

2011

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Recommended Citation

Hardcastle, F. D. (2011) "Raman Spectroscopy of Titania (TiO₂) Nanotubular Water-Splitting Catalysts," *Journal of the Arkansas Academy of Science*: Vol. 65 , Article 9.

Available at: <http://scholarworks.uark.edu/jaas/vol65/iss1/9>

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Raman Spectroscopy of Titania (TiO₂) Nanotubular Water-Splitting Catalysts

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Abstract

The phase composition of nanotubular TiO₂ films was correlated with photoelectrochemical activity as a function of O₂-annealing temperature. TiO₂ nanotubes have been shown to be more efficient than polycrystalline TiO₂ for the photocatalytic splitting of water. Raman spectroscopy was used to identify and quantify the amorphous and crystalline TiO₂ phases. The amorphous TiO₂ nanotubular array was found to consist of TiO₆⁸⁻ octahedra having the same average structure as those present in the anatase and rutile phases of TiO₂. Results show that the anatase-to-rutile transformation on Ti metal initiates at much lower temperatures compared to polycrystalline TiO₂ and this is attributed to oxygen vacancies located at the metal/oxide interface and is likely responsible for increasing the photocurrent density.

Introduction

Titanium dioxide, TiO₂, has been one of the most widely studied photocatalytic semiconducting materials since the early 1970s when Fujishima and Honda (1972) demonstrated the splitting water into H₂ and O₂ using a simple photoelectrochemical cell and illuminating a single-crystal TiO₂ photoanode (anatase) with UV light of wavelength less than 350 nm.

TiO₂ is a promising semiconducting photoanode material for water splitting using solar radiation. In addition to its low cost and availability, TiO₂ is chemically and photochemically stable, and its band edges match the redox level of water (Burda 2003). The most important requirement of a photocatalyst is its ability to generate electron-hole pairs near the catalyst surface by harvesting a significant portion of the solar spectrum. Unfortunately, the use of TiO₂ is hindered by its large band gap which allows photoconversion of only UV radiation – the band gap must be decreased if TiO₂ is to be used for visible-light applications. Much of the research to date on TiO₂-based water-splitting catalysts has focused on

narrowing the band gap by incorporating dopants into the lattice structure (Sharma 2009, Ishihara 2010). In this study, we focus on the actual phase composition of the TiO₂ which has a significant impact on its performance as a photoactive catalyst.

The two most common crystalline phases of TiO₂ suitable for photochemical applications are anatase (tetragonal) and rutile (tetragonal). Amorphous TiO₂ displays little or no photoactivity. Although rutile is more thermodynamically stable and exhibits a lower band gap than anatase (3.0 eV for rutile; 3.2 eV for anatase) (Bendavid 1999), anatase is preferred for photocatalysis. Thus, the photoactivity of the TiO₂ film should be significantly improved by taking advantage of the high surface area of anatase, present as a nanotubular array, and the lower band gap energy of rutile, and the increased efficiency of electron transport of TiO₂ nanotubes (Liu 2009).

The transformation of amorphous TiO₂ to either anatase or rutile, and the temperature at which anatase is converted to rutile, depend on many variables including the method of synthesis and the presence of foreign ions (Heald 1972) which increase the number of oxygen vacancies thereby increasing the rate of rutile formation. In this study, nanotubular TiO₂ films were characterized by Raman spectroscopy. The structural information was correlated with reported photocurrent-density measurements.

Materials and Methods

Synthesis of TiO₂ Nanotubular Arrays

The TiO₂ (titania) nanotubular films were synthesized by the UALR Nanotechnology Center, UALR (Hidetaka Ishihara, Dr. Rajesh Sharma, and Dr. Alexandru S. Biris). The films were synthesized on titanium metal foil (99.9% pure, 0.5 mm thick) using a conventional anodization process (95wt% ethylene glycol + 5wt% NH₄F; 20V). A two-electrode configuration was used for anodization. Anodization was carried out at a constant potential of 20 V using a DC voltage supply (Agilent, E3640A). The anodization

current was monitored continuously using a digital multimeter (METEX, MXD 4600 A). The anodized samples were washed with distilled water to remove the occluded ions from the anodized solutions and dried in an air-oven. The Ti foil samples were annealed in an oxygen atmosphere at 400-600 °C for 6 h in a tube furnace to convert the amorphous titania to the crystalline anatase and/or rutile forms of TiO₂.

