol % Pt (Figure 3A,D) are presented in Figure 3. The images show that the titania nanotubes prepared by the modified hydrothermal method have lengths of ca. 50–300 nm and diameters of ca. 8–12 nm. The HAAD STEM image of a 0.5 mol % Pt-doped titania nanotube is shown in Figure 3B, where the Pt particles are seen as white spots (as the Z-contrast image, the contrast is proportional to the square of element number: \( Z^2 \)). From this image the size of the Pt nanoparticles on the titania nanotube was found to be \( \sim 2–5 \) nm. The EDS point analysis of the sample (Figure 3C, spot diameter of 0.3 nm) also indicates the presence of Pt nanoclusters on the surface of titania nanotube. The 4 mol % Pt-doped titania nanotubes calcined at 400 °C exist in the nanopowder form (Figure 3E).
The specific surface area ($S_{BET}$), total pore volume, and average pore diameter of the platinum-doped samples calcined at 400°C were obtained from N$_2$ adsorption analyses and are presented in Table 1. The nitrogen adsorption–desorption isotherms of TiO$_2$ samples prepared with different concentrations of Pt are presented in Figure 4A. The adsorption isotherms of all the samples show type IV behavior with its characteristic hysteresis loop (BDDT classification), and the isotherm of undoped titania, shown in the inset of Figure 4, illustrates a typical hysteresis loop. At moderate relative pressures between 0.4 and 0.8, the adsorption–desorption curves exhibit very small hysteresis loops indicating the presence of mesopores (type IV). This is also confirmed by the corresponding pore-size distributions (Figure 4B). However, at higher relative pressure between 0.8 and 1.0, the shape of the hysteresis loops is of type H3 associated with aggregates of platelike particles, giving rise to slitlike pores. Doping with Pt decreases the surface area of the titania nanotubes. The undoped titania nanotubes have a surface area of 261 m$^2$ g$^{-1}$, whereas at 4 mol % Pt-doped titania shows a reduced surface area of 139.9 m$^2$ g$^{-1}$. The total pore volume also displays a decrease from 0.8612 to 0.5483 cm$^3$ g$^{-1}$ when comparing undoped samples to 4 mol % Pt-doped titania. The BJH pore size distributions are in two different regions. The pore size less than 10 nm corresponds to the inner diameter of the nanotubes and the larger pores (10–100 nm) are attributed to the aggregation of the nanotubes. These smaller pores (<10 nm) are not present in the samples having Pt amounts more than 1 mol % (Figure 4B), confirming that the titania samples doped with greater than 1 mol % Pt and calcined at 400°C lose the structural integrity of nanotubes displaying the associated characteristics of reduced surface area and altered pore structure. These measurements are consistent with the SEM and TEM results.

The diffuse reflectance electronic absorption spectra of the undoped and Pt-doped titania nanotubes are presented in Figure 5A. The spectra show that TiO$_2$ nanotubes absorb moderately around 385 nm and strongly around 300–350 nm, due to the presence of segregated anatase crystallites. This absorption is attributed to the excitation of electrons from the valence band to the conduction band in TiO$_2$. The optical absorption is enhanced significantly in the region of 300–700 nm, owing to the presence of Pt, in comparison to the pure anatase nanotubes. The absorbance...
Pt doping of titania nanotubes exert a variety of concentration-dependent effects at the titania surface. Pt not only extends the photoresponse of the titania but also decreases the recombination rate by 45% at higher Pt loading and the visible light activity of the platinized nanotubes, we employed EPR spectroscopy. In Figure 7 the EPR spectrum of H2 treated titania nanotubes under reducing conditions and their effect on the structural changes induced by the calcination of the nanotubes under reducing conditions and their effect on the visible light activity of the titania. The Pt centers facilitate the transfer of photoexcited electron from the titania to Pt making the photogenerated holes more available for photooxidation reactions. However, Tahiri et al. reported that higher amounts of Pt-doping increase the negative charge on the titania surface, which inhibits the adsorption of negatively charged oxidants (e.g., superoxide) involved in photooxidation reactions. Moreover, in the negative charge on the surface of titania at higher Pt loading may promote the recombination of photogenerated holes, offsetting the charge separating effects of Pt. In addition, higher levels of Pt loading block the light absorption centers of the titania causing a decrease in photoactivity.

It is well documented that the treatment of TiO2 powders with hydrogen under elevated temperatures produces defect sites both on the surface (at temperatures <450 °C) and in the lattice (at higher temperatures). In order to investigate in greater depth the structural changes induced by the calcination of the nanotubes under reducing conditions and their effect on the visible light activity of the platinized nanotubes, we employed EPR spectroscopy. In Figure 7 the EPR spectrum of H2-treated titania nanotubes in the absence of light and at 4.5 K revealed the formation of oxygen vacancies (OV) and Ti4+ species. A sharp resonance signal with g = 2.002 is associated with oxygen vacancies. Similar signals due to the formation of oxygen vacancies and/or O2− located at surface oxygen vacancies have been observed with various oxide surfaces, such as copper complexes in a silica glass matrix or on the surfaces of SnO2.

The band gap of the Pt-doped titania is calculated with a Tauc plot (Figure 5B). Where \( F(R) = (1 - R)^{1/2} R \), where \( R \) is the diffuse reflectance.

The photoactivity of the various Pt-doped titania catalysts are compared by the following oxidation of acetaldehyde, a model air contaminant and a principal odor causing gas in indoor air. The visible light photoactivity of the undoped and Pt-doped titania are studied using a solar lamp that not only simulates solar radiation but is also commonly used in household lighting applications. The irradiance spectrum of the lamp is shown in Figure S1 (Supporting Information). The choice of acetaldehyde as a model pollutant in this study is based on the fact that it is a principal odor causing gas in indoor air and generated by furniture bond, cigarette smoke, and residential wastes. The degradation of acetaldehyde in the presence of \( O_2 \) is known to proceed via radical chain reactions on the TiO2 surface along two possible pathways. Acetic acid is found to be the intermediate of the process and degrades to form carbon dioxide and water. The complete mineralization of acetaldehyde can be depicted as (eqs 2, 3, and 4)

\[
\text{CH}_3\text{CHO} + 2\text{OH} + \text{O}_2 \rightarrow \text{CH}_3^* + 2\text{CO}_2 + 2\text{H}_2\text{O} \quad (2)
\]

\[
\text{CH}_3\text{CHO} + \text{OH} + \text{O}_2 \rightarrow \text{CH}_3\text{COOH} + \text{HOO}^* \quad (3)
\]

\[
\text{CH}_3\text{COOH} + h^+ \rightarrow \text{CO}_2 + \text{CH}_3^* + h^+ \quad (4)
\]

The change in concentration of acetaldehyde as a function of reaction time is plotted in Figure 6A. The undoped titania nanotubes and Degussa P25 standard titania show similar, very limited decay (10%) of acetaldehyde. At 0.1 and 0.5 mol %, the Pt-doped titania nanotubes achieve ~45% decay of acetaldehyde under the visible radiation. At higher loadings of Pt, beyond 0.5 mol %, the reactivity diminishes and 4 mol % Pt-doped titania shows no difference in reactivity from undoped and P25 degussa titania. Assuming a pseudo-first-order reaction, the rate constant for acetaldehyde decay is plotted against the concentration of Pt in the titania matrix and presented in the Figure 6B. The 0.5 mol % Pt-doped titania nanotube shows a maximum value with a rate of 0.0034 min⁻¹, which is approximately seven times greater than commercially available P25 (0.0005 min⁻¹). The 0.5 mol % Pt-doped concentration is found to be optimum under these conditions.