Raman Spectroscopy

Raman spectra of all TiO₂ films were collected using a LabRam Micro-Raman Spectrometer (Horiba Jobin-Yvon HR800 UV) equipped with an optical microscope and 100x objective lens for a total magnification of 1000x. An argon-ion laser (514.5 nm) or helium-neon (632.8 nm) was used for laser excitation of the Raman signal with appropriate holographic notch filters for eliminating the laser line after excitation. The laser power at the sample ranged from 1 to 3 mW, and the 1/e laser spot size was about 2 μm at the sample. The slit width of the spectrometer was typically set at 700 μm. A holographic grating having 1800 grooves/mm was used for the collection of all Raman spectra and resulted in a spectral resolution of about 1.5 cm⁻¹. Spectral analysis and curve fitting was performed with GRAMS/AI 8.00 Spectroscopy software.

Results and Discussion

The Raman spectra for bulk TiO₂ reference compounds are presented in Figure 1. The thermodynamically stable rutile phase exhibits major peaks at 610, 446, and 242 cm⁻¹ and minor peaks at 818, 707, and 319 cm⁻¹. Based on the space group D_{4h}¹⁴ for rutile and assumed site symmetries for the Ti and O atoms within the unit cell, group-theoretical analysis shows four Raman-active “lattice vibrations” assigned as follows: A_{1g} (610 cm⁻¹) + B_{1g} (144 cm⁻¹) + B_{2g} (827 cm⁻¹) + E_g (446 cm⁻¹) (Balachandran 1982). In the present study, we use bond length / Raman frequency / covalency correlations that have proven quite useful and accurate for many chemical systems (Hardcastle 1990, Hardcastle 1991). Recent application of this approach to the titanates (Hardcastle, work in preparation) reveals the following relationship between Ti-O bond lengths, R, and Raman frequency shifts:

$$\nu_{\text{Ti-O}} = 722e^{-1.54946(R-1.809)} \quad (1)$$

The reported Ti-O bond lengths of 4x 1.946 Å and 2x 1.984 Å for rutile (Cromer 1955) are consistent with

observed Ti-O bands at 610, 571 (weak), 446, and 407 (weak) cm⁻¹ which yield calculated Ti-O bond lengths of 3x 1.92, 1.96, 2.12, and 2.18 Å. The O-O interactions, based on residual valence, are calculated to occur in the 252-394-cm⁻¹ region. The broad band observed near 160-240 cm⁻¹ is assigned to O-O interactions involving three- and four-coordinate oxygen. The sharp feature at 143 cm⁻¹ is consistent with Ti-Ti covalent interactions (2.96 Å; 0.29 valence units).

The peaks of crystalline rutile are initially observed for an amorphous sample after annealing at 400 °C and become sharper and more intense as the annealing temperature is increased, indicating increased crystallinity of the rutile phase. An unheated Ti foil shows amorphous titania (native oxide) and exhibits broad bands near 680, 580, and 450 cm⁻¹ assigned to Ti-O bonds (≈ 1.85, 1.95, and 2.11 Å); broad bands at 350 and 250 cm⁻¹ are assigned to O-O interactions consistent with TiO₆⁸⁻ octahedra that are slightly more distorted than those present in the rutile phase of TiO₂.

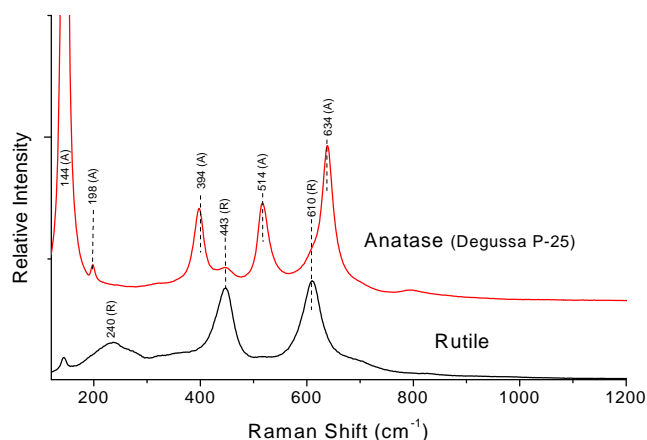


Figure 1. Raman spectra of TiO₂ bulk reference compounds: anatase (Degussa P-25) and rutile.

The Raman spectra for the Ti foil samples that were anodized to produce TiO₂ nanotubular arrays are presented in Figures 2 and 3 as a function of O₂-annealing temperature. The sample dried at room temperature, Figure 2, shows broad peaks near 612 and 467 cm⁻¹ due to amorphous titania. Using length / frequency / valence relationships for titanium-oxygen bonds, Eq. (1), these broad bands are found to be consistent with TiO₆⁸⁻ octahedra having the same average structure as those present in both anatase and rutile phases of TiO₂ with average calculated bond lengths of 5x 1.93 and 2.12 Å.

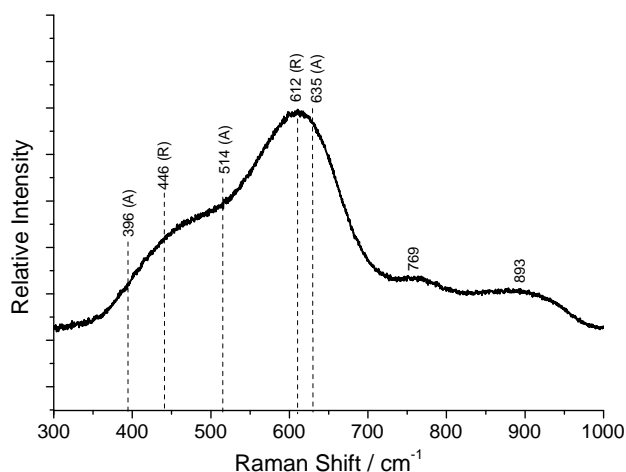
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Figure 2. Raman spectra of TiO₂ nanotubes after room-temperature drying.

In addition to TiO₂ phases, Raman spectroscopy is also used to detect and identify carbon species. For the untreated TiO₂ films, amorphous carbon is present in all the films as indicated by the characteristic bands near 1342 and 1601 cm⁻¹ assigned to sp³- and sp²-hybridized carbon, respectively (Dennison 1996); these bands are similar to those observed for carbon black. Amorphous carbonate, CO₃²⁻, is also present in all untreated TiO₂ films as indicated by the broad but characteristic peak near 1100 cm⁻¹.

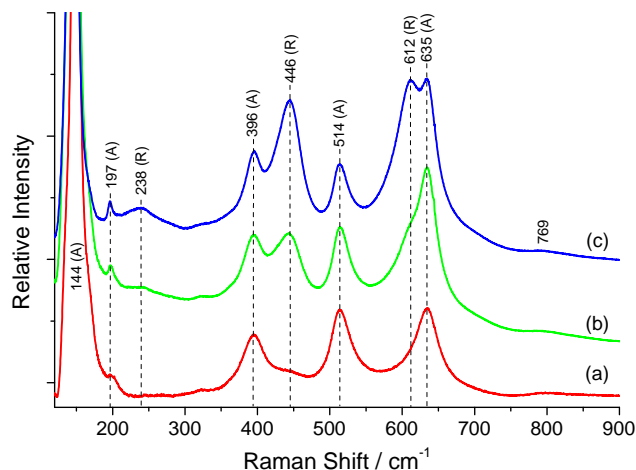


Figure 3. Raman spectra of TiO₂ nanotubular arrays after O₂-annealing at (a) 400°C, (b) 500°C, and (c) 600°C.

Annealing in oxygen at 400 °C for 6 h, Figure 3(a), results in the formation of anatase as the dominant phase in addition to a small amount of rutile. Anatase exhibits Raman bands at 635, 514, 396, and 197 cm⁻¹, as well as a very sharp and intense peak at 144 cm⁻¹.

Based on the space group D_{4h}¹⁹ for anatase and assumed site symmetries for the Ti and O atoms within the unit cell (D_{2d} for Ti; C_{2v} for O), group-theoretical analysis shows six Raman-active “lattice vibrations” assigned as follows: A_{1g} (517 cm⁻¹) + B_{1g} (640 cm⁻¹) + B_{1g} (397 cm⁻¹) + E_g (640 cm⁻¹) + E_g (147 cm⁻¹) + E_g (197 cm⁻¹) (Balachandran 1982); the weak band at 796 cm⁻¹ was assigned as the first overtone of the B_{1g} mode. The reported crystallographic Ti-O bond lengths for bulk anatase are 4x 1.9338 Å and 2x 1.9797 Å (Horn 1972). Covalence / length / frequency relations show that the observed Raman bands at 640, 517, and 397 cm⁻¹ are consistent with the moderately distorted TiO₆⁸⁻ octahedron in anatase (calculated Ti-O bond lengths: 2x 1.89, 3x 2.02 and 2.14 Å). The O-O covalent interactions are calculated near 246-351 cm⁻¹. The sharp peaks at 197 and 144 cm⁻¹ are consistent with Ti-Ti bonding present in the octahedral chains with reported Ti-Ti bond length 2.96 Å (calculated: 2.89 and 2.96 Å, respectively). As the oxygen annealing temperature is increased from 400 to 600 °C, Figure 3(a-c), the relative amount of rutile increases as evidenced by the relative intensity increase of the Raman bands at 612, 446, and 238 cm⁻¹. For the anodized sample O₂-annealed at 600 °C, Figure 3(c), both anatase and rutile are present, with rutile being the dominant phase.

The ratio of the integrated Raman peak intensity of rutile at 446 cm⁻¹ to that of anatase at 396 cm⁻¹ may be used as a semi-quantitative measure of the weight ratio of rutile to anatase. The results of a recent Raman study (Zhang 2006) investigating physical mixtures of crystalline anatase and rutile revealed the following approximate and linear relationship for the weight ratio of rutile to anatase: $W_{R/A} = 3.64 \times (I_{446}/I_{396})$. We utilize this relationship in the present study of TiO₂ nanotubular films, but with the reservation that this relationship is at best semi-quantitative because the Raman scattering cross-sections of anatase and rutile change as the degree of crystallinity changes.

The Raman data and curve fitting show that the room-temperature dried film shows amorphous TiO₂, carbonate (CO₃²⁻), and decomposition products of the ethylene-glycol electrolyte. The amorphous phase is converted to a mixture of about 3 times as much anatase as rutile 400 °C ($W_{R/A} = 0.4$), but the relative concentration of rutile increases as the O₂-annealing temperature is increased to 500 °C, where about 5 times more rutile is present ($W_{R/A} = 5$), and at 600 °C, where about 11 times more rutile is present than anatase ($W_{R/A} = 11$). The photocurrent density increases from 20 μA cm⁻² for the dried amorphous

film to $379 \mu\text{A cm}^{-2}$ for the samples O_2 -annealed at 500°C , where highly crystalline rutile is the dominant phase. It has been suggested that upon annealing, the increased crystallinity results in enhanced charge transfer and photocatalytic activity (Porter 1999). O_2 -annealing at 600°C , however, results in a decreased photocurrent density of $349 \mu\text{A cm}^{-2}$ in spite of the increased rutile content and crystallinity in the TiO_2 nanotubular film.

Figure 4 shows a plot of the ratio of the integrated Raman peaks, I_{446}/I_{396} , as a function of measured photocurrent density (shown as squares, axis on the left) for the anodized TiO_2 films. Also shown is the measured photocurrent density as a function of O_2 -annealing temperature (circles, axis on the right). For TiO_2 nanotubular films dried at room temperature, only baseline photocurrent densities of $20 \mu\text{A cm}^{-2}$ were observed for the amorphous TiO_2 film (not shown on the graph). After O_2 -annealing at 400°C , the photocurrent density increased to $58 \mu\text{A cm}^{-2}$ with the appearance of mostly crystalline anatase (72 % anatase; $W_{\text{R/A}} = 0.4$). At 500°C , the nanotubular film is predominantly rutile (83% rutile; $W_{\text{R/A}} = 5$), and the photocurrent density increases significantly to $379 \mu\text{A cm}^{-2}$, which represents the highest photocurrent density observed in this study. O_2 -annealing at 600°C , however, was detrimental to the PEC activity as the photocurrent density decreased slightly to $349 \mu\text{A cm}^{-2}$ where $\sim 8\%$ of the TiO_2 is anatase ($W_{\text{R/A}} = 11$).

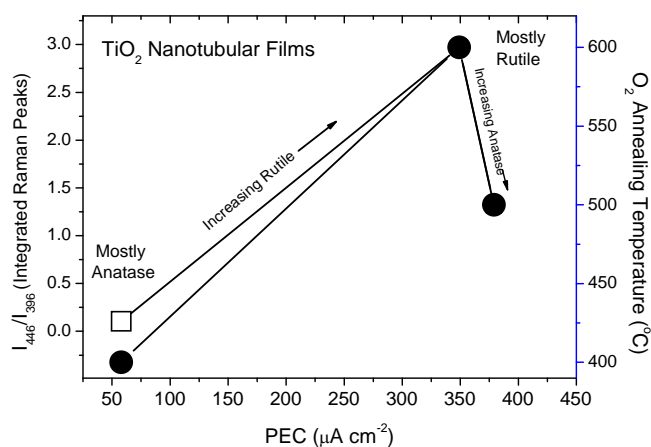


Figure 4. Plot for anodized TiO_2 films showing the photocurrent density (PEC) versus TiO_2 -rutile / TiO_2 -anatase relative concentration and O_2 -annealing temperature. The circles correspond to the annealing temperature axis (right), and the squares correspond to the ratio of integrated Raman peaks (scale on left).

Figure 5 shows a schematic diagram of Raman-identified phases in untreated and TiO_2 nanotubular films as a function of O_2 -annealing temperature and measured photocurrent density (PEC measurements: Hardcastle 2011). The anatase-to-rutile transformation occurs at much lower temperatures ($\sim 400^\circ\text{C}$) compared to those reported for bulk samples. Previous Raman spectroscopy and X-ray diffraction studies show that the anatase-to-rutile transformation for bulk TiO_2 powders starts at 500°C and is completed at about 700°C ; and for single-crystal anatase, this transformation does not occur until 900°C (Shannon 1964).

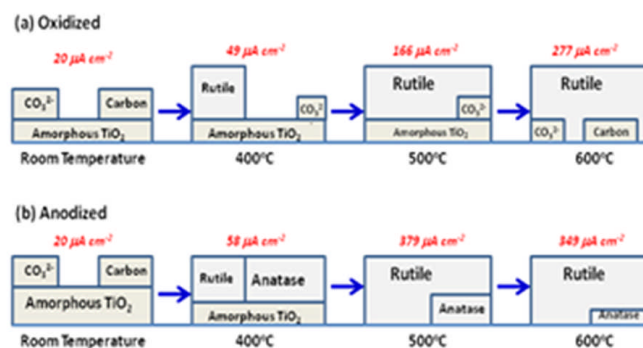


Figure 5. Scheme showing Raman-identified phases in (a) oxidized and (b) anodized films as a function of O_2 -annealing temperature and measured photocurrent density (PEC measurements from Hardcastle, 2011).

The kinetics of the anatase-to-rutile transformation depends on many variables, including the nature and amount of Ti impurity interstitials in the TiO_2 lattice in addition to oxygen vacancies. These impurity ions, in this case being titanium cations having a valence less than that of Ti^{4+} , locally increase the number of oxygen vacancies in order to maintain charge neutrality. The oxygen vacancies facilitate cleavage of the Ti-O bonds in the anatase structure, which reduces the lattice volume and results in the formation of the denser rutile phase at lower annealing temperatures.

Whereas oxidized titanium foil forms only rutile, TiO_2 nanotubes are considerably thicker, and more "bulk-like" TiO_2 behavior is expected. Similar to the untreated sample, the low-crystalline rutile phase forms at 400°C and is likely located near the oxide/metal interface, but the amorphous TiO_2 nanotubes located outside the oxide/metal interfacial region transform to anatase. At this temperature, about three times more anatase is present than rutile in the anodized nanotubular film. At 500°C , there is ~ 5 times more rutile than anatase because the rutile formed at the

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oxide/metal interface “seeded” or catalyzed the accelerated formation of rutile throughout the film. At 600 °C, the nanotubular film is mostly rutile with ~8% anatase; the anatase is presumably located at the outer edges of the film, furthest from the Ti-metal substrate. By comparison, bulk polycrystalline TiO₂ that has been O₂-annealed at 600 °C consists of 60% anatase.

The observed degradation of the nanotubular morphology by SEM (Hardcastle 2011) is expected with rutile formation because of the higher density and decreased surface area characteristic of the rutile phase of TiO₂. For a TiO₂ film on Ti metal, rutile formation initiates at the oxide/titanium interfacial region where oxygen vacancies are present. Collapse of the nanotubular film near the oxide/metal interfacial region is consistent with the morphological changes observed in the SEM images, where buckling of the film begins at 500 °C. As the annealing temperature is increased, rutile spreads out into the nanotubular layer (away from the metal surface). At 600 °C, where <10% anatase remains, the topical region of the nanotubular array is cracked and fragmented as the remaining anatase begins to transform to the more dense rutile phase at a temperature consistent with that of polycrystalline, unsupported anatase (500 - 700 °C).

We have shown using photocurrent-density measurements and Raman spectroscopy that the photoactivity of TiO₂ nanotubular arrays increases with rutile content, but reaches a maximum value at 500 °C, then decreases as the nanotubular morphology degrades at 600 °C. The increased photoactivity is attributed to the increased amount of rutile combined with the high surface area morphology. The maximum photocurrent density measured for oxidized films is 277 μA cm⁻² compared to 379 μA cm⁻² for the nanotubular films (O₂-annealed at 500 °C). This difference is attributed to the increase in rutile surface area provided by the TiO₂ nanotubular array architecture resulting in increased rutile photoactive sites and increased efficiency of electron transport.

Conclusions

TiO₂ is one of the most widely studied photocatalytic materials for splitting water, but the photoelectrochemical activity strongly depends on the phase composition of the material or film. The more ordered arrangement of the nanotubular TiO₂ arrays shows promise over polycrystalline TiO₂ because of observed increased efficiency of electron transport.

In this study, the photocurrent density of nanotubular TiO₂ films was correlated with the phase

composition of the film as a function of oxygen annealing temperature. Raman spectroscopy was used to identify the amorphous and crystalline TiO₂ phases present in the films.

It was found that amorphous TiO₂ is converted to predominantly anatase (~72% anatase) at 400 °C, where the photocurrent density is comparable to that of the oxidized (untreated) film. The highest photocurrent density (2.3x that of the oxidized film) is achieved for the nanotubular film at 500 °C, where ~83% of the TiO₂ is rutile. At this temperature, there is enough anatase within the nanotubes to sustain its architecture and act as a support for the rutile that forms at the surface. The dramatic increase in photocurrent density is attributed to the increase in rutile surface area and corresponding photoactive sites.

At 600 °C, more rutile is formed (92% rutile) in the TiO₂ nanotubular film, but this is countered by the significant loss of rutile surface area due to degradation of the nanotubular array architecture. SEM images show significant degradation (from 500 to 600 °C) and cracking of the film as sintering occurs to accommodate the formation of the denser rutile structure. In spite of the increased rutile content, the photocurrent density decreases slightly from its value at 500 °C.

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