Pt doping exerts a variety of concentration-dependent effects at the titania surface. The Pt not only extends the photoresponse of the titania but also decreases the recombination rate by separating the electron hole pair, leading to an increase in the photoefficiency of the titania. The Pt centers facilitate the transfer of photoexcited electron from the titania to Pt making the photogenerated holes more available for photooxidation reactions. However, Tahiri et al. reported that higher amounts of Pt-doping increase the negative charge on the titania surface, and water. The complete mineralization of acetaldehyde can be characterized by a shift in the optical absorption edge to longer wavelengths with broad absorbance and the absence of a distinct absorbance peak in the visible region.

The photoactivity of the various Pt-doped titania catalysts are compared by following the oxidation of acetaldehyde, a model air contaminant and a principal odor causing gas in indoor air. The visible light photoactivity of the undoped and Pt-doped titania are studied using a solar lamp that not only simulates solar radiation but is also commonly used in household lighting applications. The irradiance spectrum of the lamp is shown in Figure S1 (Supporting Information). The choice of acetaldehyde as a model pollutant in this study is based on the fact that it is a principal odor causing gas in indoor air and generated by furniture bond, cigarette smoke, and residential wastes. The degradation of acetaldehyde in the presence of \( O_2 \) is known to proceed via radical chain reactions on the TiO2 surface along two possible pathways. Acetic acid is found to be the intermediate of the process and degrades to form carbon dioxide and water. The complete mineralization of acetaldehyde can be depicted as (eqs 2, 3, and 4)

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\]
H$_2$-treated anatase, and CuO/rutile. The signal with $g = 1.93$ is assigned to Ti$^{3+}$ ions on the surface of anatase nanotubes.

Figure 8 shows the EPR spectra recorded under UV and visible light illumination of undoped nanotubes calcined under oxidizing and reducing conditions and the 0.5 mol % Pt-doped nanotubes (synthesized under reducing conditions). The axially anisotropic signal, having $g_x = 2.003, g_y = 2.016$, and $g_z = 2.025$ observed for all samples (Figure 8a,b,c,e,f except for oxygen atmosphere heated titania nanotubes under visible light, Figure 8d), corresponds to the photogenerated holes localized at the surface of nanotubes as oxygen-centered radicals. The signals (with $g < 2.0$) that correspond to photogenerated electrons in the anatase nanotubes differ between oxidized and reduced TiO$_2$ samples. When nanotubes are calcined under a flow of oxygen, the stoichiometry of TiO$_2$ is preserved, and the EPR spectrum (Figure 8a UV, black line) indicate that photo-generated electrons localize both in the bulk ($g_\perp = 1.990$) and at the surface of anatase nanoparticles ($g = 1.930$) under UV light illumination. When illuminated at $\lambda > 400$ nm (Figure 8d visible, black line), the photon energy is inadequate to excite electrons from the valence to conduction band of anatase; thus the EPR spectrum exhibits the absence of any signals for oxidized nanotubes.

The calcinations under reducing conditions (under flow of hydrogen) both in the presence and in the absence of chloroplatinic acid result in the formation of oxygen deficiencies in the nanotubes. It has been demonstrated previously that nonstoichiometry, and the presence of partially reduced Ti, both account for the visible-light photocatalysis. EPR spectra confirmed formation of photogenerated charges under visible light excitation (Figure 8e,f, blue and red lines). The UV excitation yields the same EPR features, though with higher intensities (Figure 8b,c; blue and red lines). The $g$-tensor value for photogenerated electrons localized on reduced nanotubes, $g = 1.982$, differs significantly from the values for stochiometric TiO$_2$ (1.990) and Ti$_2$O$_3$ (1.970). From a structural point of view, heat-induced breaking of the Ti–O bond, under an oxygen-deficient atmosphere, can result in formation of both 5-fold pyramidal and 4-fold tetrahedral Ti$^{4+}$ species. The measured $g$-value for reduced anatase nanotubes is close to the one reported for tetrahedral Ti at the interface of mixed phase TiO$_2$, $g = 1.979$. Additionally, the calcination of the nanotubes under hydrogen yields only a limited number of these unsaturated Ti sites, as EPR revealed a strong signal from electrons localized on an anatase surface (labeled as $A_{surf}$ on graph, with $g = 1.930$). The presence of defects on the TiO$_2$ surface can suppress the recombination of electron–hole pairs and hence extend their lifetime. When Pt nanoparticles (shown for 0.5 mol %) are present on the surface of nanotubes, an increase of intensity of a $g = 1.982$ signal was observed (Figure 8c,f). This can be explained by suppressed charge recombination in these samples or by the visible light photosensitization of possible platinum clusters, metallic Pt, Pt(OH)$_2$, or PtO$_2$.

**Conclusion**

This paper describes the synthesis of Pt-doped titania nanotubes by a hydrothermal method. Pt-doping decreases the band

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**References**

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5. The signals (with $g < 2.0$) that correspond to photogenerated electrons in the anatase nanotubes differ between oxidized and reduced TiO$_2$ samples.
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8. The calcinations under reducing conditions (under flow of hydrogen) both in the presence and in the absence of chloroplatinic acid result in the formation of oxygen deficiencies in the nanotubes.
9. It has been demonstrated previously that nonstoichiometry, and the presence of partially reduced Ti, both account for the visible-light photocatalysis.
10. EPR spectra confirmed formation of photogenerated charges under visible light excitation (Figure 8e,f, blue and red lines).
11. The UV excitation yields the same EPR features, though with higher intensities (Figure 8b,c; blue and red lines).
12. The $g$-tensor value for photogenerated electrons localized on reduced nanotubes, $g = 1.982$, differs significantly from the values for stochiometric TiO$_2$ (1.990) and Ti$_2$O$_3$ (1.970). From a structural point of view, heat-induced breaking of the Ti–O bond, under an oxygen-deficient atmosphere, can result in formation of both 5-fold pyramidal and 4-fold tetrahedral Ti$^{4+}$ species.
13. The measured $g$-value for reduced anatase nanotubes is close to the one reported for tetrahedral Ti at the interface of mixed phase TiO$_2$, $g = 1.979$. Additionally, the calcination of the nanotubes under hydrogen yields only a limited number of these unsaturated Ti sites, as EPR revealed a strong signal from electrons localized on an anatase surface (labeled as $A_{surf}$ on graph, with $g = 1.930$).
14. The presence of defects on the TiO$_2$ surface can suppress the recombination of electron–hole pairs and hence extend their lifetime.
15. When Pt nanoparticles (shown for 0.5 mol %) are present on the surface of nanotubes, an increase of intensity of a $g = 1.982$ signal was observed (Figure 8c,f).
16. This can be explained by suppressed charge recombination in these samples or by the visible light photosensitization of possible platinum clusters, metallic Pt, Pt(OH)$_2$, or PtO$_2$.
gap of titania from 3.16 eV up to 2.64 eV for 4 mol % Pt. The nanotube morphology of the titania is lost at higher Pt-doping (>1 mol % Pt). The surface area and total pore volume decrease as the concentration of Pt in the titania nanotube matrix increases, which corresponds to the collapse of nanotube structure at the high Pt-doping levels. EPR spectroscopy data indicate that the oxygen vacancies and associated Ti$^{3+}$ ions created at the surface of nanotubes in synthesis (calcination under reducing conditions) promote visible light absorbance and excitation of electrons from these surface defect sites to the conduction band of titania. As indicated by the increase in the signal at $g = 1.982$, Pt in the titania matrix suppresses the recombination of electron–hole pair on the visibly activated titania. This would be the reason for the increased photocatalytic activity of the Pt-doped titania under visible light. The 0.5 mol % Pt-doped titania would be responsible for the increased photodegradation of the P25 titanium. These results suggest the potential for incorporating Pt-doped titania nanotubes with commercial light sources for practical applications that photo-oxidize indoor air contaminants.

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Supporting Information Available: Figure of emission spectra of the natural daylight bulb used in the experiment. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes