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Titanium dioxide functions as an electron transport medium in dye sensitized solar cells. Nanotubular anatase titanium dioxide is expected to be a better photoanode because of the direct path of the electrons from injection to the working electrode due to the ordered nanotube walls. However, the performance of titanium dioxide nanotube-based solar cells lags behind the nanoparticulate-based. In this work, the crystallographic and defect properties of titanium dioxide nanotubes are examined with spectroscopic and materials characterization techniques in order to understand their electrical properties. Defects in the crystal structure lead to trap states within the bandgap which either assist or hinder electron collection. Shallow traps, those within the range of kT from the conduction band help in increasing the density of states thus increasing conduction. Deep traps capture the electrons and increase the probability of recombination with the oxidized form of the electrolyte. To probe these intra-band states, intra-band photoluminescence spectroscopy was used.
Nanotube photoluminescence consists of three types of emission at approximate peak positions of 425 nm (2.9 eV), 550 nm (2.2 eV), and 650 nm (1.9 eV), which are attributed to recombination of the following nature: exciton, mobile electrons to trapped holes, and mobile holes to trapped electrons, respectively. These defects are similar to that found in nanoparticulate anatase. Although the nature of the defects is the same, the emission intensity in nanotubes is lower than that of nanoparticles. However, comparison with single nanotube photoluminescence revealed that quenching in “bulk” array is caused by significant charge transport in the lateral direction (between neighboring nanotubes).

The orientation of the nanotube wall length is parallel (with slight angular deviations) to the c-axis direction of the unit cell as shown by electron backscatter diffraction. This leads to exposed planes of (100), (110), and (101). Single nanotube photoluminescence in epi-illumination showed that the walls are uniform with respect to defect densities. However, a focused laser beam gave satellite emissions from the ends of a nanotube that show recombination of mobile electrons with trapped holes giving a visual indication of electron transport in the nanostructure.
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Dedication

To Earl, Eodene, & Drew
CHAPTER 1

Introduction

Titanium dioxide is a mineral that occurs in nature commonly as rutile or anatase, both with tetragonal unit cell and crystal structures. It is traditionally viewed as an insulator with a bandgap around 3.0 eV,\textsuperscript{1,2} however, recent developments have opened new fields to the application of TiO\textsubscript{2} in gas sensing, hydrogen-splitting, and dye sensitized solar cells. Figure 1.1a shows the long and narrow tetragonal anatase unit cell with lattice constants $a = b = 3.786$ Å and $c = 9.517$ Å.\textsuperscript{3} The equilibrium unit cell Wulff construction is shown in figure 1.1b and is consistent with most anatase crystals found in nature.\textsuperscript{4} The highest surface energy is the (001) facet while the most thermodynamically stable is the (101).\textsuperscript{4,5}

Fig. 1.1 a) Anatase unit cell and b) equilibrium crystal shape. c) Illustration of the indirect bandgap of the anatase phase.
The anatase phase is the focus of this research because its electrical properties are useful in a type of photovoltaic cell which will be described in the next section. Anatase is stable in small dimensions of less than ~50 nm, unlike the other TiO₂ polymorph, rutile, which can be grown into large single crystals. However, anatase has a major advantage compared to rutile: the mobility of electrons in anatase is found to be greater than that in rutile.

1.1 Dye Sensitized Solar Cells (DSSC)

The first dye-sensitized solar cell was introduced in 1991 by O'Regan and Grätzel. The cross-section is shown with an illustration in figure 1.2. The photoanode is composed of a dye adsorbed onto the surface of the n-type anatase titanium dioxide mesoporous nanoparticulate film and platinum coated FTO is the cathode. The redox potential energy of the excited state of the dye is higher than the conduction band of the TiO₂, which upon excitation, enables the dye to inject an electron into the TiO₂. The oxidation reaction is $D^* \rightarrow D^+ + e^-$ where $D^*$ is the dye in the excited state and $D^+$ is the oxidized dye. The dye is regenerated by the reduced species of the redox couple and the oxidized species is reduced at the counter-electrode, $I_3^- + 2e^- \rightarrow 3I^-$. Two major advantages of DSSCs are the low cost of materials and manufacturing and the ability to generate current even in low light conditions.

Separation of the electrons in the semiconductor and the holes in the electrolyte is a characteristic of the DSSC not common with other photovoltaic devices. Electron injection is fast due to the positive difference between the energy of the lowest unoccupied molecular orbital and the conduction band ($E_{LUMO}-E_{CB}$) of anatase and also because of the availability of a larger density of states per unit area in the anatase than in the dye.

After injection, the electrons are transported through the network of interconnected
particles by diffusion.\textsuperscript{11,12,13}  Transport is adequately modeled by a random walk motion.\textsuperscript{14} However, this motion is interrupted by frequent trapping and detrapping in lattice imperfections.\textsuperscript{15,16,17,18} In low illumination, only deep traps are within the quasi-fermi level resulting in slower transport.\textsuperscript{19} At high illumination, these traps are filled and only shallow traps participate resulting in faster transport.\textsuperscript{5,20,21} Surface states and defects act as deep-level electron traps and reduces carrier lifetime by increasing the probability of electron recombination with the electrolyte as shown in figure 1.2a.\textsuperscript{22,23,24,25,14}

![Diagram of solar cell](image)

**Fig. 1.2** a) Physical layout of the solar cell showing electron injection and transport through the titanium dioxide. b) Energy diagram of the solar cell showing the recombination of a trapped electron with the oxidized species of the electrolyte. The defects are shown as deep and shallow traps.
1.2 Photoluminescence Spectroscopy and defects in semiconductors

The use of light to excite an electron to a higher energy state causing the emission of light upon relaxation is called photoluminescence spectroscopy (PL). Surface and interface states as well as bulk recombination can be determined by varying excitation wavelengths and looking at the emission spectrum.\cite{26} The mechanisms of luminescence excitation and relaxation are:

\[
S_0 + h\nu_{\text{exc}} \rightarrow S_1 \quad \text{(excitation)}
\]

\[
S_1 \rightarrow S_0 + h\nu_{\text{em}} + \text{heat} \quad \text{(emission)}
\]

These are shown schematically in figures 1.3a and 1.3b below for cases of interband and intraband transitions, where \(S_0\) is the ground electronic state, \(S_1\) is the first excited state, \(h\nu_{\text{exc}}\) is the excitation and \(h\nu_{\text{em}}\) is the photoluminescence.

Fig. 1.3 Photoluminescence relaxations a) Interband photoluminescence and b) intraband photoluminescence. Intraband PL is the relaxation of importance in determining defects in semiconductors.
Defects in crystals create perturbations in the potentials of the lattice resulting in the formation of localized domains called traps.\(^{27}\) If a substitutional impurity or a vacancy results in a localized level just above the valence band, these are called hole traps. When they create distortions in the potential that captures an electron and prevents it from reaching the ionized atom, it is an electron trap.\(^{27}\) Defect states can have various energies within the bandgap, thus the energy of the intraband photoluminescence is important information in identifying the nature of the defect. In this work, as mentioned earlier, we refer to states close to the conduction band as electron traps – this is also called a donor state because occupation of these states will provide additional electrons available for excitation to the conduction band. Hole traps are called acceptor states because of their propensity to donate holes and thus accept electrons.

Because of the larger surface to volume ratio, surface traps become more predominant in nanostructured materials. Dangling bonds which result in under-coordinated atoms could adsorb surface groups like surface –OH which forms a hole trap and releases a hydroxyl radical when occupied.\(^{28}\) Point defects like oxygen vacancies also occur near surfaces\(^{29}\) and defect reactions have shown that increase in concentration of oxygen vacancies gives a proportional increase in titanium interstitial.\(^{30}\) Oxygen vacancies become neutral, singly charged, or doubly charged F-centers\(^{30,31,32}\) or electron traps, which result into Ti\(^{3+}\) when occupied.\(^{33}\)

Photoluminescence has been used to study defects in silicon solar cells using the band-gap emission as indication of the minority carrier diffusion length. In band-to-band transitions, longer diffusion length shows as more intense PL and gives higher conversion efficiency.\(^{34}\) Intra-band PL intensity is proportional to the number of radiative defects – its relationship with
the total number of defects is still to be established, however, recent results have been published for silicon that intraband PL can also be an indicator of device performance.\textsuperscript{35}

1.3 Photoluminescence of nanoparticulate films of anatase

The study on intraband photoluminescence of nanoparticulate anatase was done to understand the nature of its defects. In figure 1.4a, the PL spectra in various environments are shown – the spectrum in argon represents the amount of luminescent intraband states of the nanoparticle, the spectrum in air represents the effect of mobile electron scavenging by oxygen, and the one in ethanol represents scavenging of holes in the valence band. Photoluminescence in argon occurs over a broad range of wavelengths in the visible; exposure to oxygen causes quenching of the entire photoluminescence and exposure to ethanol causes a shift in the peak position to 530 nm and a change in the spectral shape to a narrower, more defined peak. Based on these behaviors, the proposed model for anatase nanoparticle photoluminescence was derived as a composite of two types:

\[ e_{CB}^- + h_{tr}^+ \rightarrow h\nu_{PL}(green) \]

\[ h_{VB}^+ + e_{tr}^- \rightarrow h\nu_{PL}(red) \]

An illustration of these processes is shown in figure 1.4b.
1.4 Research Goals

Device performance issues of the nanoparticulate film in dye sensitized solar cells – hopping transport and trapping and recombination into the electrolyte – are the motivation for the search for an alternative to conventional nanoparticles. It has been shown experimentally\textsuperscript{36} and by Monte-Carlo technique\textsuperscript{37,38} that improvement in the particle interconnection and ordering can improve electron transport. Titanium dioxide nanotube is seen as a feasible option. Figure 1.5 shows a comparison between a nanoparticulate-based device and the nanotubular device. The green arrows indicate the transport of electrons through the titanium dioxide. It is expected, due to the morphology of the nanotubes that transport would proceed along the length of the tube until the charges are collected at the electrode.

Fig. 1.4 Photoluminescence of mesoporous nanoparticulate film of anatase showing: a) changes in the spectrum when exposed to different environments and illustration of electron and hole scavenging by air and ethanol respectively (inset), b) PL model from the observations on environmental effects on the spectra.
Simple calculations of the total surface area also showed that the nanotube morphology has a higher surface-to-volume ratio than nanoparticles, see appendix A1. There are two advantages, therefore in going from a nanoparticulate to a nanotubular morphology – increase in available surface area for dye adsorption and better charge collection, both leading to increase in solar cell efficiency. However, efficiencies of nanotubular devices are still much lower than nanoparticulate ones. Impedance spectroscopy studies showed that the transport between nanoparticulate and nanotubular morphologies are the same, however, recombination is lower in nanotubes.\textsuperscript{39} Thus, it is the goal of this study to gain better understanding of the titanium dioxide nanotube. It aims to characterize the trap states of nanotubes and to understand their

Fig. 1.5 Illustration of expected electron transport in nanoparticulate and in nanotubular array films (original image from The Photochemistry Portal photochemistry.wordpress.com)
transport and recombination behavior.

The following hypotheses will be tested:

- Nanotubes have fewer defects than nanoparticles
- Defects in nanotubes and nanoparticles are different in nature
- There is transport of charges within the nanotube and between adjacent nanotubes

An investigation of the nature and distribution of defects in titanium dioxide nanotubes will provide guidelines in their applications, one of which is as an active area in dye sensitized solar cells. Knowing the location and concentration of the defects spatially will determine the strategies in improving the performance of TiO$_2$ nanotube (NT) DSSCs, for instance by decreasing the area of surfaces where recombination is likely to occur.

1.5 Formation and characterization of TiO$_2$ nanotubes

The first report on the formation of ordered nanoporous TiO$_2$ was published by Zwilling et al. after observing the structure upon subjecting a titanium film to a dilute HF solution.$^{40}$ In 2001, Grimes et al. showed the formation of nanotubes by anodization of titanium foils in an electrolyte containing HF.$^{41}$ Since then several studies have been published on the relationship between the process parameters and the resulting structure (pore size, tube length, wall diameter, etc.).

TiO$_2$ nanotubes are formed when a film of high purity titanium metal is anodized in fluoride containing electrolytes with voltages ranging from 2 to 65 V$^{42,17}$ opposite a platinum counter electrode. There are several factors to consider, voltage applied$^{43,44}$ (including ramp, pulsed, etc.), surface of the titanium foil, temperature and viscosity of the electrolyte.$^{45,46}$
composition of the electrolyte\textsuperscript{17,22} (amount of F\textsuperscript{-}, presence of NH\textsubscript{4}\textsuperscript{+} ions, amount of water), viscosity of the electrolyte, distance between the electrodes, and anodization time. This type of growth is often referred to as self-organized and although with respect to processing it is relatively simple, the mechanisms involved in the formation of the tubes is more complex.

The structure of TiO\textsubscript{2} nanotubes is different from others (i.e. carbon nanotubes); they are open on the surface, thus from the top you will see only an array of circular tube openings. The bottom is rounded and closed (see figure 1.6). Several papers have described the mechanism of formation of TiO\textsubscript{2} nanotubes as a combination of the following key processes (illustrated in figure 1.7): 1) metal oxide formation, 2) chemical dissolution, 3) vacancy diffusion.\textsuperscript{17,43,47}

1. \[ \text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^- \]

2. \[ \text{TiO}_2 + 6\text{HF} \rightarrow (\text{TiF}_6)^{2-} + 2\text{H}_2\text{O} + 2\text{H}^+ \]

Fig. 1.6 Morphology of an ordered array of nanotubular TiO\textsubscript{2} in various magnifications.
3. \( V_{Ti}^{4+} \) diffusion

![Diagram of TiO\(_2\) nanotubes and processes](image)

The mechanism of wall formation follows the point-defect model for vacancy condensation mechanism for alumina\(^{48}\) and is explained as follows: When the oxide layer undergoes field-assisted dissolution, the Ti\(^{4+}\) diffuses into the solution leaving cation vacancies. These \( V_{Ti}^{4+} \) are attracted to the anode and migrate toward the metal-oxide interface. These are areas where the rate of annihilation of vacancies is overcome by the rate of arrival of new vacancies, thus leading to condensation of voids. In Ref. 48, it was mentioned that oxygen vacancies are also formed to maintain charge neutrality, however, the behavior of this species was not described. The initially prepared TiO\(_2\) is amorphous and converted into crystalline anatase by heating to 450°C in air. Figure 1.8 shows the development of the Raman modes of the anatase as samples were heat treated in various temperatures. The peak position of the \( E_{g\ell(1)} \) mode showed a shift to a lower frequency accompanied by a narrowing of the peak width.
attributed to improvement in crystallinity. Annealing of the films at temperatures from 600 °C to 800 °C results in grain growth and transformation to rutile.\textsuperscript{49,50,51}

Fig. 1.8 Development of the anatase morphology with different sintering temperatures. The $E_g(1)$ mode is analyzed and fitted to Gaussians and the peak position and peak width are shown.

The absorbance of the nanotubular films on titanium substrate was taken by diffuse reflectance UV-Vis spectroscopy, see appendix B for experimental details. Figure 1.9 shows the reflectance against wavelength with maximum reflectance in the blue wavelengths and sharply falling to below 5\% in the UV region – the reflectance at 350 nm is \textasciitilde 10\%. Kubelka-Munk transform (appendix B) was done to estimate the bandgap of the film and resulted in energy of around 3.2 - 3.3 eV, comparable to the reported value of 3.34 eV.\textsuperscript{45}
The nanotubes are formed by non-equilibrium processes, and their crystallographic texture may differ from the equilibrium crystal shape shown earlier. Transmission electron microscopy is a way to determine crystal planes and orientations in nano-sized samples; however, its interpretation often leads to confusion when studying surfaces. Electron Back-Scatter Diffraction (EBSD) provides a way to determine the crystal orientation of surfaces (see appendix B for details) not possible with other techniques. Figure 1.10 below shows a region of a fracture surface of ordered nanotube arrays with the corresponding crystallographic texture map. The orientation of the anatase unit cell is indicated in several areas of this map. From the data, it can be seen that the nanotubes grow along the 001 direction and the crystal planes exposed are parallel to this direction with some variation in angle.
Fig. 1.10  a) Electron diffraction lines from a point in the samples area and the indexing of these diffraction patterns. b) Sample area where the crystallographic map was taken. c) Crystallographic texture map of the nanotube with the inverse pole figures showing the orientation of planes along nanotube walls; the legend is shown on the right.
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CHAPTER 2

Defect Photoluminescence of TiO₂ Nanotubes

Attribution:

The following work was done and written by the author and was presented at the 2010 Spring Meeting of the Materials Research Society and peer-reviewed and published as part of the conference proceedings.


Abstract

Photoluminescence (PL) spectroscopy of nanocrystalline TiO₂ using ultraviolet light excitation reveals a range of intra-bandgap defect states which emit at visible wavelengths. In this study we use 350 nm excitation to probe the luminescent defect states of TiO₂ nanotubes fabricated by anodization of titanium. The nanotubes show a broad visible luminescence from 450 to 700 nm with a peak at 520-550 nm or 2.4-2.3 eV. The intensity of nanotube PL is orders of magnitude lower than that of nanoparticulate anatase and P25 (mixed-phase anatase/rutile) films of comparable thickness. Similar to the PL of the nanoparticles, the nanotube PL is increased by vacuum annealing. The nature of the nanotube defects is investigated through shifts in the intensity and shape of the PL spectra in hole or electron scavenging environments. We
find the PL intensity of the nanotubes to be less dependent on environment than that of conventional TiO$_2$ nanoparticles. We conclude that there are two inter-related reasons for decreased intensity and decreased environmental dependence of PL from TiO$_2$ nanotubes as compared to nanoparticles: decreased density of defect states and improved carrier transport.

2.1 Introduction

Titanium dioxide nanotubes formed on the surface of titanium foils after anodization exhibit a good vertical alignment and uniformity of dimensions.$^{1-4}$ Because of the ordered structure, they are seen as an alternative$^5,^6$ to the TiO$_2$ nanoparticles frequently used in dye-sensitized solar cells (DSSC). Their walls could provide a direct path for the electrons to travel thus minimizing recombination that occurs when the electrons encounter the electrolyte as they hop from one particle to another.$^6,^7$ Currently, DSSCs with nanotubular TiO$_2$ reach up to 6.9% energy conversion efficiency and incident-photon-to-electron conversion efficiency (IPCE) of 80%.$^1$

Nanotubes formed by anodization of Ti are initially amorphous but sintering above 280 $^\circ$C transforms them into nanocrystalline anatase.$^8$ The nanotubes are open on the top side and closed on the bottom and upon closer inspection each tube is isolated from the other except for small connections that may result from a vacancy condensation mechanism during the formation of the tubes.$^9$ Transmission electron microscopy showed that nanotubes are composed mostly of (101) planes along the walls.$^{10}$ Because the morphology of the nanotubes is different from that of TiO$_2$ nanoparticles, the objective of this study is to understand the nature of defects and their distribution and to relate these to the device characteristics of the dye-sensitized solar cell.
2.3 Experimental details

The nanotubes were fabricated by anodization of titanium foils (Aldrich) in a two-electrode cell following the procedure of Ref. 10, using 0.5% NH$_4$F and 2% water in ethylene glycol as the electrolyte and anodization voltage of 10V to 60V supplied from a dc source. The films were then sintered in air at 450°C for 3 hours in a muffle furnace. The titanium dioxide phase was verified using Raman spectroscopy excited by a Kr ion laser operating at an excitation wavelength of 413.1 nm. The power at the sample was 5 mW and the scattered light was dispersed and detected with a SPEX double monochromator and photomultiplier tube. Photoluminescence spectroscopy was done using 10 mW and 350.7 nm excitation from the same laser. The emitted light was filtered using a 385 nm long pass filter, dispersed with a single monochromator, and detected with a thermoelectrically cooled CCD. All measurements were done at room temperature, using a quartz cuvette as a sample holder to vary the environment of the sample. Raman spectra were recorded in air and PL spectra were recorded in argon, air, and ethanol. Vacuum annealing was done in a mild vacuum (~ 50 mtorr) at approximately 230 °C for 30 minutes. Dimensions and morphology were observed through a field emission scanning electron microscope.

2.4 Discussion

Anodization of titanium foils to produce titanium dioxide films result in ordered nanotubes with an inner and outer diameter around 100nm and 190nm respectively (Fig. 2.1a). The length ranges from 6 µm to 9 µm. After anodization, the nanotubes were amorphous, as
verified by Raman spectroscopy. The nanotubes transformed into the anatase phase after sintering at 450 °C for 3 hours (Fig. 2.1b).

![Fig 2.1 (left) SEM picture of the titanium dioxide nanotubes showing the tube dimensions and (right) Raman spectra showing the anatase phase obtained after sintering.](image)

In our previous studies of the PL of anatase and mixed-phase P25 (25% rutile, 75 % anatase) nanoparticles,12,13 we observed weak visible PL that could be resolved into contributions from trapped holes and trapped electrons based on the effect of electron and hole scavengers on the spectrum. In that work, we found the PL to be strongly quenched in air owing to the ability of O₂ to scavenge conduction band electrons. In the presence of ethanol and other hole scavengers, the red PL resulting from the radiative recombination of trapped electrons with valence band holes is suppressed leaving a PL spectrum which peaks in the green, assigned to the radiative recombination of mobile electrons (from the conduction band and shallow traps) with trapped holes. We therefore examined the PL of TiO₂ nanotubes in air, argon and ethanol.
The PL of the nanotubes excited at 350 nm in the presence of argon is shown in Fig. 2.2. Fig. 2.2a compares the typical PL of the nanotubes (NTs) to that of anatase and P25 nanoparticle films on the same scale, and normalized to the same intensity in the inset. The nanotubes reveal a much weaker PL than the nanoparticles, with a shape more similar to that of P25 than anatase. As shown in previous work, the PL of red-emitting electron traps is quenched in P25 leaving the green hole trap emission. The PL spectrum of the nanotubes shows a peak in the green at around 520-550 nm with a slight shoulder around 600 nm and a wing that extends to 700-750 nm. The intensity and shape of the nanotube PL spectrum compared to that of the nanoparticles suggest that the nanotubes have a lower density of defects and that the green-emitting hole traps dominate over the red-emitting electron traps. Upon vacuum annealing (Fig. 2.2b), the weak red shoulder is diminished and there is a large increase in intensity, consistent with the formation of oxygen vacancies which emit in the green. Oxygen vacancies are important defects in nanocrystalline TiO$_2$ and known to limit transport and enhance recombination in TiO$_2$-based solar cells. Thus the weak PL from the nanotubes before vacuum annealing is consistent with their superior transport properties as compared to nanoparticles.

We also considered the possibility that differences in film thickness could be responsible for the higher PL intensity of the nanoparticles compared to nanotubes. However, the absorption coefficient of TiO$_2$ nanotubes is 22,000 cm$^{-1}$ at the excitation wavelength, resulting in a penetration depth of about 0.5 μm. Since this is considerably less than the film thickness of both the nanoparticle and nanotube films, the lower PL intensity of the nanotubes is likely to be a consequence of their lower defect density. At the same time, the efficiency of carrier transport may also be at work, since radiative recombination of trapped and mobile charge carriers
depends on their spatial overlap. Enhanced carrier transport in nanotubes as opposed to nanoparticle films may also contribute to the weaker PL of the former.

![Photoluminescence spectra of anatase and P25 nanoparticles and TiO$_2$ nanotubes taken in argon. The inset shows the same data after normalization. b) PL of TiO$_2$ nanotubes before and after vacuum annealing.](image)

The PL spectrum of the unannealed nanotubes was fit to three Gaussian functions (Fig. 2.3a). The first peak is around 450 nm or 2.8 eV, the second at 540 nm (2.3 eV), and the third at 700 nm (1.7 eV) with FWHMs of 0.3, 0.4, and 0.5 eV respectively. The peak at 450 nm is thought to result from a bulk self-trapped exciton. In accord with our previous work, we assign the peak at 540 nm to the radiative recombination of mobile electrons with trapped holes (Type 1 PL) and that at 700 nm to the recombination of trapped electrons with valence band holes (Type 2 PL). The resulting trap state distributions are depicted schematically in Fig. 3d. Since this assignment was based on the response to electron (O$_2$) and hole (ethanol) scavengers, the PL of the (unannealed) TiO$_2$ nanotubes was measured in air and ethanol (Fig. 2.3b). Surprisingly, the nanotube PL is not strongly quenched by oxygen, but the intensity is diminished in ethanol with no change in shape. This is in contrast to the results for anatase nanoparticles where O$_2$
completely quenches the PL and ethanol results in decreased red emission and increased green emission. We have previously speculated that the electron and hole traps of nanocrystalline anatase are spatially isolated on different crystal planes. Though the more stable (101) planes of anatase constitute a larger proportion of the surface than the (001) planes in conventional nanoparticles, the exposed surfaces of the nanotubes are even more skewed toward contributions from the (101) planes. Thus the shape of the nanotube PL spectrum would be explained if the green- and red-emitting traps are localized on the (101) and (001) planes, respectively. The vacuum annealing results of the present work suggest that oxygen vacancies\textsuperscript{14,15} contribute strongly to the green emission.

Fig. 2.3 a) Fit of the nanotube PL spectrum to three Gaussian functions. b) Nanotube PL in the presence of argon, air and ethanol. c) PL spectrum of a two-phase nanotube sample obtained by anodization at 10 V, exhibiting anatase (visible) and rutile (near-IR) PL. The spectra were recorded first in argon (1), then in air (2), then again in argon (3) and again in air (4) d) Proposed trap state distributions for anatase from Ref. 13. The transition associated with the Type 1 PL of rutile is shown for comparison.
The failure of oxygen to significantly quench the nanotube PL may indicate that adsorption of O$_2$ at surface defects, i.e. oxygen vacancies, is required for electron scavenging. The fewer number of these defects and the possible sequestering of these defects along the seams between the nanotubes could account for the weak quenching by oxygen. As reported separately,$^{16}$ natural bulk anatase crystals which evidence a high density of oxygen vacancies exhibit strong PL which is not significantly quenched by O$_2$, probably owing to a low surface concentration of these defects.

More puzzling is the decrease in PL on exposure to ethanol, shown in Fig. 2.3b. Other solvents (e.g. acetonitrile and dimethylsulfoxide) were also examined and found to generally exert only a weak effect on the nanotube PL intensity. We suspect that the strong solvent dependence of the PL of anatase and P25 nanoparticles$^{13}$ derives in part from solvent contributions to the barrier to interparticle electron transfer. The morphology of the nanotubes may diminish the importance of this interparticle transport and results in decreased solvent dependence of the PL intensity.

The nanotube spectra of Fig. 2.2 are typical of samples that have been anodized at 20 to 50 V. Anodization at lower voltages yields spectra that have two prominent peaks, one at ~530 nm, characteristic of the anatase phase, and one at 800-850 nm assigned to the rutile phase.$^{12,13}$ This is illustrated in Fig. 3c which shows the PL spectrum of a nanotube sample obtained by anodization at 10 V. In the presence of air, the rutile PL is enhanced at the expense of the visible PL. The effect is quasi-reversible in that the anatase PL only partially recovers on exposing the nanotubes to argon again. This behavior is similar to that reported in Ref. 13 for mixed phase nanoparticle samples, and is indicative of interphasial carrier transport. It would appear that in
the presence of electron scavengers, there is a competition for electrons between hole traps in the anatase (green PL) and rutile (near-IR PL) phases. The effect is seen only for shorter nanotubes obtained at lower anodization voltage. From structural studies of nanotubes, rutile is known to reside on the oxide layer at the bottom of the nanotubes. Since the PL is excited through the top of the nanotube film, it is reasonable that this effect is seen only with shorter nanotubes grown at lower voltage. These results highlight the transport properties of the nanotubes by showing that electrons from the anatase phase can travel in shallow traps to recombine with the hole traps in the rutile underlayer.

2.5 Conclusions

The photoluminescence of TiO₂ nanotubes is found to be orders of magnitude weaker than that of TiO₂ nanoparticles, a consequence of fewer defects and improved carrier transport. In contrast to nanocrystalline anatase, the PL of TiO₂ nanotubes is dominated by the green PL associated with hole traps with only weak red PL from electron traps. The much weaker solvent dependence of the nanotube PL compared to that of nanoparticles is tentatively attributed to faster transport and diminished role of interparticle electron transfer.

2.6 Acknowledgment

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CHAPTER 3

Photoluminescence of Dense Nanocrystalline Titanium Dioxide Thin Films: Effect of Doping and Thickness and Relation to Gas Sensing

Attribution:

The optical spectroscopy was done by the primary author; the samples for analysis and the gas sensor data were provided by Dr. Seeley.


Abstract

The photoluminescence (PL) of dense nanocrystalline (anatase) TiO2 thin film is reported in varying calcination temperature, thickness, and tungsten and nickel doping. Investigation of the optical absorption, Raman spectra, and PL spectra as a function of heat treatment and dopants reveals the role of oxygen vacancies, crystallinity, and phase transformation in the performance of TiO2 films used as gas sensors. The broad visible defect PL of compact and undoped TiO2 films is found to be much brighter and less sensitive to the presence of oxygen than that of mesoporous films. The dense nanocrystalline grains and the nanoparticles comprising the mesoporous film are comparable in size, making the difference in morphology an important
factor in understanding the nature of photoluminescent defects. At higher calcination temperatures, the transformation to rutile results in the appearance of a dominant near-infrared peak. This characteristic change in the shape of the PL spectra demonstrates efficient capture of conduction band electrons by the emerging rutile phase. The W-doped samples show diminished PL with quenching on the red side of the emission spectrum occurring at lower concentration and eventual disappearance of the PL at higher W concentration. The results are discussed within the context of the performance of the TiO2 thin films as CO gas sensors.

**KEYWORDS:** dense nanocrystalline film, titanium dioxide, photoluminescence, gas sensors, Ni-doping, W-doping

### 3.1 Introduction

Nanoparticulate TiO2 has several physical properties that can make it an ideal gas sensing material such as good thermal stability, high surface area, and, most importantly, electrical resistance that depends on the presence of oxidizing and reducing gases. For TiO2, intrinsic oxygen vacancies are responsible for the n-type semiconducting properties.1 In the common bulk phase of TiO2, i.e. rutile, conductivity decreases with increasing partial pressure of O2 and increases with the number of donor states associated with oxygen vacancy formation.2,3 The removal of an oxygen atom and its associated −2 charge from the TiO2 lattice leads to defects such as Ti3+ centers, and F+ and F centers where one or two electrons, respectively, are trapped at vacancies.4 Using Kroeger-Vink notation, oxygen vacancy formation can be represented as:

\[
2TiO_2 \rightarrow 2Ti_{\bar{Ti}}^{x^+} + 3O_\bar{O}^{x^-} + V_{\bar{O}}^- + \frac{1}{2}O_2 + 2e'
\]  

(1)
O₂ adsorption at these surface oxygen vacancies then leads to the formation of O₂⁻, O', or O²⁻ species,⁵ resulting in electron scavenging and an increase in resistivity. Conversely, reducing gases such as CO, which react with adsorbed oxygen species, decrease the film resistivity.⁶

A variety of optical spectroscopic techniques have revealed the presence of different kinds of electron and hole traps associated with defects.⁷,⁸ We have recently reported the visible defect PL of nanocrystalline TiO₂ that is observed on illumination with photon energies above the band gap of 3.2 eV.⁹,¹⁰,¹¹ By observing the PL of mesoporous TiO₂ films prepared from nanocrystalline anatase in the presence of electron and hole scavengers, we have resolved the overall broad visible PL into contributions from hole and electron traps.¹⁰ The PL which peaks at a green wavelength ~530 nm is assigned to the recombination of mobile (conduction band and shallow-trapped) electrons with trapped holes. The PL from the recombination of trapped electrons with valence band holes, on the other hand, extends into the red and near-infrared with a peak between 600 and 650 nm. Conditions which favor an increase in the number of mobile electrons such as vacuum annealing to create n-donors in the form of oxygen vacancies, result in increased emission at green wavelengths.¹¹,¹²

The PL of the rutile phase of TiO₂, on the other hand, occurs in the near-IR and is much brighter and narrower than the PL spectrum of anatase. Nakato et al. have assigned the rutile PL at ~840 nm to recombination of conduction band electrons with holes trapped on oxygen atoms on the (110) and (100) facets.¹³ In commercially available P25 nanoparticles (Aeroxide® from Degussa), which contain about 75% anatase and 25% rutile, PL associated with red-emitting electron traps of anatase is apparently quenched, as is the rutile PL, and only the green emission from hole traps is observed.⁹ Nanocrystalline anatase in the presence of hole scavengers such as ethanol gives rise to PL similar to that of P25 as the recombination of the trapped electrons is
Conversely, thermally treated anatase films containing only minor amounts of rutile show a PL spectrum dominated by the minority phase, owing to facile interphasial electron transport and the much larger quantum yield for rutile PL as opposed to that of anatase. Thus the intensity of PL depends not only on the concentration of luminescent traps but also on the ease with which nascent electron-hole pairs can be separated. The electron and hole traps of nano-TiO₂ strongly influence carrier transport in nanoparticulate TiO₂ as well as the binding of adsorbates, which influence this carrier transport. Photoluminescence spectroscopy is therefore a useful technique for investigating the physical basis for the performance of TiO₂-based gas sensors that respond through changes in conductivity. Here, we examine the effects of calcination temperature, n-type (W), and p-type (Ni) dopants on the PL of compact nanocrystalline TiO₂ films and relate these to gas sensing efficiency. We also report striking differences between the PL of compact anatase films compared to that of previously studied mesoporous films. Our results shed light on the physical basis for trap state luminescence while revealing how dopants and thermal treatment influence sensor performance.

### 3.2 Experimental

Titanium-based metal-organic sols were created by dissolving titanium (IV) isopropoxide (Ti[OCH(CH₃)₂]₄, 97% min., Alfa Aesar) in 2-methoxyethanol (CH₃OCH₂CH₂OH 99.3+%, Alfa Aesar) in an argon atmosphere. Tungsten (VI) isopropoxide (W[OCH(CH₃)₂]₆, Alfa Aesar), and nickel(II) methoxyethoxide (Ni(OCH₂CH₂OCH₃)₂, Alfa Aesar) were used as the dopant sources. Sol were created with metal ion compositions of 0, 2.5, 5, 10 at.% W, and 10 at.% Ni balanced by Ti. Metal ionic concentration was kept at 0.5 M for all sols. The solutions were refluxed in an oil bath at 120 °C for 6 h under constant argon flow to ensure homogeneity.
TiO$_2$-based thin films were created by spin-coating the Ti sols onto a quartz substrate described in more detail in Ref. 15. Films were created in two thicknesses by controlling the number of spin coated depositions; 2 or 12. After every 4th deposition, the films were calcined, oxidized, and crystallized in a furnace between 600 and 900°C. Film resistance and gas sensing measurements were performed in a quartz tube furnace with controlled flowing gas atmosphere and temperature. Scanning electron microscope and x-ray diffraction techniques were used to characterize the morphology and crystal structure.

UV-visible absorption spectra of thin films were measured using UV-2501PC Shimadzu spectrophotometer scanning from 800 to 250 nm wavelengths. The Raman spectra were measured using 5 mW 413.1 nm Kr$^+$ excitation, a double monochromator, and a PMT detector. The photoluminescence spectra were taken in backscattering geometry using a 20 mW 350.7 nm Kr$^+$ excitation with a 385 nm long pass filter before the slit of an ACTON SpectraPro 2300i spectrometer.

3.3 Results and Discussion

1. Characterization of dense nanocrystalline TiO$_2$ Films

The X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and resistivity properties of undoped dense TiO$_2$ films calcined at 600, 700, 800 and 900 °C were previously reported.$^{15}$ Relevant to the present study, the FE-SEM images of Ref. 15 reveal nonporous films and grain sizes which increase from about 60 to 150 nm for calcination at 600 to 900 °C, respectively. XRD measurements showed an increase in crystallinity between 600 and 700 °C, grain growth between 700 and 800 °C and the onset of rutile formation in the 900 °C sample. In Fig. S1 of the Supporting Information, the Raman spectra of the undoped samples at all calcination temperatures show that anatase is the dominant phase. The samples are divided

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into two sets – 12-layer 2-layer films. Each spin-coated layer contributes between 70 and 80 nm to the film thickness and therefore the 12-layer and 2-layer films are about 800-1000 nm and 140-160 nm thick, respectively.

2. Photoluminescence of Undoped Thin Films

![Figure 3.1 PL from a 12-layer dense nanocrystalline TiO$_2$ film, calcined at 600 °C, in air and in argon compared to that from a mesoporous anatase film in air and in argon.](image)

Figure 3.1 compares the PL spectrum of a dense TiO$_2$ film calcined at 600 °C to that of a mesoporous TiO$_2$ film prepared from 6-nm anatase particles sintered at 450 °C according to the procedure of Ref. 16. Both samples are in the anatase phase and the shape of their PL spectra is similar. The apparent structure in the emission spectrum of the thin film sample is a result of interference. Thus the main difference is the order of magnitude more intense PL from the dense film and very weak quenching by oxygen. The penetration depth of the incident light at the 350 nm excitation wavelength is about 0.5 μm based on the absorption coefficient of ~20,000 cm$^{-1}$ reported in Ref. 17. However, this data is for a mesoporous film of TiO$_2$ nanotubes, hence the
penetration depth in the thin film may smaller. The thickness of the dense film is about 0.8 to 1 μm and that of the ~50% porous nanocrystalline films is on the order of 10 μm. Thus both films are thicker than the penetration depth of the incident light and thus the intensity difference between them is not due to an increase in the amount of TiO₂ sampled in the dense film. We attribute the more efficient PL quenching by air in the case of the mesoporous film, which is approximately 50% porous, to the much larger surface area available for adsorption of O₂ and thus greater scavenging of conduction band electrons. As in the case of rutile,¹⁸ and other gas sensing oxides,¹⁹,²⁰,²¹ evidence suggests O₂ adsorbs on surface oxygen vacancies of anatase.

Since luminescent defects reside on the nanoparticle surface,⁹ more intense PL from the dense film is surprising at first glance. However, the intensity of defect PL in TiO₂ also depends on carrier transport, which competes with radiative recombination, as well as the defect density. We hypothesize that more intense PL from the dense nanoparticle film results from grain boundaries, which impede interparticle electron transport. Carrier transport is related to the width of the neck between nanoparticles.²² In the conceptual depiction of a TiO₂ gas sensor film,²³ particle interconnectivity is controlled to prevent transport of charges within the film and thus maximizing the charges available for the sensing mechanism. The different intensities of the dense and mesoporous films seen here might reflect differences in both carrier transport and defect density. This conclusion seems reasonable in light of studies which suggest that presence of grain boundary barriers associated with interface trap states,²⁴ and their greater importance in microcrystalline as compared to nanocrystalline TiO₂ films.²⁵ The weaker quenching effect of ambient O₂ in the case of the dense TiO₂ films is attributed to the lower accessibility of oxygen vacancy binding sites at these buried interfaces. However, as shown in Fig. S2 of Supporting Information, O₂ has a greater quenching effect on the PL of samples calcined at 700, 800, and
900 °C than for the 600 °C sample. Based on the Raman and X-ray data for the latter sample, we hypothesize that the amorphous TiO$_2$ content of the 600 °C sample, presumably on the surface, is unfavorable to binding O$_2$.

Fig. 3.2 shows the PL of undoped TiO$_2$ films that were subjected to calcination at 600, 700, 800 and 900 °C. In all cases anatase is the majority phase as shown by Raman spectroscopy and XRD, with a small amount of rutile evident in the XRD of the 900 °C film. As shown in Fig. S1 (supporting information) the normalized intensity of the 143 cm$^{-1}$ Raman peak shows little variation in width or frequency for the four samples. This peak is known to broaden and shift when significant numbers of oxygen vacancies are present.$^{26}$ However, the general increase in intensity of anatase Raman lines with higher calcination temperature is in agreement with an increase in crystallinity as reported in Ref. 15 on the basis of XRD and SEM.

The samples calcined at 600 and 700 °C show only the visible PL of anatase, while the 800 and 900 °C samples reveal the near-IR PL of minor amounts of rutile. The quantum yield of
rutile PL is orders of magnitude larger than that of anatase, making the PL spectrum much more sensitive for detecting small amounts of rutile. In addition, the conduction band edge of rutile is about 0.2 eV lower than that of anatase, enabling interphasial transport of conduction band electrons from anatase to rutile. Between 600 and 700 °C there is a slight increase in anatase PL with no change in shape. We think that the photoluminescent hole and electron traps of anatase are sequestered on different exposed crystal planes of anatase. It is worth noting that the typical anatase PL shown in Figs. 3.1 and 3.2 are not present in amorphous TiO₂ nanoparticles where more blue emission is observed. The slight increase in intensity of PL in the 700 °C sample compared to the 600 °C film could be correlated to enhanced crystallinity. On increasing the calcination temperature from 700 to 800 °C, there is a further overall increase in the anatase PL accompanied by a blue-shift in the peak. This blue-shift is associated with increased formation of oxygen vacancies and correlates well with the decrease in baseline resistivity in this temperature range. In addition, the near-IR PL of rutile emerges for the 800 °C sample. After calcination at 900 °C, there is an overall decrease in both the anatase and rutile components of the PL, despite the increase in rutile content. The peak at about 540 nm in the anatase PL for this sample is significantly less intense. This suggests quenching of the red-emitting electron traps as seen previously in mesoporous anatase films heated at 900 °C and also containing small amounts of rutile. The rutile PL does not arise from defects but rather from holes trapped on three-fold coordinated oxygen atoms of the exposed (110) and (100) surfaces. Hence the decrease in rutile PL from 800 to 900 °C could be the result of increase in size of the rutile particles and thus decrease in the surface-to-volume ratio. As reported previously, FE-SEM images and XRD reveal increase in grain size from 800 to 900 °C, explaining the overall decrease in the intensity of PL from surface defects. At the same time, less intimate connection of anatase and rutile
phases in the 900 °C sample would decrease the ability of the rutile phase to act as a sink for conduction band electrons from anatase, also contributing to weaker rutile PL.

As shown in Fig. S2, the PL of the 12-layer dense films becomes more sensitive to oxygen for films subjected to higher calcination temperature. The PL of the 700 °C is slightly reduced in air compared to argon. This effect is small compared to a reduction from 2 to 3 times for the 800 °C film. Exposure of the 900 °C film to air instead of argon resulted in almost complete quenching of the anatase emission with only a slight reduction in the rutile PL. These observations may indicate an increase in oxygen vacancy content in the 800 °C sample over that of the films calcined at lower temperature, which results in both more intense PL as well as greater sensitivity to O₂ as an electron scavenger. Increased oxygen vacancy content is also suggested by the decreased resistance of the films with increasing calcination temperature between 700 and 900 °C. Note that the near-IR PL from pure rutile nanoparticles is not very sensitive to oxygen.¹⁰ Greater quenching of the rutile component of the PL by air in the case of the 800 °C versus the 900 °C sample is also evidence that the particles of the two phases are in better electrical contact in the former film than in the latter, accounting for the increased rutile emission in the 800 °C film.

Fig. 3.3 shows the effect of the efficient hole scavenger ethanol (EtOH) on the PL from the 12-layer 600 °C film. In the presence of air, the PL from the dense film shows an envelope that matches the scaled PL spectrum from a mesoporous anatase film. Exposure of the dense films to EtOH shuts off the red PL from the recombination of trapped electrons with valence band holes, leaving a spectrum which resembles that of P25, which is in agreement with our previous results.¹⁰ Thus despite the smaller exposed surface area of the compact film compared to the mesoporous film, EtOH can still efficiently scavenge valence band holes. This is in
contrast to effect of oxygen as an electron scavenger, for which scavenging depends on the accessibility of adsorption sites.

The PL of the dense film in Fig. 3.3 shows definite structure that hasn’t been seen in mesoporous films. These peaks were found to be more pronounced when the excitation beam was more tightly focussed at the sample. Assuming that this structure results from interference, the thickness $d$ of the film was calculated from $2n(\lambda)\lambda = i/d$, where $i$ is the peak number, and $n(\lambda)$ is the refractive index at wavelength $\lambda$. Taking $n(\lambda)$ as the average of the values at 320 nm (3.6 eV) and 400 nm (2.9 eV) for anatase,\textsuperscript{30} the film thickness was calculated to be 1000 nm, comparable to the value taken from SEM images, i.e. between 800 and 1200 nm and as reported in Ref. 15.

The same defects, which give rise to visible PL, could also lead to band tails in the absorption spectrum.\textsuperscript{16} An alternative explanation is that the band tails are associated with amorphous TiO$_2$
which should decrease with increasing calcination temperatures. The absorption spectra of 2-layer films, which are thin enough for measurement in transmission, were obtained as a function of calcination temperature. Fig. 3.4 shows the absorbance and PL spectra of 2-layer films that were subjected to calcination at 600, 700, 800 and 900 °C. The absorbance spectra in all films show a maximum at around 250 nm (4.9 eV) and a shoulder at 300 nm (4.1 eV). Some variations in the band tail region were present and showed the 700°C film as having the largest maximum absorbance and the steepest absorption edge.

![Absorbance and PL spectra](image)

**Fig. 3.4** Absorbance (left) and photoluminescence (right) of 2-layer dense films of nanocrystalline anatase, as a function of calcination temperature. The inset shows the absorbance spectra normalized to the same maximum. The PL spectra were recorded in argon.

As shown in Fig. 3.4, the PL spectra of the 2-layer films exhibit some important differences compared to the spectra of the thicker films shown in Fig. 3.2. Interference fringes are absent as expected for the thinner film. Though the intensity trends with calcination temperature are similar to those seen in the thicker film, there is no hint of rutile emission while the visible emission from anatase shows a peak at about 550 nm. This anatase peak is blue-shifted compared to the anatase PL from the thicker film. The most intense PL was observed in
the film with the steepest band edge, calcined at 700 °C, however, there are no clear trends for
the remaining films and the variation in PL are larger than the variations in the normalized
absorption spectra. This lack of correlation may be tied to the importance of carrier transport in
determining the intensity of the PL, or may be a result of both amorphous materials and oxygen
vacancies contributing to the band tails.

The absence of a rutile peak, even for the 900 °C sample, may be related to the size-
dependent stability of anatase and rutile nanoparticles. The rutile phase is favored for crystallite
dimensions above 50 nm, therefore the 140 to 160 nm thickness of the 2-layer film is not as
favorable to rutile nanoparticle formation as the thicker (~1000 nm) films. Another striking
difference compared to the thick films is the greater sensitivity to oxygen in the case of the 2-
layer films. The PL data shown in Fig. 3.4 were recorded in argon and can be compared to the
same data recorded in air where the intensity is reduced by roughly a factor of two (Fig. S2).
This is attributed to the larger ratio of exposed surface area to illuminated volume. Since the PL
spectra of the thin and thick films were recorded with the same incident power density, the
appearance of a peak in the green for thin layer films corresponds to a higher photogeneration
rate of electron-hole pairs and thus PL is dominated by the radiative recombination of conduction
band electrons with trapped holes.

2. Doped thin films

The thin films were doped with nickel and tungsten resulting in either p-type or n-type
electrical behavior, respectively. The following defect reactions occur upon doping:

\[
TiO_2 \xrightarrow{W} W^{6+} + 2e^+ + 2O^X \quad (2)
\]

\[
TiO_2 \xrightarrow{N} Ni^{2+} + 2O^X + 2h^* \quad (3)
\]
Calcining of films doped with aliovalent cations nickel and tungsten was done at different temperatures for each dopant because of the different phase stability of the anatase-rutile transformation in doped TiO$_2$ and to avoid the formation of unwanted phases such as tungsten oxide with increasing heat treatment temperature.\textsuperscript{33} As shown by the Raman spectra of Fig. S3, the W-doped film calcined at 700 °C is in the anatase phase while the Ni-doped film at 900 °C shows conversion to rutile, even though the undoped sample at this temperature remained predominantly in the anatase phase. This is evidence that nickel as a substitutional impurity enhances the formation of rutile in accord with similar observations in the literature.\textsuperscript{34}

Fig. 3.5 PL spectra of W-doped (left) and Ni-doped 12-layer films calcined at 700 °C and 900 °C, respectively. The inset at left shows the spectra of the W-doped films scaled to the same maximum. The PL of the Ni-doped film at right is compared to a scaled PL spectrum of a mesoporous film of rutile nanoparticles from Ref. 10.

The PL spectra of the doped films are shown in Fig. 3.5. In the case of tungsten, dopant concentrations from 2.5 to 10 % result in a strong green PL, consistent with the greater availability of mobile electrons in this n-doped sample. The intensity of PL decreases with increasing W content, suggesting that the dopant itself is acting as a donor rather than merely facilitating the formation of oxygen vacancies. In the case of the Ni-doped sample, both the
Raman data (Fig. S3) and the PL of Fig. 3.4 suggest complete conversion to rutile on calcination at 900 °C. Interestingly, the Ni-doped film shows a peak at about 820 nm corresponding to the holes trapped on the (110) surface, while the 840 nm peak associated with the (100) surface is absent. The absence of PL from the (100) surface may be the result of the nature of the growth of the rutile particles from the pre-existing anatase particles.

3. Relation to gas sensing

Gas sensor performance is gauged through the ratio of film resistance exposed to the target gas against the resistance when exposed to the background gas. Evidence exists that for TiO₂ in both the rutile and the anatase phases, O₂ is adsorbed in the immediate neighborhood of a vacancy where it scavenges trapped electrons. The ratio, therefore, of the photoluminescence in argon and to that in air might be expected to correlate to the sensitivity of the film’s resistance to its environment. In undoped samples, the ratio most different from unity was seen in the film calcined at 800 °C, followed by 900 °C, then by 700 °C (Fig. S2). However, as shown in Ref. 15, the response to both O₂ and CO was larger for the films calcined at 600 - 700 °C, for which there is only a small effect of air on the intensity of PL. The basis for this apparent discrepancy may lie in the competing effects of defect density and transport on the intensity of anatase PL and the extraordinary role of minor amounts of rutile. For the undoped sample calcined at 800 °C, the PL spectrum evidences rutile even though the amount is too low to be detected by XRD. Thus although the PL for this film in air reveals efficient electron scavenging by adsorbed oxygen, the transport is dominated by rutile sinks and thus the film resistance is not as oxygen-dependent as that of the films calcined at lower temperature and lacking the rutile phase. It is possible that while higher calcination temperature improved the crystallinity of the films (allowing for more oxygen vacancies to be close to the surface), the
transport of the charges are also improved. One important thing to keep in mind is the difference in condition between PL measurement and resistivity testing. Sensing tests were performed at higher temperatures and the absorption and desorption reactions may occur at different rates.

Oxygen vacancies are sites of O$_2$ adsorption and dissociation$^{35}$ and the adatom formed reacts with the target gases (carbon monoxide for instance) causing the change in film resistance. From the defect reactions, doping with tungsten creates n-type carriers; creation of oxygen vacancies also results in similar charges. As mentioned earlier, the PL decreased upon addition of small amounts of tungsten supporting the possible consequence of tungsten-doping as pointed out by the defect reaction which is the decrease in the driving force for oxygen vacancy formation. To understand the reason behind the apparent contradiction between the results of tungsten doping, PL, and the gas response ratio, it is important to note the source and location of the dissociation of O$_2$. Studies by Du et al.$^{35,18}$ on rutile surfaces show that the charges that transfer from the surface to the adsorbed O$_2$ are electrons from oxygen vacancies and that these charges can migrate through the lattice making them delocalized over the vicinity of the vacancy. This means that not just a single oxygen vacancy contribute its charge to the dissociation but several. From Ref. 18 also, the O$_2$ dissociation was seen to be on the Ti rows where the electrons are delocalized. Upon tungsten doping the carrier charges (electrons) are still created upon substitution and these could still travel to the surface. Although this study was done in rutile (110) surfaces, similar behavior is thought to be the reason of the improved gas sensing with tungsten doping. In undoped samples, the charges are associated with the creation of oxygen vacancies, which were seen to be healed by some O-adatoms, thus there are less O-adatoms available for the reaction with target gases. On the other hand, W-doping makes more n-type
carriers or electrons available for dissociation O2 and more O-adatoms are created and available for the reaction with target gases. Nickel-doped samples showed the presence of significant amount of rutile and has been observed to have p-type conductivity\textsuperscript{1} at elevated temperatures and seen to be responsible for the p-type sensor behavior.\textsuperscript{33,36}

3.4 Conclusions

The photoluminescence of titanium dioxide is an indication of the amount of intra-band gap states. Data suggests that the green PL of anatase is attributable to the amount of oxygen vacancies. The difference in the intensity of peak photoluminescence in argon and air show the relative amount of sites that are available to bind O\textsubscript{2} for it to scavenge electrons. This difference is highest between 600 to 700°C calcining temperatures. Presence of rutile in the sample results to inter-phase scavenging and decreases the efficiency of the sensor for samples calcined at 800 to 900 °C. Rutile is stable at larger dimensions and by limiting the sample thickness to approximately 150 nm, its formation can be suppressed. Thin film PL is stronger than nanoparticulate PL due to slower charge transport (dissipation) within the film as a result of the presence of grain boundaries.

Tungsten doping results in an overall decrease in the PL with increasing amount of dopant suggesting a decrease in the amount of oxygen vacancies while keeping the carriers required for O\textsubscript{2} dissociation. Nickel doping lowers the transformation temperature of anatase to rutile, resulting to a large percentage of rutile in the doped sample leading to its p-type sensor behavior.

**Supporting Information Available:** Photoluminescence and raman spectra of other samples and other conditions

44
Supporting Info:

Fig. S1. Raman spectra of TiO₂ undoped films as a function of calcination temperature. The inset shows the normalized 143 cm⁻¹ shift peak showing very little variation on the width.

Fig. S2. PL of the 2-layer films. The spectra on the left shows the PL when exposed to argon and the PL on the right was taken with the samples exposed in air.
Fig. S3. Raman spectra of tungsten and nickel-doped films calcined at 700°C and 900°C (left). PL spectrum of Ni-doped (right).
REFERENCES


CHAPTER 4

Location of Hole and Electron Traps on Nanocrystalline Anatase TiO$_2$

Attribution:

*The spectroscopy was done by the author; the samples were courtesy of Dr. Ichimura and Ms. Usmani from Department of Chemistry and Biochemistry, San Francisco State University, San Francisco, CA 94132. The Electron Backscattered Diffraction Analysis was done by Dr. Saraf.*


Abstract

The defect photoluminescence from TiO$_2$ nanoparticles in the anatase phase is reported for nanosheets which expose predominantly (001) surfaces, and compared to that from conventional anatase nanoparticles which expose mostly (101) surfaces. Also reported is the weak defect photoluminescence of TiO$_2$ nanotubes, which we find using electron back-scattered diffraction to consist of walls which expose (110) and (100) facets. The nanotubes exhibit photoluminescence that is blue-shifted and much weaker than that from conventional TiO$_2$ nanoparticles. Despite the preponderance of (001) surfaces in the nanosheet samples, they exhibit
photoluminescence similar to that of conventional nanoparticles. We assign the broad visible photoluminescence of anatase nanoparticles to two overlapping distributions: hole trap emission associated with oxygen vacancies on (101) exposed surfaces, which peaks in the green, and a broader emission extending into the red which results from electron traps on under-coordinated titanium atoms, which are prevalent on (001) facets. The results of this study suggest how morphology of TiO$_2$ nanoparticles could be optimized to control the distribution and activity of surface traps. Our results also shed light on the mechanism by which the TiCl$_4$ surface treatment heals traps on anatase and mixed-phase TiO$_2$ films, and reveals distinct differences in the trap-state distributions of TiO$_2$ nanoparticles and nanotubes. The molecular basis for electron and hole traps and their spatial separation on different facets is discussed.

4.1 Introduction

The spatial and energetic distribution of surface defects of nanocrystalline TiO$_2$ are of tremendous importance in applications such as solar energy conversion,$^{1,2}$ photocatalysis,$^{3,4,5}$ and sensing.$^6$ Photovoltaic and photoelectrochemical applications of nanocrystalline TiO$_2$ motivate a desire to understand and control the activity of surface traps, which may mediate carrier diffusion if they are shallow$^7$ or promote recombination into the electrolyte if they are deep.$^8$ Intra-band gap trap states also influence the photocatalytic properties of TiO$_2$. Reports$^9,10$ of facet-dependent photoredox reactions on shape-tailored TiO$_2$ nanoparticles have generated much interest in understanding the potential for spatial separation of photogenerated electrons and holes, which may in turn be related to the nature of traps on different exposed crystal planes. Though numerous electrochemical and spectroscopic studies have revealed aspects of the energetic distribution and density of surface traps of nanocrystalline TiO$_2$, $^{11,12,13}$ the molecular
nature of these traps has not yet been elucidated. Under-coordinated Ti$^{4+}$ and oxygen vacancies are often cited as likely sites for electrons to be trapped, while surface hydroxyls have been implicated as sites for trapping holes. In the present work, we examine the defect photoluminescence of shape-tailored and conventional nanoparticles of anatase-TiO$_2$ in order to explore surface trap-state distributions on different exposed crystal planes.

We have previously examined the broad visible defect photoluminescence (PL) of conventional nanocrystalline TiO$_2$ in nanoporous$^{14,15,16,17,18}$ and compact$^{19}$ films. Based on the influence of environment including electron and hole scavengers, we have resolved this PL into contributions from two distributions of traps:

\[
\text{Type 1: } e^{-}_{CB} + h^{+}_{e} \rightarrow h \nu_{\text{green}} \quad \text{(Scheme 1)}
\]

\[
\text{Type 2: } h^{-}_{VB} + e^{+}_{e} \rightarrow h \nu_{\text{red}} \quad \text{(Scheme 2)}
\]

where Type 1 and Type 2 PL refer to emission associated with hole and electron traps, respectively. Since each type of PL involves the recombination of trapped holes or electrons with oppositely charged mobile carriers in the conduction or valence band, respectively, the intensity of this emission increases with increasing density of trap states and diminishes with increasing efficiency of carrier transport. Electron traps dominate the emission spectrum of conventional anatase nanocrystals, which show a broad PL spanning the visible spectrum with a peak at about 650 nm, hereafter referred to as “red PL.” We have assigned this red PL to the radiative recombination of trapped electrons, about 0.7 to 1.6 eV below the conduction band edge, with valence band holes. In the presence of hole scavengers such as ethanol, this emission
is quenched leaving the Type 1 “green PL” characteristic of radiative recombination of mobile electrons (from the conduction band and shallow traps) with trapped holes. This emission peaks at about 540 nm and can be used to deduce a distribution of hole trap states about 0.7 to 1.4 eV above the valence band edge. In the widely-used two-phase P25 nanoparticles, which are about 80% anatase and 20% rutile, the red emission of electron traps is quenched and only the green PL is seen.\textsuperscript{14,15} The expected strong near-infrared emission of the rutile phase, associated with the (Type 1) radiative recombination of conduction band electrons with holes trapped at oxygen atoms on (100) and (110) facets,\textsuperscript{20} is also absent in P25. Both of these features of the P25 PL might be a consequence of electron transfer from the anatase to the rutile phase, as suggested by EPR experiments.\textsuperscript{21} We speculate that this interphasial carrier transport could be facilitated by adlineation of the anatase and rutile facets on which the relevant traps would reside in the pure phases. The enhancement of the green emission of anatase on vacuum annealing\textsuperscript{17} suggests that this PL is associated with oxygen vacancies, which are widely held to be responsible for the n-type intrinsic semiconductor behavior of undoped TiO\textsubscript{2}.\textsuperscript{22} The assignment of the red PL to electron traps associated with undercoordinated Ti\textsuperscript{+3} (when occupied) is consistent with spectroelectrochemical and EPR measurements which have located surface traps at energies about 0.5 to 1.0 eV below the conduction band.\textsuperscript{23,24,25,26}

![Anatase crystal structure](image)

**Fig. 4.1** Anatase crystal structure showing a) five-fold coordinate Ti on (001) plane and b) 5-fold and 6-fold Ti on (101) plane. c) Wulff construction of an anatase nanocrystallite.
The present work addresses the location of hole and electron traps on specific facets of anatase nanocrystals. Conventional TiO$_2$ nanoparticles prepared via sol-gel chemistry expose mostly the more stable (101) planes and to a lesser extent the higher energy (001) facets.$^{27,28}$ (Fig. 4.1) This is consistent with the Wulff construction for the crystal: a truncated octahedron in which the lower energy (101) facets make up more than 90% of the surface.$^{29,30}$ The (001) facets are more reactive and as shown in Fig. 4.1a, all Ti atoms on the ideal (001) surface are five-fold coordinated. On the other hand, half the Ti atoms on the (101) facets (Fig. 4.1b), are five-coordinate and half are six-coordinate. Recently, the preparation of TiO$_2$ nanocrystals rich in exposed (001) planes has been reported.$^{31,32}$ TiO$_2$ nanotubes prepared from the anodization of Ti metal,$^{33}$ on the other hand, are shown in the present work to have walls that expose (100) and (110) surfaces. By comparing the photoluminescence of nanosheet (NS) and nanotube (NT) films to that from conventional anatase nanoparticle (NP) films, we obtain evidence that green-emitting hole traps are favored on (101) surfaces while red-emitting electron traps are more prevalent on the (001) facets. In each case the response of the photoluminescence (PL) to electron scavenging oxygen and hole-scavenging ethanol provides insight into the molecular nature of electron and hole traps.

4.2 Experimental Section

Photoluminescence (PL) spectra for all samples were recorded at room temperature with 350 nm excitation using previously described instrumentation.$^{15}$ Typically laser powers at the front-illuminated sample films were 1 mW.
Conventional TiO$_2$ nanoparticles (NPs) in the anatase phase, nominally 20 nm in size, were purchased from Aldrich. NPs were dispersed in surfactant-free ethanol and subjected to prolonged stirring as described in Ref. 34. Films were then doctor-bladed onto quartz substrates which had been previously cleaned using Piranha treatment, a 1:2 mixture of 30% H$_2$O$_2$ and concentrated H$_2$SO$_4$. (Caution! Mixing these reagents is highly exothermic and the resulting solution should be handled with care.) The resulting films were sintered in air at 450 °C for 30 min. P25 nanoparticles, nominally 25 nm in size and consisting of approximately 80 % anatase and 20 % rutile, were a generous gift from Degussa. Films of P25 NPs were prepared in the same way as for anatase NPs.

The TiO$_2$ nanotubes (NTs) were grown by anodizing titanium in an electrolyte composed of 0.5% NH$_4$F, 2% water, and ethylene glycol, following the method of Grimes et al. Nanotubes for photoluminescence measurements were prepared by anodization at 40 V for 24h, resulting in nanotubes approximately 9 μm in length, with wall thicknesses of about 50 nm. Nanotubes for use in EBSD (vide infra) were prepared by anodization at 50 V for 72 hours resulting in tubes about 12 μm in length, with ~80 nm thick walls. The samples were then sintered at 450 °C for 3 hours. To investigate the effect of fluoride on nanotube PL, anodization was also performed in 0.1M aqueous perchloric acid at 10 V for 10 min, following Ref. 36. The PL data for NTs prepared in this fashion are shown in Supporting Information, while the data presented below are for NTs prepared following Ref. 35. Raman spectroscopy was used to confirm the anatase phase of the nanotubes, using excitation from a 413.1 nm line of a Kr$^+$ laser and a double monochromator with photomultiplier detector. The nanotube samples for photoluminescence were approximately 9 microns in length. NT sampled for EBSD
measurements were anodized in the NH$_4$F-based electrolyte for 72 hrs at 50 V to get thicker films. PL spectra of NT samples still attached to Ti substrate were recorded by illuminating the TiO$_2$ side of the as-prepared sample. PL spectra of detached but contiguous NT films attached to quartz substrate were also examined.

The crystallographic texture of the TiO$_2$ nanotubes was determined with electron back-scattered diffraction (EBSD), using a dual beam focused ion beam/scanning electron microscope (FIB-SEM). FEI Quanta 3D was utilized for EBSD and imaging analysis. The energy dispersive spectroscopy (EDS) elemental analysis of the samples was done using a detector from EDAX Instruments with Genesis software interface. The e-beam energy during EDS analysis was 30 kV at 4 nA. The EBSD analysis was performed using Orientation Imaging Microscopy (OIM) from EDAX/TSL and with the help of a Hikari high speed camera. During EBSD experiments, as shown below in Fig. 4.3, the TiO$_2$ nanotubes were aligned parallel to the substrate surface. The EBSD data collection was performed at speeds between 20-50 frames/second. To analyze inverse pole figure (IPF), grain misorientations and the band quality image from Kikuchi patterns, misorientation angle calculator and other analysis tools in OIM interface were used. The e-beam energy during EBSD measurements was 30 kV @ 23 nA. The Hough pattern setting for EBSD camera was set using a classic algorithm which uses a convolution mask to detect the peaks. The classic algorithm at low resolution uses a binned pattern. The convolution mask settings were 9 x 9 with minimum peak magnitude 5, minimum peak distance 15 and a peak symmetry setting of 0.5. The binned pattern size was 96 with theta step size of 2 degrees. The Rho fraction was considered 86% which means that bands from the outermost 14% area of the
circular EBSD camera were not considered in the calculations. The maximum and minimum peak count settings were 12 and 3, respectively.

TiO₂ nanosheets with enhanced {001} texture were prepared by immersing a gold or silicon substrate into the Teflon liner of a Parr acid digestion bomb containing 12 mL of 50 mM aqueous TiF₄. The gold substrate was prepared by first cleaning a silicon (100) wafer with RCA-1 solution for ten minutes, rinsing the wafer with deionized water and ethanol, and finally drying under a stream of argon. The silicon wafer was placed in a bell-jar and baked out for several hours until the pressure was 10⁻⁷ torr. Then, 5 nm of chromium and 200 nm of gold were deposited onto the wafer. The substrate was secured vertically in the Teflon liner and was completely immersed in the TiF₄ solution. The sealed Parr reactor was heated at a rate of 0.4 °C/min to 120 °C and held at temperature for four hours. The cooling rate was also 0.4 °C/min. After removal of the substrate from the bomb, the anatase film was rinsed with deionized water and dried at 60 °C overnight. To remove fluorine from the TiO₂ film surfaces and bulk, the anatase films were annealed at 600 °C for two hours in air. Annealed and unannealed anatase films were characterized by grazing angle X-ray diffraction (gXRD) using a Bruker D8 Advance diffractometer equipped with a Goebel mirror and thin film slit assembly. A Carl Zeiss Ultra 55 FESEM was used to acquire electron micrographs of the NS films. Removal of fluorine from the annealed nanosheet samples was confirmed using XPS spectroscopy with an AXIS-165 electron spectrometer (Kratos Analytical Inc., Manchester, UK) using the monochromatized Al Kα line at 1486 eV with a power of 195 W.

4.3 Results
Physical Characterization

Fig. 4.2 shows SEM images for the nanoparticle (NP), nanosheet (NS), and nanotube (NT) samples used in the present work. All TiO$_2$ samples (except for P25) were confirmed to be in the anatase phase as revealed by Raman spectroscopy and X-ray diffraction. The SEM image of the NPs (Fig. 4.2a) confirms the nominal ~20 nm particle size and reveals larger agglomerates obtained by sintering. The NS samples reveal (001) surfaces on the order of 400 nm in diameter. SEM images of the top view of the NT film (See Supporting information.) reveals inner and outer diameters on the order of 100 nm and 200 nm, respectively. In all cases, the thickness of the films exceeds the penetration depth of the incident light for the PL measurements, which is about 0.5 μm at a wavelength of 350 nm. Thus intensity differences reported below are not a consequence of different film thicknesses. SEM images of P25 films, top-view of NT films, and side-view of NS films are shown in supporting information. Though the conventional NPs used here are not large enough to infer the crystallographic texture from the SEM images, we assume the predominance of {101} surfaces as reported in the literature.$^{27-30}$

![SEM images of TiO$_2$](image)

Fig. 4.2 SEM images of TiO$_2$ a) nanoparticles, b) nanosheets, and c) nanotubes. The scale bar in each image is a) 200 nm, b) 400 nm, and c) 500 μm.
TiO$_2$ nanosheets present a unique opportunity to study the facet-dependence of photoluminescent surface traps because of the dominant \{001\} texture of the films. Anatase films prepared on gold substrates using a fluoride route yield highly oriented films that have the c-axis normal to the substrate.\(^3\) As shown in Figure 4.2b, the surface is characterized by \{001\} facets approximately 450 nm on a side. In the absence of fluoride in the synthesis solution, the majority facet is \{101\}. Grazing angle XRD, shown in Fig. S2 of Supporting Information, shows that the (004) and (105) diffraction peaks are the most intense in the NS sample while the (101) peak is weak and others such as (112), (200), (211), (213), and (220), which are typically present in the powder pattern, are notably absent. The edge view of the film shows that it is 1.08 \(\mu\)m thick and composed of grains that extend from the gold substrate growing larger as they reach the external surface. After annealing, the overall morphology of the anatase grains does not change but changes in the Raman spectra on annealing (see Supporting information, Fig. S3) suggest enhanced crystallinity of the NSs. As particles coarsen during annealing, the crystallites grow in random directions due to loss of fluorine, the crystallographic controlling agent, resulting in a larger powder component to the gXRD. The \{001\} texture persists, however, and SEM images show that there is no change in the film thickness or grain size after annealing.

Fig. 4.3 (a-e) shows the EBSD analysis of horizontally aligned TiO$_2$ NTs annealed at 450 °C for 3 hrs. The sample analysis was difficult due to uneven nanocrystalline surfaces that created challenges to satisfy the EBSD angle requirement. Existence of amorphous overlayers also affected the quality of band indexing. Due to the narrow width (less than 100 nm) of TiO$_2$ NTs, the e-beam scan step size for EBSD measurement was maintained at 20 nm. The determination of orientation was performed on those areas that have continuous similar
orientation (for example, the blue region that is circled in Fig. 4.3a) along the nanotube length for more than 200-300 nm. The quality and accuracy of the measured backscattered diffraction patterns (confidence index) was calculated using automated indexing of the diffraction patterns.\textsuperscript{38,39} For any given diffraction pattern, there could be several possible indexing solutions and orientations.

Fig. 4.3 EBSD of TiO\textsubscript{2} nanotubes. (a) Top view SEM image of horizontally aligned and 70\textdegree tilted (for EBSD measurements) TiO\textsubscript{2} nanotubes. Colored image on top is an IPF orientation map collected from the same region. The marked region represents (110) orientation. (b) Schematic representation of Kikuchi bands collection from horizontally aligned TiO\textsubscript{2} nanotube. (c) TiO\textsubscript{2} crystal view and (001) pole figure representing TiO\textsubscript{2} surface from the marked region in (a). (d) & (e) (110) orientation bands detected using EBSD camera from the marked region in (a) and an overlap of standard (110) anatase TiO\textsubscript{2} orientation bands matching with detected bands proving (110) orientation.
A ranking system is developed using a voting mechanism, accuracy = \( \frac{V_1 - V_2}{V_{\text{ideal}}} \) where \( V_1 \) and \( V_2 \) are the number of votes for the first and second index solutions and \( V_{\text{ideal}} \) is the total possible number of votes from the detected bands. Fig. 4.3a shows the inverse pole figure (IPF) map generated from the marked section shown in SEM image. IPF in EBSD provides information about orientation of a particular grain or crystal direction with respect to the reference frame of that crystal. The (110) orientations were confirmed along the nanotube walls, as indicated in the circled region in Fig. 4.3a. There is also some indication of (100) texture (the green spots in Fig. 4.3) but there is less continuity of this region compared to the (110) orientations. The schematic in Fig. 4.3b is shown for visualization purposes indicating that the measurements were performed along the length of the nanotubes. Fig. 4.3d indicates the anatase crystal alignment from the detected area with pole figure measured along 001. Figs. 4.3d and e show as recorded EBSD Kikuchi diffraction bands from the marked area. The solution indexing confirmed the structure and orientation.

Photoluminescence Emission Spectra

Fig. 4.4 compares the PL from an annealed nanosheet sample (NS) to that from nanoparticle (NP) and P25 films, normalized to the same peak intensity, recorded in argon and excited at 350 nm. As previously reported, the P25 film gives a maximum at 530 nm compared to about 600 nm for the anatase NP film.\(^ {14,15} \) The apparent structure in the NS film is the result of optical diffraction by the thin film sample. The overall envelope of the emission spectrum of the NS sample, with a peak in the vicinity of 600 nm, overlaps well with the spectrum of anatase NPs, despite the much smaller proportion of (001) surfaces in the NP sample.
Fig. 4.5 shows the PL spectrum of the NS sample before and after annealing to remove fluorine. While the normalized spectra of the two samples are similar, repeat measurements for three different NS samples always showed greater PL intensity for the annealed compared to the unannealed samples when the spectra are recorded in argon. As confirmed by XPS measurements in this study (see Fig. S4 of Supporting Information), annealing removes the fluoride ions which stabilize the (001) surface through coordination to Ti,\textsuperscript{31} thus the results of Fig. 4.5 strongly suggest that the electron traps associated with red PL result from under-coordinated Ti. In the case of the as-prepared (fluorinated) sample, there is little effect of air on the intensity of the PL. This is in strong contrast to the PL from nanoporous films of conventional anatase NPs,\textsuperscript{14,15} for which the PL is almost completely quenched in air. In contrast, after annealing to remove fluorine, the PL intensity in air is only half as intense as that recorded.
in argon. Thus removal of the surface fluorine results in NS samples for which oxygen is capable of quenching the defect PL but to a much lesser extent than in the case of conventional NPs.

![Graph showing PL from annealed and as-prepared NS samples.](image.png)

**Fig. 4.5** PL from annealed (green and blue) and as-prepared (black and red) NS samples, excited at 350 nm. The green and black traces are the spectra recorded in argon, and the blue and red traces are spectra recorded in air. The spike at ~700 nm is an artifact from the excitation laser.

Fig. 4.6a compares the PL from TiO₂ NTs to that from P25 and anatase NPs. Notably, the intensity of PL from a film of conventional NPs is about four times as large as that from the NT sample. The peak in the NT emission spectrum, at 554 nm, is blue shifted from the peak observed at 608 nm for the NP sample, while the peak in the P25 spectrum is observed at 530 nm. As shown in Fig. 4.6b, air has only a slight quenching effect on the PL from the NT sample, in contrast to its strong quenching effect on the PL from P25 and NP films.¹⁵ The wavelength range of the PL spectrum of the NTs is intermediate between that of the NPs and P25, with a
peak in the green yet intensity in the red region as well.  As we have previously shown, the PL from both NT\textsuperscript{16} and NP\textsuperscript{17} samples shifts to the blue after vacuum annealing, becoming more similar to that of P25. This observation might suggest that the hole traps associated with green PL are from oxygen vacancies. However, as considered further below, it should be kept in mind that vacuum annealing increases the concentration of conduction band electrons, which according to Scheme (1) are responsible for the green PL.

Transport and PL intensity are closely linked because radiative recombination can only take place when there is spatial overlap of the mobile and trapped charges. Thus improved transport resulting from, for example, enhanced particle necking in sintered films\textsuperscript{15} results in decreased intensity of defect PL. Though the carrier transport times of TiO\textsubscript{2} NTs have been reported to be

![Fig. 4.6 a) PL of TiO\textsubscript{2} nanotubes (NT) compared to a film of nanoparticles (NP) and P25, all recorded in argon. b) Comparison of NT PL in argon and in air.](image)
comparable to those in NPs, recombination rates are slower for nanotubes.\textsuperscript{40,41,42} Since the NT PL data in Fig. 4.6 were measured on a Ti foil substrate as opposed to a quartz substrate for the NP PL measurement, we considered the possibility that electrons created in the nanotubes could be driven to the metal substrate owing to its lower Fermi level. As shown in Supporting Information (Fig. S5) however, the PL intensity of contiguous, detached NT films is similar to that of the same film on Ti foil, indicating that transport along the length of the NTs does not significantly reduce radiative recombination. NTs were also obtained by anodization of Ti foil in a fluoride-free electrolyte following Ref. 36, resulting in similar PL spectra to that from the NTs prepared in electrolyte containing NH$_4$F, as shown in Fig. S5 of Supporting Information.

![Graph](image)

Fig. 4.7 Effect of ethanol (EtOH) on the PL emission of as-prepared and annealed nanosheets. The sharp peaks above ~700 nm are unfiltered plasma lines from the 350 nm excitation laser.

The shape of the NT PL from samples prepared in fluoride-free electrolyte is somewhat different from that seen in the conventional NT preparations, probably owing to differences in
morphology as reported in Ref. 36 and confirmed in our work. Nevertheless, the intensity difference in the two samples is no larger than sample-to-sample variations, revealing that lower PL intensity of NTs compared to NPs is not the result of by passivation of luminescent defects by fluoride.

Fig. 4.7 illustrates the effect of ethanol (EtOH) on the PL of the annealed and unannealed NS samples, compared to the same samples in air and argon. For reference, we have previously seen that the PL from anatase NPs in the presence EtOH is increased and blue-shifted relative to the same sample in argon or other non-hole scavenging environment,\textsuperscript{15} adopting a shape virtually identical to that of the P25 PL spectrum. Though unavoidable interference peaks seen in Fig. 4.7 distort the envelope of NS spectrum, it is still clear that EtOH causes a blue-shift similar to what is observed for NPs. However, there is no increase in intensity.

4.4 Discussion

The data presented above strongly suggest that under-coordinated Ti, which are more prevalent on the (001) surface than on (101) surfaces, are responsible for the red PL associated with recombination of trapped electrons with valence band holes. Despite the large contribution of (101) surfaces to conventional nanoparticles, the PL of NP films is very similar to that from nanosheets which expose a great deal of (001) texture. There is much experimental and theoretical evidence\textsuperscript{43,44} that O\textsubscript{2} adsorbs to under-coordinated Ti on reduced TiO\textsubscript{2}, which then transfers an electron to produce superoxide anion:

\[
\text{Ti}_{5c}^{3+} \cdots \text{O}_2 \rightarrow \text{Ti}_{5c}^{4+} \cdots \text{O}_2^- \quad \text{(Scheme 3)}
\]
In the present work, we propose that band-gap illumination of TiO$_2$ NPs and NSs results in trapped electrons which reduce five-fold coordinated surface Ti from the +4 to the +3 oxidation state. The recombination of these trapped electrons with valence band holes gives rise to the broad “red PL” observed in the absence of oxygen (Scheme 2). The reported Fermi level of $E_F = 2.4$ eV for stoichiometric TiO$_2$ does not preclude the presence of occupied electron traps in the dark, which then recombine with valence band holes created by UV illumination. Based on the assumption that the broad red PL of anatase NPs represents a range of vertical transition energies, we have derived electron trap depths of 0.7 to 1.6 eV that are in good agreement with other estimates. However, we need to understand why oxygen quenching is much less significant for the NS than the NP samples, and why EtOH affects the two samples differently.

The increase in nanosheet PL and increased quenching by O$_2$ on removal of fluorine supports the conclusion that the broad red PL arises from under-coordinated Ti atoms. As in the present work, fluoride is employed in the synthesis of nanosheets for its ability to stabilize the (001) facet through coordination to five-coordinate Ti. Surface binding of fluorine to anatase TiO$_2$ is reported to convert Ti$^{3+}$ to Ti$^{4+}$, hence, when fluorine is removed on annealing, more trapped electrons are available and PL increases. At the same time, more binding sites for O$_2$ are made available, permitting PL quenching according to Scheme 3, albeit less than for conventional NPs.

In previous work, we showed that the PL of anatase NPs is almost completely quenched by oxygen, and that in contact with EtOH an enhanced green PL similar to that of P25 is observed. The conversion of anatase PL from predominantly red (Type 2) to green (Type 1) after vacuum annealing strongly suggests that oxygen vacancies play a role in the green PL.
Surface and sub-surface oxygen vacancies have been shown to influence substrate binding on anatase (101) surfaces.\textsuperscript{48,49,50,51} and oxygen vacancies are widely held to be sites for $O_2$ adsorption.\textsuperscript{52,53} Recent work shows that the (101) facets of anatase are quite reactive to $O_2$,\textsuperscript{54} a feature which is explainable in light of greater density of oxygen vacancy defects on the (101) surface than on (001).\textsuperscript{55,56} Thus, increased adsorption of $O_2$ on the abundant (101) surfaces of NPs compared to the NSs serves to enhance the ability of oxygen to scavenge conduction band electrons from the NPs. Apparently the well-known hole-scavenging ability of EtOH results in quenching of the red-emitting electron traps of both NP and NS samples. To explain the increased intensity of green PL for NPs but not for NSs in the presence of EtOH, we propose that this intensity increase is a reasonable result of the well-known tendency of photooxidized alcohols to undergo further oxidation by injecting electrons into the conduction band (CB),\textsuperscript{57,58} favoring Type 1 PL (Scheme 1). This electron injection should be favored when EtOH is adsorbed on the surface. In the case of conventional NPs, dilute solutions of EtOH in non-hole scavenging (acetonitrile) environment are capable of causing the transition from red to green PL, suggesting preferential adsorption of the alcohol.\textsuperscript{15} Adsorption of alcohols at oxygen vacancies on bulk rutile TiO$_2$ is well-known.\textsuperscript{59} The present results would be explained if EtOH adsorbs preferentially on anatase (101) rather than (001). Indeed, in previous work using natural bulk anatase samples,\textsuperscript{17} we found no effect of EtOH on the PL when the (001) facet of the crystal was illuminated, and a quenching effect for PL from the (101) facet.\textsuperscript{60} If the hole traps associated with Type 1 PL are isolated on the (101) facets, this too would contribute to the different effect of EtOH on NP and NS PL. In either case, when scavenging of valence band holes by EtOH quenches red PL, radiative recombination of CB electrons with trapped holes dominates the emission causing a blue shift in the spectrum. However, the greater abundance of (101) facets
for the NP samples then translates into more intense green PL than from NS samples when both are in contact with EtOH.

We favor associating the green PL with hole traps on (101) facets. The electron traps (red PL) on the other hand, might be present on both (101) and (001) facets because both contain five-fold coordinated Ti. However, we tentatively propose that electron traps are sequestered on the (001) facets of the conventional NPs. Supporting these claims, we note the absence of red PL from P25. The structure of these mixed-phase nanoparticles is controversial, and conflicting HR-TEM measurements report both predominant (001) and (101)/(100) exposed surfaces. Conflicting reports of P25 nanoparticle morphology could be the result of its heterogeneity, nevertheless, our PL studies reveal that P25 is not a mere mixture of separate anatase and rutile NPs; i.e., both phases are present within the same nanoparticle. The mutual quenching of anatase red PL and rutile near-IR PL has led us to propose that the red-emitting traps on anatase are covered by the rutile phase. Theory suggests that stable anatase-rutile interfaces are those that complete the Ti coordination sphere. In light of the present results and considering the higher surface energy of the (001) compared to (101) surface, we propose that the (001) anatase surface is not exposed in P25 NPs. The present results are consistent with spatial isolation of electron and hole traps on (001) and (101) surfaces, respectively.

Another question is the chemical nature of the green-emitting hole traps. Increase in intensity of green PL on vacuum annealing could result from participation of oxygen vacancies as hole traps or from the increased availability of mobile electrons recombining with some other kind of hole trap. The prevailing notion in the literature is that surface hydroxyl groups, Ti-OH, trap holes to produce hydroxyl radicals. Exposure of TiO₂ to aqueous NaOH is sufficient to
result in a hydroxylated surface. In separate studies of anatase NP films in contact with aqueous media, we find no effect of solution pH on the intensity of green traps. Thus we propose that oxygen vacancies, more prevalent on (101) than (001) surfaces, give rise to luminescent hole traps which our PL studies place about 0.7 to 1.4 eV above the valence band edge. Removal of a bridging oxygen atom leaves behind two electrons which can reduce two neighboring two Ti$^{4+}$ to Ti$^{3+}$. The latter could then trap holes created by UV illumination. Alternatively, electrons trapped at oxygen vacancies (F-centers) could give rise to the green-emitting hole traps. The existence of deep traps associated with oxygen vacancies might seem to conflict with the well-known intrinsic n-type semiconductor property of TiO$_2$ which is widely held to result from these defects. While oxygen vacancies are favorable to majority carrier transport, at the same time they have been shown to be detrimental to the performance of dye-sensitized solar cells, leading to deep traps that inhibit transport. The removal of an oxygen atom from the TiO$_2$ lattice can lead to a variety of singlet and triplet states. Di Valentin et al. used density functional theory to show that one of these states may be a relatively deep trap level while the other is a delocalized state that accounts for the enhanced conductivity of n-type TiO$_2$. Thus, oxygen vacancies may be associated with both shallow and deep traps. Our results suggest that oxygen vacancies on (101) surfaces give rise to hole traps associated with green PL.

With these conclusions, we can revisit our earlier work on the effect of TiCl$_4$ treatment on the green and red emission. In an ideal (001) plane, all the Ti sites are five-coordinate. The failure of TiCl$_4$ treatment to remove red-emitting traps is thus readily understood, since fresh deposition of TiO$_2$ can’t affect traps associated with these “normal” Ti sites. In contrast, the TiCl$_4$ treatment eliminates green-emitting hole traps in both P25 and conventional anatase NP.
This is in accord with the conclusion that the green emission comes from oxygen vacancies, or from Ti$^{3+}$ associated with neighboring oxygen vacancies which can be healed by fresh deposition of TiO$_2$. The breadth of this PL is likely associated with the presence of a heterogeneous distribution of Ti$^{3+}$ sites as has been suggested for example by theory, EPR spectroscopy, and spectroelectrochemistry. In our model, the Type 2 recombination is analogous to a Ti(3d) $\rightarrow$ O(2p) charge transfer transition, and homogeneous broadening from a phonon progression of Ti-O stretching modes could conceivably contribute to the spectral width.

While the present results support our hypothesis that electron and hole traps are sequestered on different crystal planes, the conclusion that electron traps are found on the (001) surfaces and holes traps on (101) is opposite to our previous conjecture. Some reports of facet-dependent photocatalysis provide support for our present model. For example, oxidative decomposition of organic compounds is shown to be more efficient on anatase (101) than on the (001) surfaces, while the latter are more effective for H$_2$ production. However, it must be cautioned that our results only relate to luminescent traps, and in addition interfacial redox chemistry may involve free rather than trapped charges. Murakami et al., for example, found the products of photooxidation and photoreduction to be respectively deposited on the (001) and (101) surfaces of anatase nanocrystals. The reported facet-dependence of the UV-induced hydphilicity of TiO$_2$ surfaces, which has been interpreted in terms of more facile removal of bridging oxygens on (101) than (001) surfaces, provides support for our present conclusions.

Finally, we consider the nature of the PL observed from TiO$_2$ nanotubes, which is found in this work to be intermediate between the red and green PL typical of NPs and P25,
respectively. Though it’s been stated that the walls of the NTs consist of (101) surfaces,\textsuperscript{40} we find using EBSD in the present work that the nanotube walls expose (110) and possibly (100) facets. The (110) surface is not prevalent in conventional anatase NPs but has been observed in a few preparations.\textsuperscript{78,79} For an equilibrated crystal the formation energy of the (100) surface is just slightly higher than that of the (101) surface, while formation of the (110) surface requires still higher energy.\textsuperscript{80} DFT calculations showed that (100)-walled nanometer-size nanowires are the most stable for anatase, while a combination of (110) and (100) walls were less stable.\textsuperscript{81} Both (110) and (100) facets would, in the ideal case, contain highly reactive four-coordinate Ti, thus they are likely to undergo significant reconstruction. The lack of quenching of NT PL by air, in accord with results for NSs, results from a scarcity of oxygen vacancies which bind O\textsubscript{2}. While there is insufficient data at present to characterize the chemical nature of luminescent defects of TiO\textsubscript{2} NTs, we can draw tentative conclusions about the basis for reduced PL intensity in NTs compared to NPs. (Fig. 4.6). This could arise from two inter-related effects: improved transport and decreased density of oxygen vacancies. Given that transport times are reported to be no shorter in NTs than in NPs, the present data suggest fewer oxygen vacancies in the nanotubes, though there is the possibility that inter-tube electron transport provides a quenching mechanism in contiguous films. A reduced defect density in NTs compared to NPs would account for the observation that recombination into the electrolyte is reduced in NT-based dye-sensitized solar cells. Differences in the defect distributions of anatase NTs and NPs have been previously surmised based on their performance in dye-sensitized solar cells.\textsuperscript{41} Such differences are, in this work, proposed to be the result of different distribution of exposed planes.

4.5 Conclusions
In summary, examination of the photoluminescence of TiO$_2$ nanosheets and nanotubes provides evidence that hole traps are located on (101) planes and derive from oxygen vacancies, while electron traps arising from under-coordinated Ti are preferentially located on the (001) planes but may also reside on the majority (101) surfaces. Knowledge of the spatial location and molecular nature of these traps will provide a basis for shape-tailoring and surface modification of TiO$_2$ nanoparticles for a particular application.

4.6 Acknowledgments

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Supporting Information Available: SEM images of P25, side view of nanosheets, top view of nanotubes (Fig. S1), Grazing-angle X-ray diffraction pattern of nanosheets (Fig. S2), Raman spectra of nanosheets (Fig. S3), XPS spectra of nanosheets (Fig. S4), and PL of detached nanotubes and of nanotubes prepared in perchlorate electrolyte (Fig. S5). This information is available free of charge via the Internet at http://pubs.acs.org.

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**Supporting Information:**

Fig. S1 SEM images of a) P25 b) side view of nanosheets, after annealing c) top view of nanotube films. The scale bar is 200 nm in a) and 400 nm in b) and c).

Fig. S2 Grazing angle x-ray diffraction pattern of anatase nanosheet films (a) before and (b) after annealing at 600 °C for two hours. The * indicate diffraction peaks from the gold substrate.
Fig. S3 Raman spectrum of the ~142 cm⁻¹ anatase line, excited at 413 nm, of two nanosheet samples before annealing (red and blue), and after annealing (magenta and black), compared to the Raman spectrum of conventional anatase nanoparticles (green).

Fig. S4 XPS spectra in the F 1s region of two nanosheet samples before (a and b) and after (c and d) annealing.
Fig. S5 a) PL of TiO$_2$ nanotubes on Ti substrate (black) and detached (red). b) PL of TiO$_2$ nanotubes prepared by anodization in perchlorate electrolyte (red) and ammonium fluoride electrolyte.
REFERENCES


60. Note that in this study, the mineral anatase samples were lightly colored and probably highly doped. Therefore, they showed green PL from all facets owing to abundant extrinsic donor defects.


67. Knorr, F. J.; McHale, J. L. to be submitted.


CHAPTER 5

Observation of Charge Transport in Single Titanium Dioxide Nanotubes by Micro-Photoluminescence Imaging and Spectroscopy

Attribution:

The spectroscopy and experimentation was done by the author. The micro-photoluminescence set-up was built by Dr. Knorr.

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Abstract

In this work, we present the first report of photoluminescence spectra and images of single TiO$_2$ (anatase) nanotubes. In previous work using ensembles of conventional TiO$_2$ nanoparticles, we interpreted the broad photoluminescence (PL) spectrum to be a superposition of hole trap emission, peaking in the green, and broad red PL arising from electron traps. Photoluminescence spectra of individual nanotubes in inert environment show a similar broad emission, with peaks at around 560 to 610 nm. The PL from single nanotubes, however, differs from the more blue-shifted PL of ordered nanotube films. The intensity of PL is found to be larger for single nanotubes than for ordered arrays, as a result of competition from transport in the contiguous samples and from introduction of additional trap states when the nanotubes are dispersed. PL images of single nanotubes show the emission to be concentrated in the area of excitation, but
the peaks in the red and green components of the PL are not spatially coincident. Remote PL, occurring away from the excitation point, is observed in the green (~510 nm), showing the possible contribution of charge transport to the observed PL. While the PL from ensembles of TiO₂ nanotubes is fairly insensitive to contacting media, exposure of single nanotubes to air and ethanol changes the shape and intensity of the PL spectrum. Our results point to a very different trap state distribution in TiO₂ nanotubes compared to that of conventional TiO₂ nanoparticles, which we attribute to differences in exposed crystal facets. In addition, separation of nanotubes introduces additional photoluminescent trap states and changes the character of the emission from excitonic in the array to trap-mediated in single nanotubes.

KEYWORDS: TiO₂ nanotubes, single nanoparticle spectroscopy, trap states, transport

Surface defects strongly influence macroscopic properties and device performance in applications of TiO₂ nanoparticles. For example, intra-band gap states resulting from defects play an important role in carrier recombination and transport in TiO₂-based dye-sensitized solar cells (DSSCs). While inefficient interparticle electron transfer hinders charge collection in conventional nanoporous TiO₂, it was expected that the ordered structure of TiO₂ nanotube films would result in faster transport. However, measurements showed that transport in nanotube-based devices is not significantly faster than that in films containing conventional TiO₂ nanoparticles, although recombination rates are lower in the former. It has been suggested that differences in trap-state distributions result in more efficient charge collection in TiO₂ nanotubes than in conventional TiO₂ nanoparticles, and that excitonic states limit transport in nanotubes. Transport in nano-TiO₂ occurs by diffusion mediated by shallow traps, while deep traps promote deleterious recombination. Additional factors that may influence transport are local electric
fields, solvent environment, particle interconnectedness, and, in the case of nanotubes, the morphology of the ordered films. Trapping and detrapping events may be the major contributors to lower mobility in nano-TiO₂ compared to the bulk material, and it is therefore of great interest to understand how trap states of conventional TiO₂ nanoparticles may differ from those of TiO₂ nanotubes.

We have previously used photoluminescence (PL) spectroscopy of nanocrystalline TiO₂ films to explore the dependence of trap-state emission on contacting solvent, surface treatment and crystalline phase, sintering, and nanoparticle morphology. Based on these studies we have formulated a model for the visible trap state emission of anatase TiO₂, which we assign to the radiative recombination of spatially isolated trapped electrons and holes with mobile carriers in the valence or conduction band, respectively. Recombination of mobile electrons with trapped holes results in emission that peaks in the green (~530 nm), while the recombination of trapped electrons with valence band holes leads to a broader PL spectrum with a peak in the red (~600 nm). We hypothesize, based on results summarized in Ref. 20, that trapped holes are isolated on the (101) surfaces of conventional anatase nanoparticles while electron traps associated with undercoordinated Ti⁴⁺/³⁺ on the (001) planes are responsible for the PL that peaks in the red. In conventional TiO₂ nanoparticles (NPs), the (101) surfaces make up the majority of the surface, with the more reactive (001) surfaces contributing about 10 %. In the case of ordered anatase titanium dioxide nanotubes (NTs), the emission is centered at 550 nm and is much less intense and less responsive to environment than the PL of NP films. Since radiative recombination of trapped and mobile carriers depends on their spatial overlap, the intensity of trap state PL diminishes when transport is faster. Thus the weaker intensity of PL from TiO₂ NTs compared to
NPs could result from a lower density of intraband-gap states and/or from improved transport. In addition, we have found\(^{20}\) that the walls of the NTs expose (110) and (100) facets, which are not prevalent in conventional NPs. Hence different distributions of exposed surfaces could be tied to different trap state distributions and different PL spectra.

Hindering any study of surface trap states in nano-TiO\(_2\) is the heterogeneity of the particles and their surfaces. Single nanoparticle luminescence addresses this problem by obtaining PL spectra of individual nanoparticles or small aggregates thereof. A few previous single nanoparticle PL studies of TiO\(_2\) have been reported. Tachikawa \textit{et al.} reported PL spectra and images of single nanowires of TiO\(_2\)-B\(^{23}\) and of Eu\(^{3+}\)-doped TiO\(_2\) nanoparticles,\(^{24}\) while Jeon \textit{et al.} reported PL blinking dynamics of single TiO\(_2\) nanodisks.\(^{25}\) In this work, we present the first report of PL spectra and images of individual TiO\(_2\) nanotubes and address the nature of their trap states as compared to those of conventional TiO\(_2\) nanoparticles as well as nanotube arrays.

**RESULTS AND DISCUSSION**

\textit{SEM images}

Fig. 5.1 SEM images of dispersed TiO\(_2\) nanotubes spin-coated onto a quartz cover slip a) single NT and fragments b) nanotube array fragment
Fig. 5.1 shows SEM images of the nanotubes. Ultrasonic dispersion of nanotube (NT) arrays resulted in single NTs and fragments shorter than the original thickness of the NT array (Fig. 5.1a), and fragments of the NT array (Figs. 5.1b and 5.1c). Fig. 5.1b shows the top view of a fragment of the NT array revealing the perpendicular alignment of the tubes on the quartz substrate, while the single NT images shown below will be for NTs with their long axes parallel to the surface. The lengths of the single NTs analyzed were from 1 to 5 µm, while the original NT length in the ordered arrays was 10 µm. The nanotubes have external diameters ranging from 150 to 170 nm and wall thicknesses around 18 nm. In what follows, we will refer to arrays such as that shown in Fig. 5.1b and c as “array fragments” to distinguish them from the contiguous NT arrays prepared on Ti substrate. TEM images of separated NTs, shown in Fig. S1 of Supporting Information, reveal that the surfaces of the dispersed tubes are littered by broken fragments of nanotubes, mainly due to the TEM sample preparation where a drop of the suspension is allowed to dry on the copper grid. However, as will be shown below, the PL from the smaller fragments does not appear to be fundamentally different from that of more intact NTs.

Raman Spectra

As shown in Fig. 5.2, Raman spectroscopy confirms that the TiO$_2$ NTs are in the anatase phase, in agreement with the XRD results shown in Fig. S1 of Supporting Information. Fig. 5.2 compares the Raman spectrum of an isolated NT (or perhaps a small bundle) to that of a fragment of the NT array and a cluster of anatase TiO$_2$ NPs. The relative intensities of the $A_{1g}$ (399 cm$^{-1}$), $B_{1g}$ (519 cm$^{-1}$) and $E_g$ (639 cm$^{-1}$) peaks are similar for the single NT and NT array fragment, but the absolute intensities are of course smaller for the single NT. The relative
intensities of these three peaks are different for nanotube (NT) and conventional nanoparticle (NP) samples owing to differences in nanoparticle morphology.

![Raman scattering spectra](image)

**Fig. 5.2** Raman scattering spectra excited at 413.1 nm of a NT array fragment, a single NT (SNT), and anatase NP clusters. Optical images are shown on the right.

_Photoluminescence Spectra_

Fig. 5.3 shows the micro-PL spectrum of a single NT (SNT) compared to that of a contiguous NT array (NTA) and a cluster of dispersed NPs as a function of excitation power. The corresponding (representative) SEM images of the three samples are also shown. In obtaining micro-PL spectra of films and isolated particles, the power density is of interest because, as shown in Supporting Information (Fig. S2), higher powers can change the shape of the PL spectrum. For conventional anatase NPs, a blue-shifted spectrum at higher power densities results from increased contribution from the radiative recombination of mobile
electrons with trapped holes. The similar normalized spectral lineshapes in Fig. 5.3 show that the spectra are not being perturbed by high power densities of the microscope. The lineshapes of the three different samples are clearly different. The micro-PL spectrum of a fragment of the NP film (Fig. 5.3c) is identical to our previously reported spectra of both mesoporous\textsuperscript{17,18} and dense\textsuperscript{26} anatase NP films, while the emission spectrum of the NTA is narrower and blue-shifted relative to that of the NPs. The emission spectrum of the SNT, however, is intermediate between the two and shows enhanced emission in the red relative to the NTA. Though all three samples in Fig. 5.3 show a broad range of emission wavelengths, both isolated and clustered nanotubes show PL spectra for which the peak is blue-shifted relative to the PL spectrum of NPs. In addition, there is a decreased width of the PL spectrum of the NT array compared to the spectrum of an isolated NT.

Fig. 5.3 SEM images and normalized micro-PL spectra of a) a contiguous NT array b) a single NT and c) a film of anatase NPs, as a function of laser power.
Fig. 5.4 compares the peak PL intensity of single NTs, a contiguous NT array, and a NP film as a function of incident laser power. As previously reported, the PL of the NTA is less intense than that of a NP film. However, it is significant that the PL intensity of the SNT is greater than that of a NTA. This is especially striking since the penetration depth of the incident light, about 0.5 µm based on the absorption coefficient at 350 nm from Ref. 27, is larger than the outer diameter of the NTs but smaller than the lengths of the ordered NTs. Thus the incident light excites a much greater sample volume in the case of the ordered array. This hints at the importance of transport in limiting the PL intensity. However, the electric field vector of the incident laser is oriented differently in the two samples, being coplanar with the long axis of the single NTs and perpendicular to the long axes of the ordered NT arrays. The polarization of the laser could select a different distribution of trap state emissions for NTs which are parallel versus perpendicular to the substrate. To check for this possibility, ensemble PL spectra of the as-prepared NT array were excited using a near-backscattering (~135°) geometry, and both vertically and horizontally polarized incident light. As shown in Fig. S3 of supporting information, there is no difference in the PL spectra for these two experiments; thus, the difference in the spectra of single NTs and NT arrays is not a consequence of the different alignments of the tubes relative to the incident electric field vector. Alternatively, the interparticle connections in the NT arrays could passivate a subset of more red-emitting traps, or permit interparticle transport that competes with the radiative recombination from these traps. The higher PL intensity of a single NT compared to a NT array, while surprising at first, may be a consequence of the higher probability of radiative recombination of trapped and mobile carriers when the nascent electron-hole pairs are confined to a smaller sample volume. In addition, the enhanced emission in smaller nanoparticles could result from diminished competition from...
nonradiative relaxation channels, since the rate of PL quenching by electron or energy transfer decreases in confined geometries.\textsuperscript{28}

Closer examination of the slopes of the plots in Fig. 5.4 provides more insight into the nature of the emission in the different samples. In general, the intensity of photoluminescence \( I_{PL} \) is proportional to \( P^k \), where \( P \) is the incident power and \( k \) is an exponent that can reveal the nature of the radiative recombination.\textsuperscript{29} For the case of single NTs and conventional NPs, slopes close to unity (\( k = 1.15 \pm 0.7 \) for NPs and 1.13 \( \pm 0.9 \) for the SNT) were observed in the log-log plots of Fig. 5.4, decreasing slightly at higher powers. This behavior is consistent with

![Fig. 5.4 Dependence of peak PL intensity on incident laser power for an anatase NP film (triangles), a single NT (circle) and a contiguous NT array (black square). The red line is a least squares fit.](image)

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recombination of mobile and trapped carriers, in accord with our previous model for the green and red PL components of conventional anatase NPs. For the contiguous NT array, however, we find $k = 1.42 \pm 0.06$. As discussed in Ref. 29, this is suggestive of a donor- or acceptor-bound excitonic transition. As will be considered further below, this indicates that separation of NTs changes the nature of their luminescent trap states.

![Fig. 5.5 Peak intensity of single NT PL as a function of NT length.](image)

Further consideration of the role of sample size is given in Fig. 5.5, which reveals a weak trend toward decreased intensity of emission with increase in NT length. We interpret this to result from increasing competition from nonradiative recombination in longer NTs. The geminate electron hole pairs created in the illuminated volume diffuse away from the laser spot at different rates owing to different electron and hole mobilities. Smaller particle sizes increase the chance that trapped and mobile carriers will overlap spatially and undergo radiative
recombination. The scattered nature of the data in Fig. 5.5 might result from our inability to distinguish bundles of NTs from single NTs in optical microscopy; hence there may be intensity variations that result from probing different numbers of NTs.

Fig. 5.6 shows PL images of dispersed NTs under epi-illumination and with various filters. The images obtained with the 510 nm bandpass filter are brighter than those obtained with longer wavelength light. The corresponding line profiles show that bright and dark areas of the NT are similar for the 510 nm filtered PL and unfiltered PL images. The PL intensity is

Fig. 5.6 Photoluminescence of a SNT under epi-illumination with 20 mW of 350.7 nm laser a) without a filter, b) with the 510 nm bandpass filter, c) with the 610 nm longpass filter, d) SEM image of the same area. The corresponding line scans on the right show the intensity along the white line in the PL image (black lines) compared to the background (red dotted lines).
distributed along the entire length of the tube and there is no evidence that PL at green and red wavelengths emanates from different regions of the NT. Additional epi-illumination images of dispersed NTs and their corresponding SEM and optical images are shown in Fig. S4.

Fig. 5.7 shows the correlated PL and SEM images of a single NT and a NT array fragment, along with the PL spectra obtained from the same illuminated region. As in Fig. 5.3, the emission spectrum of the SNT shows more intensity in the red than that of the ordered array. Good correlation between the optical images (shown as insets to the PL images) and SEM images is observed showing the ability to locate the same structure in both experiments.
Fig. 5.8 demonstrates the interesting observation of satellite emission. Using either the 385 nm longpass or the 510 nm bandpass filter to determine the PL image, a satellite luminescence is observed near one end of the ~4 μm nanotube. The satellite is not observed using the red longpass filter. This behavior is similar to that observed in nanowires of TiO₂-B,²³ although the remote emission that was observed in that study was red (~600 nm). It is tempting to interpret the remote PL of NTs using our previously developed model for the trap state emission of conventional NPs,²⁰ where the emission peaking in the green is associated with mobile electrons recombining with hole traps on (101) exposed planes. However, (101) planes do not appear to make up a large portion of the NT surface.²⁰ Alternatively, we considered that
the satellite emission results from waveguiding, as has been observed for example in ZnO$^{31}$ and TiO$_2^{23}$ nanowires. However, the wall thicknesses of our NTs, less than 20 nm, are much smaller than the dimensions of the nanowires used in Refs. 23 and 31. It is likely that diffraction effects would limit the ability of our NTs to confine visible light, and it is therefore reasonable to assign the remote emission to carrier transport. In this picture, mobile carriers formed in the illuminated region diffuse and recombine with pre-existing trapped charges at remote locations.

Fig. 5.9 shows the PL images obtained from a pair of crossed NTs excited at four different positions. The presence of remote luminescent spots can be seen when illuminated in

Fig. 5.9 Optical image (top center) of a pair of crossed nanotubes and PL images (1 through 4) obtained upon excitation at the indicated positions. Recorded with a 385 nm long pass filter.
regions 2 to 4, revealing weak but observable emission from the shorter nanotube when the longer one is illuminated. On the contrary, excitation of the shorter tube (at region 1 in Fig. 5.9) gave a completely dark longer tube. Excitation of the longer NT results in remote emission near the end of the tube.

![Figure 5.10](image)

Fig. 5.10 PL spectrum of a single nanotube 1) in Ar, 2) after 1 hour in air, 3) immediately after introducing ethanol vapor, 4) after 30 minute exposure to ethanol vapor, and 5) in liquid ethanol.

Fig. 5.10 shows the effect of air and ethanol on the PL spectrum of a single NT. We have previously shown\textsuperscript{17} that, for conventional anatase NPs, air almost completely quenches the PL owing to electron scavenging, and ethanol acting as a scavenger of valence-band holes\textsuperscript{32} quenches the red emission from electron traps. In addition, we found that the PL of contiguous NT films is less dependent on environment than that of mesoporous anatase films, showing very little PL quenching when exposed to air.\textsuperscript{20,22} As shown in Fig. 5.10, the PL of single NTs also has a very different dependence on air and ethanol (EtOH) compared to the PL of bulk NP samples. In the SNT, air quenches the emission slightly on the red side. EtOH also quenches the emission on the red side of the spectrum but in addition causes an overall decrease in the emission intensity. In contrast, ethanol causes an increase in the intensity and a larger blue-shift
in the emission of anatase NPs, which we have attributed to a current doubling mechanism.\textsuperscript{20,33,34} The data of Fig. 5.10 suggest that the assignment of the red and green regions of the NT PL is different from that of NPs.

Fig. 5.11 provides further insight into the effect of air on the PL. As shown there, the spatial distribution of the PL in argon is a symmetric Gaussian peak while prolonged exposure to air resulted in a PL image that is elongated to follow the dimension of the nanotube, and decreased in intensity. Evidence suggests that O\textsubscript{2} adsorbs on oxygen vacancies in rutile and anatase.\textsuperscript{34,26} In conventional anatase NPs, green emission appears to be associated with hole traps (\textit{i.e.}, deep electron traps) from oxygen vacancies.\textsuperscript{20} The results in Fig. 5.11 hint at the role of oxygen vacancies in the NT emission and in impeding transport. Prolonged exposure to air could heal these vacancies, improving transport and resulting in a PL image which extends along the length of the NT.

Fig. 5.11 Intensity (top) and spatial distribution (bottom) of emission (from left) in argon, after 5 min in air, and after 12h in air. The right-most image is the 100x optical image of the excited area with microscope illumination.
Surprisingly large intensities are observed for the PL of single TiO$_2$ nanotubes, considering the weak PL of their contiguous ordered arrays. At the same time, emission on the red side of the PL spectrum of single NTs is apparently quenched in the ordered arrays, more so as the size of the fragment increases, as shown in Fig. 5.12. These results suggest that there is significant charge transport perpendicular to the long axis of the tubes in the ordered arrays. The diminished red-edge PL in the ordered arrays could result from passivation of traps residing along the tube walls when the tubes are inter-connected. The power dependence data of Fig. 5.4 indicates a bound excitonic component to the PL of the NT array, consistent with conclusions of Ref. 9, that is absent in the separated NTs. Both oxygen and EtOH are capable of quenching the red edge of the single NT PL spectrum (Fig. 5.10), and both are known to bind to oxygen vacancies. Differences between the PL of single NTs (SNTs) and NT arrays (NTAs) can be understood if we hypothesize that oxygen vacancy defects or other trap states are more numerous or more accessible in SNTs than in NTAs. It is reasonable to suppose that a larger number of trap states in SNTs than NTAs is responsible for the change in PL from a trap-assisted excitonic recombination in the array to recombination of trapped and mobile carriers in the individual NT, in agreement with the power dependence of Fig. 5.4. The excitonic character of the NTA PL is consistent with observed$^{20,22}$ weaker dependence of the spectrum on electron and hole scavenging environments compared to SNTs and NP films.

Our results suggest that both TiO$_2$ SNTs and NTAs have an entirely different distribution of emissive traps compared to that of conventional TiO$_2$ NPs. (An exception to this is the narrow peak at about 700 nm that is present in all anatase nanostructures and is likely assigned to electrons trapped at undercoordinated Ti sites.) Conventional TiO$_2$ NPs are well-known to have
surfaces dominated by lower energy (101) facets, where hole traps associated with oxygen vacancies are located, while electron traps associated with under-coordinated Ti atoms prevail on the minority (001) surfaces.\textsuperscript{20} TiO$_2$ NTs, on the other hand, exhibit growth along the [001] direction; therefore, not surprisingly, their walls expose (100) and (110) facets, which are not common in conventional NPs.\textsuperscript{20} Thus the model of trap state emission we developed previously for conventional NPs, and for nanosheets exposing a lot of (001) surfaces, is not applicable to NTs. For example, PL quenching by oxygen may require a sufficient number of O$_2$ binding sites, which are known to be found on anatase (101). The presence of this surface also appears to be tied to the current-doubling mechanism that makes PL of conventional NP films increase in intensity in the presence of ethanol, a phenomenon which is not observed in the PL of NTs. We note that the effects of both ethanol and air on SNT PL is very similar to their effects on the PL of TiO$_2$ nanosheets with predominately (001) texture. We suggest the strong effects of ethanol and air on the PL of conventional anatase NPs depend on their ability to bind at oxygen vacancies on the (101) surfaces. In the intact NT films, the surfaces of the NTs may be unable to bind O$_2$ and thus no quenching is seen in air.\textsuperscript{20}

Fig. 5.12 a) Normalized PL spectra of different samples showing the diminished intensity of red PL for single NTs and NT arrays. b) Characteristic PL intensity of single NTs compared to that of various sizes of NT array fragments.
Conclusion

Photoluminescence spectroscopy and imaging of single TiO$_2$ nanotubes permits the observation of carrier transport and radiative recombination of mobile and trapped charges. The emission spectrum of a single nanotube revealed more intensity on the red side of the spectrum compared to the spectra of ordered nanotube arrays. The power-dependence of the PL from single NTs and NT arrays suggests that separation of the NTs changes the nature of the PL from that of a bound exciton to that of recombination of trapped and mobile carriers. We speculate that individual NTs possess more surface defects than NTs in contiguous arrays, and that these defects contribute to the red-edge PL that is seen in SNTs but not in NTAs. Supporting this, we found that emission at red wavelengths can be quenched by both oxygen and ethanol, presumed to bind at oxygen vacancies, when the nanotubes are separated. Decreased lateral charge transport in separated NTs, along with increased trap state activity, explains why the PL is orders of magnitude brighter in SNTs than in NTAs. The excitonic character of the NTA PL and scarcity of binding sites explains our previously puzzling observation$^{22}$ that this PL is fairly insensitive to the presence of electron and hole scavengers. Though the exposed surfaces and trap state distributions of SNTs differ from those of conventional NPs, the present results suggest a similar assignment of the PL at green and red wavelengths to recombination of trapped holes and trapped electrons, respectively, with oppositely-charged mobile carriers. Given the longer diffusion length of electrons compared to holes in anatase,$^{35,36}$ the observation of remote PL in SNTs at green, not red, wavelengths could be explained if PL in the green derives from recombination of mobile electrons with neutral acceptors, i.e., hole traps. Ethanol, which scavenges valence band holes but not trapped holes,$^{37}$ can’t quench this green PL, but does
diminish the PL on the red edge, which is then attributed to recombination of trapped electrons with valence band holes. While this model is similar to that for conventional anatase NPs, the shapes of the PL of NPs and NTs differ because the surface traps are situated on different facets.

Assuming the emission in the NT array is that of a donor-bound exciton, the energy of the emission is $h\nu = E_g - E_x - E_D$, where $E_D$ is the donor binding energy, $E_x$ the exciton binding energy, and $E_g = 3.2 \text{ eV}$ is the band gap. The recombination of trapped electrons with valence band holes, on the other hand, (e.g., the “red PL” of conventional anatase NPs) occurs at $h\nu = E_g - E_D$. Similar equations can be written to compare acceptor-bound excitonic transitions to the green PL of anatase NPs (the recombination of mobile electrons with trapped holes), by replacing $E_D$ by the acceptor binding energy $E_A$. Thus the large Stokes shift and breadth of the PL in either case is a consequence of the range and depth of electron (or hole) traps, in addition to probable phonon progressions. In the model proposed here, suggested by the difference in the power dependence of the PL of SNTs and NTAs, the introduction of additional trap states, which could be either donors or acceptors, when the nanotubes are dispersed, changes the nature of the PL from a donor- or acceptor-bound exciton, in the NTA, to radiative recombination of trapped and mobile carriers, in the SNT. The excitonic character of the PL of the NTA, along with the lower density of active traps that can bind air and ethanol, explains the very weak dependence of the PL on the presence of electron and hole scavengers. Many TiO$_2$ samples, including amorphous nanoparticles, show a narrow emission at ~420 nm that is insensitive to surface treatment, which we assign to a self-trapped exciton.$^{17,18,38}$ Thus the binding energy $E_x$ of about 0.25 eV contributes to the Stokes shift of the PL from NTAs.
The difference in the nature of the photoluminescence in individual NTs versus NT arrays might appear to obscure the question of the influence of lateral carrier transport on the intensity of PL. However, the orders-of-magnitude increase in PL intensity in the SNTs appears difficult to account for by a mere increase in trap density. Consistent with the conclusions of Ref. 16, we invoke lateral carrier transport between connecting NTs in the array, which serves to quench the PL from recombination of free and trapped carriers, in the contiguous NT arrays.

Returning to one of the original questions we hoped to address by single nanoparticle spectroscopy, our results show that the breadth of the PL spectrum is not an ensemble effect, since different SNTs give identical spectral shapes. Broadening by phonon modes is one example of a homogeneous broadening effect that could account for the observed emission spectral widths. Further, the epi-illumination images show luminescent traps to be dispersed along the entire length of the NT, with no evidence for spatial separation of traps emitting at different wavelengths. Future work will be aimed at determining the molecular nature of these traps.

**Experimental**

Titanium foils (99.7% from Aldrich) were anodized at 50 V in 3% NH₄F, 2% water, and ethylene glycol electrolyte for 48 h. The resulting TiO₂ nanotube films were then washed with ultrapure water and sintered in air at 450 °C for 3 h, then ultrasonically dispersed in ethanol for 30 min and spin-coated onto clean quartz cover slips and air dried. The morphology of the dispersed film was checked with a scanning electron microscope. Material characterization was done with the following: Siemens D-500 X-ray diffractometer, JEOL 1200EX transmission electron microscope, and PerkinElmer UV/Vis/NIR spectrophotometer with an integrating sphere and a Spectralon reference. Micro-PL was measured using an Olympus IX70 microscope.
with an oil immersion 100X UV fluorescence objective (Immersol 518F and UPLSAPO, respectively). The excitation was a 350.7 nm line of a Kr ion laser. The power at the laser head was ~20 mW in most measurements, except for the experiments in Fig. 5.3 where it was varied from 5 to 60 mW. Considering the losses in imaging beam transmission of the entire set-up and the beam spot size, the power density at the sample is on the order of $10^6$ to $10^7$ mW/cm$^2$. (See Supporting Information, Figs. S5 and S5.) The emission filter was either a 385 nm longpass, a 610 nm long pass, or a 510 nm (teal) band-pass filter (Schott GG385, RG610, and BG-12 respectively), as noted in the text. The emission spectra were collected by an Acton SP2300i SpectraPro single monochromator and detected with a Spec-10 CCD camera. Imaging was done using an Andor Clara interline-CCD camera. Exposure times were 10s and 0.1s per frame for the two cameras, respectively. Raman spectra were taken using the same microscope and objective with 10 mW, 413.1 nm excitation from a Kr ion laser passed through a holographic bandpass filter to remove plasma lines. A holographic notch filter following the sample was used to reject the scattered laser light. PL spectra of bulk samples were measured using the configuration described in Ref. 17, using a near-backscattering geometry as shown in Fig. S3 of Supporting Information. Bulk samples were intact films of TiO$_2$ nanotubes on Ti foil substrate or sintered films of 20 nm anatase nanoparticles (Aldrich) prepared as described in Ref. 19. Emission was recorded either in ambient air, in argon using 14 L/min flow of the gas; or in ethanol vapor as noted in the text. Dispersed films of conventional anatase TiO$_2$ nanoparticles (NPs) for micro-PL measurements were prepared starting from sintered films which were then sonicated and spin-coated onto quartz using the same procedure as described above for the nanotubes. For correlated SEM and micro-PL measurements, a grid was made by lithographic patterning with a positive
resist and sputtering gold on quartz substrate (cleaned by acetone, isopropanol, and DI water and then air dried).

Acknowledgment

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Supporting Information Available: TEM images, XRD, and diffuse reflectance spectra (Fig. S1), power dependence of PL from a NP film (Fig. S2), experimental configuration for measuring polarization dependence of NTA emission spectrum (Fig. S3), epi-illumination, optical, and SEM images of dispersed NTs (Fig. S4), determination of spot size and power density at the sample for 100X magnification (Figs. S5 and S6). This information is available free of charge via the Internet at http://pubs.acs.org.

Table of Contents Graphic
Observation of Charge Transport in Single Titanium Dioxide Photoluminescence Imaging and Spectroscopy

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SUPPORTING INFORMATION

Fig. S1. Materials characterization of the titanium dioxide nanotubes. a) Transmission electron microscope image and selected area diffraction, b) x-ray diffraction spectrum showing the anatase phase, c) diffuse reflectance spectrum showing approximately 12% reflectance at 350 nm and the Kubelka-Munk transform of the data (a fit of the linear region gives $E_g$ at 3.26eV).
Fig. S2 Photoluminescence spectrum of nanocrystalline film of conventional TiO$_2$ nanoparticles in contact with acetonitrile excited with different power densities. The arrow shows the increase in intensity and blue shift in the spectrum when the exciting light is more tightly focused on the sample.
Fig. S3 a) Set-up of the variable polarization excitation experiment b) PL spectra in argon showing no variation in intensity and shape of emission.
Fig. S4. Photoluminescence of dispersed nanotubes under epi-illumination with 20 mW 350.7 nm laser a) without filter b) with the 510 nm (teal) c) 610 nm filter (arrows indicate the scale bar for the intensity d) optical transmission image e) scanning electron image of the same area and magnified image of the nanotube f) SEM and g) PL in the upper left-hand corner of a through e.
Fig. S5. Determination of the beam spot size with 100x objective lens. Dilute (< 1% by weight) aqueous silver nitrate was dropped on a thin anatase film. The film was then exposed to the UV laser focused by the 100x objective. The dark spot was then observed with regular microscope illumination and the graduation of the color/darkness of the film. The measured spot is larger than the actual focused beam area because the silver colloid tended to bleed through the film.
Fig. S6. Power and power density calculation a) 100x UPLSApo Transmission. Source: Olympus b) Transmittance of the 350.7 nm bandpass filter c) Table of the calculated power densities. The cone of spread of the light after the 100x objective is too large to effectively measure the power using conventional power meters. To determine the power at the focused area, the power was measured without the bandpass filter and the objective. The value was then corrected with the transmittance of the filter and the objective.

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CHAPTER 6

Efficiency of Plant Pigment Dye-Sensitized TiO₂ Nanotube Solar Cell in Iodide/Triiodide Electrolyte

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Abstract

The sustainability and environmental compatibility of dye sensitized solar cell (DSSC) technology can be further improved with the use of a natural dye to replace the metal-based dyes that are currently in-use. Betanin is a plant pigment with 535nm peak absorption in solution (500nm when adsorbed on TiO₂) and a molar absorptivity as high as 65,000 M⁻¹cm⁻¹. In this work, we used it to sensitize nanotubular TiO₂ films of anatase. Electrolytes from iodide / triiodide redox couple in various solvents – acetonitrile, methoxypropionitrile, and ethanol – were used in the solar cell. Dye loading in TiO₂ nanotubes for betanin and N3 are measured and optical absorption spectra of the films were taken to determine the shifts in peak absorbance on adsorption on TiO₂. DSSCs based on titanium dioxide nanotubes with betanin and the ruthenium-based dye, N3 were fabricated and photovoltaic properties are compared.

Introduction
Current dye sensitizers are based on synthetic molecules containing a transition metal center that absorb visible light. One example is the Ru-based RuL₂(NCS)₂2H₂O (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid), commonly called “N3.” Ruthenium availability is limited and it is potentially toxic.¹ Thus, our objective is to present a natural dye as a viable option for the sensitizer in DSSCs.

In an earlier work, betanin-sensitized solar cells with nanoparticulate titanium dioxide as the photoanode have reached ~2.7% in power conversion efficiency and incident-photon-to-electron conversion efficiency of ~90%.² ³ The betanin solar cell reached ~14 mA/cm² for the short circuit current density, however, the low open circuit voltage ~0.35- 0.44V makes the overall efficiency lower compared to ruthenium-based dyes. Although the overall efficiency is lower for this sensitizer, the incident-photon-to-electron conversion efficiency (IPCE) is higher at more than 80% compared to N3 sensitized cells which peaks at 60-70%. The contradictory values of IPCE and Vₒc reflect the large amount of recombination that occurs in betanin sensitized cells but the mechanism on how this recombination occurs is still being investigated.

![Fig. 6.1 The energetics of the dye sensitized solar cell and the physical parts comprising it.](image-url)
One of the possible causes of this lower efficiency is the presence of minute amounts of water in the solar cells after sensitizing. Betanin is only soluble in water, thus a TiO$_2$ film is sensitized in pH 4 aqueous betanin solution. However, recent studies showed that presence of \(~10\text{-}20\%\) water in the electrolyte increases the efficiency by around 0.5\%.\textsuperscript{4,5,6} From photoluminescence studies of nanoparticulate and nanotubular anatase, it was found that the titanium dioxide nanotubes respond less to the environment than nanoparticles (as discussed in Chapters 2 and 5) thus the use of this morphology as an active area in betanin-sensitized solar cells can be explored. Since recombination is a problem in betanin-sensitized cells and TiO$_2$ nanotubes has been shown to have less recombination than nanoparticles,\textsuperscript{7} it is postulated that adsorption on nanotubes would result in less recombination. Figure 6.1 illustrates a dye sensitized solar cell with nanotube as the active area. It is perceived that nanotubes have a more direct path for electron transport from the point of injection by the sensitizer dye to the working electrode and this configuration would result in increased charge collection efficiency.\textsuperscript{8} Because of the lack of response of the nanotube photoluminescence to contacting environment, we also speculate that the effect of solvent in nanotubular (NT)-based DSSC will be different from that of nanoparticle-based DSSCs. One of the goals of this study was to compare the solvents (e.g. ethanol), commonly yielding low power conversion efficiency in nanoparticulate DSSCs, with solvents that yield higher efficiencies (e.g. acetonitrile or methoxypropionitrile).

The natural dye betanin is a plant pigment with 535 nm peak absorption in aqueous solution (500 nm adsorbed on TiO$_2$) and molar absorptivity of 65,000 M$^{-1}$cm$^{-1}$.\textsuperscript{2} Betanin belongs to the betalain family. The molecular form is shown in figure 6.2.
Methodology

A series of grinding and filtration steps were used to get an extract from beets (*Beta Vulgaris*) with a small amount of ultrapure water as an extractant. A phosphate buffer was added to stabilize the solution. The red-purple pigment was separated into betanin and other natural dyes by reverse-phase medium pressure liquid chromatography (MPLC) in methanol and water media (10:90). Two batches of solutions were used during extraction – one with a phosphate buffer (pH 6) and the other with dilute HCl (pH 3-5). Further purification was done by lyophilization of the solution and running it through MPLC for a second time. The nanotubes were fabricated by anodization of titanium in 0.5% NH₄F in ethylene glycol with ~2% water following Appendix A1. The sample was then annealed in air at 450°C for 3 hrs.

After annealing, the nanotube films were acidified in a solution of 0.1M HCL in ethanol for 30 minutes and dried. Dried films were immersed in the betanin solution for at least 12 h.
before testing. A few (2-3) drops of the electrolyte were put on the sensitized NT films and the platinum-coated fluorine-doped tin oxide (FTO) counter electrodes were pressed against the film. Thin strips of plastic foil or parafilm were used as spacers to prevent electrical contact between the titanium metal and the counter electrode and to prevent the electrolyte from seeping out. The cell was secured by metal clips and a piece of glass was used to prevent contact of the clip with the titanium metal (see figure 6.3).

Solar cell I-V measurements were done with a 103 mW/cm² Xe arc lamp illumination with UV and IR filters. A Keithley 2400 supplied the voltage and recorded the current. The cell was illuminated through the counter electrode – platinum on fluorine-doped tin oxide (FTO) – details in Appendix A3. Succeeding treatment of the NT film with 0.1M titanium (IV) tetrachloride (TiCl₄) in ultrapure water was done for 12 h in refrigeration, the film was then washed, dried, and sintered at 450°C for 30 minutes in air.
Results and Discussion

a. Betanin purification

Figure 6.4 shows the absorption of the betanin upon purification in comparison to that of the raw beet extract and indicaxanthin. Indicaxanthin is a yellow dye present with the purple dye betanin in the beet extract; it has a peak absorption in the blue (with lower molar absorptivity of 48,000 M⁻¹ cm⁻¹)⁹,¹⁰ and competes with betanin in anchoring to the TiO₂. This results in a less favorable light harvesting; thus the indicaxanthin is separated out from the betanin before sensitization.

![Fig. 6.4 UV-vis spectra of the beet extract and its component dyes – betanin and indicaxanthin](image)

b. Betanin-sensitized Nanotube DSSC

Initial DSSCs based on titanium dioxide nanotubes sensitized with betanin were compared with N3-sensitized cells. Sample to sample comparison showed that betanin-sensitized
films have lower $I_{sc}$, $V_{oc}$, and fill factor resulting in a lower overall efficiency. This is different from NP-based Betanin-DSSC where the $I_{sc}$ is ~ same as that for N3-DSSC (as mentioned earlier). A possible cause is the PO$_4^{3-}$ in the buffer used to stabilize betanin which blocks dye binding sites resulting in lower dye loading. Another batch with HCl to control the pH showed a small improvement; Table 6.1 lists the summary of the $I_{sc}$, $V_{oc}$, fill factor, and efficiency of the solar cells.

Table 6.1. Maximum recorded values of the key parameters of Bet-NT DSSC

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NT/Bet in MPN</td>
<td>3.8</td>
<td>0.36</td>
<td>0.32</td>
<td>0.35</td>
</tr>
<tr>
<td>NT/Bet in ACN</td>
<td>2.2</td>
<td>0.23</td>
<td>0.31</td>
<td>0.28</td>
</tr>
<tr>
<td>NT/Bet in EtOH</td>
<td>0.5</td>
<td>0.27</td>
<td>0.32</td>
<td>0.07</td>
</tr>
<tr>
<td>NT/Bet (PO$_4^{3-}$ buffer) in MPN **</td>
<td>3.6</td>
<td>0.31</td>
<td>0.24</td>
<td>0.21</td>
</tr>
<tr>
<td>NT/Bet in MPN TiCl$_4$ treated</td>
<td>2.1</td>
<td>0.27</td>
<td>0.37</td>
<td>0.20</td>
</tr>
<tr>
<td>NT/N3 in MPN</td>
<td>8.01</td>
<td>0.35</td>
<td>0.24</td>
<td>0.66</td>
</tr>
</tbody>
</table>

MPN = Methoxypropionitrile, ACN = Acetonitrile, EtOH = ethanol. All Betanin sensitizers uses HCl for controlling the pH except where indicated by ** which used a phosphate buffer.

DSSCs based on nanotubes have lower efficiency than those with mesoporous films for several reasons. The I-V curve is affected by current leakage attributed to cracks in the nanotube film. This is still seen even after TiCl$_4$ treatment following the procedure done for nanoparticulate film which resulted in an increase in the efficiency. The deposition of a thin layer of TiO$_2$ by TiCl$_4$ reaction with water is usually done to improve particle interconnection.
and heal surface defects. Device architecture is also another reason for lower efficiency.

Nanotube solar cells are illuminated from the counter electrode side because the working electrode is titanium metal. The absorption of the electrolyte, the glass electrode, and the thin Pt layer result in lower incident light intensity than in the nanoparticulate device. Lastly, lower dye loading is seen in nanotubular film compared to nanoparticulate. Dye loading of TiO$_2$ nanotubes measured with N3 was significantly lower ($1.3 \times 10^{-8}$ mols/cm$^2$) than that of a mesoporous film of comparable thickness ($8.5 \times 10^{-8}$ mols/cm$^2$). The dye loading experiment is done with the sensitized film immersed in a dilute (0.1M) NaOH aqueous solution to break the attachment of the carboxylic group with the TiO$_2$. However, betanin is most stable within pH 3.5 to 5 and immersion in NaOH caused the dye to decompose, as a result the dye loading experiment was done with N3.

Table 6.1 showed the highest attained efficiency for the dye sensitized solar cells with betanin as sensitizer, figure 6.5 shows the distribution of the efficiencies in the devices fabricated.

![Fig. 6.5 Distribution of efficiencies of nanotube/betanin-based solar cells in various electrolyte solvents – ACN (4 cells), ethanol (4 cells), MPN (8 cells), and with TiCl$_4$ treatment (4 cells).]
From figure 6.5, we can see that the electrolytes in ACN and MPN performed similarly. In Ref. 2, the best performing cell was measured in ACN at $\eta = 2.7\%$, significantly higher than with the MPN at 2.2%. However, the best performing nanotube cell was measured in MPN (although the range of efficiencies is broad). This could mean that the nanotube/betanin solar cell does not differentiate between solvents of the same functional group (acetonitrile and methoxypropionitrile). On the other hand, the performance of the nanotube/betanin solar cell in ethanol is significantly lower which indicates a solvent related-effect.

c. Solar cell equation

Figure 6.6 shows the equivalent circuit diagram of a solar cell. The I-V curve is modeled by the equations:

For an ideal cell:

$$I = I_L - I_D$$  \hspace{1cm} (1)

$$I_D = I_o \{[\exp(qV/nkT)] - 1\}$$  \hspace{1cm} (2)

Where $I_o$ is the saturation dark current and is a measure of the recombination in a device, $q$ is the absolute value of the charge of the electron, $k$ is Boltzmann’s constant, $n$ is a diode ideality factor, and $T$ is temperature in K.

For a normal cell:

$$I = I_L - I_o \{\exp \left[\frac{q(V + IR_s)}{nkT}\right] - 1\} - \left(\frac{V + IR_s}{R_{sh}}\right)$$  \hspace{1cm} (3)
where $I$ is the current through the device, $I_L$ is the load current, $I_D$ is the diode current. In a normal cell, resistances caused by several aspects of device fabrication are introduced changing the diode current, eq. 2, into the form

$$I_o \left\{ \exp \left[ \frac{(q(V + IR_s))/nkT}{} - 1 \right] - \frac{(V + IR_s)}{R_{sh}} \right\}$$

where $R_s$ and $R_{sh}$ are the series and shunt resistances, respectively.\textsuperscript{11} Unfortunately, this equation can only be modeled numerically, however, the effects of the resistances are shown in the model calculated in MatLab for a using the values typical for a DSSC at ambient temperature and 1 Sun (figure 6.7).

The short circuit current ($I_{sc}$), open circuit voltage ($V_{oc}$), and fill factor (FF) are key parameters to measure solar cell performance. The overall cell efficiency is calculated from:

$$\eta = \frac{V_{oc}I_{sc}FF}{P_{in}} \quad (4)$$

Where $V_{oc}$ is the open circuit voltage, $I_{sc}$ is the short circuit current, $FF$ is the fill factor, and $P_{in}$ is the incident power.\textsuperscript{12}
The open circuit voltage, $V_{oc}$, is the photovoltage without any load on the device, for a dye sensitized solar cell the maximum possible $V_{oc}$ is the difference between the Fermi level, $E_F$, of the titanium dioxide and reduction potential of the electrolyte.\textsuperscript{13} The short circuit current, $I_{sc}$,
is the current at very low (~0) impedance, in DSSCs the maximum value corresponds to the photocurrent generated by the device.\textsuperscript{14} The fill factor is a ratio of the maximum power given by the cell (considering the effect of the two resistances) over the maximum power obtainable by considering the $I_{sc}$ and $V_{oc}$ values (equation 5).

$$FF = \frac{(IV)_{max}}{I_{sc}V_{oc}}$$  \hspace{1cm} (5)

The open circuit voltage is an indication of the amount/degree of charge recombination in the device. By rearranging the solar cell equation 3 and letting $I = 0$ for an open circuit (and neglecting shunt and series resistances),

$$0 = I_L - I_o \left\{ \exp \left[ \frac{(qV)}{nkT} \right] - 1 \right\}$$  \hspace{1cm} (6)

$$V_{oc} = \frac{nkT}{q} \ln \frac{I_L}{I_o}$$  \hspace{1cm} (7)

The $I_o$ is the reverse saturation current or the saturation dark current and (as mentioned earlier determines the amount of recombination in a diode.\textsuperscript{12} Thus from equation 7, the $V_{oc}$ varies directly as the $\ln \left( \frac{1}{I_o} \right)$. It can also be shown that $I_L$ is equal to the short circuit current (at $V = 0$). Thus recombination manifests as a reduction in the $V_{oc}$ of a device.

d. **Shape of the Bet-NT-DSSC measured I-V curve**

Comparing figure 6.8 below to the model I-V curves, these cells are showing power loss due to shunts and series resistances. The slope of the line (as $V \to 0$) at the $I_{sc}$ is zero from
\( R_{sh} \to \infty, \frac{dI}{dV} = 1/\infty \), however in the case of MPN, the \(|\text{slope}|\) is increasing as \( V \) decreases, indicating shunts between electrolyte to the electrode – as this behavior is also seen in dark current measurements for MPN (see figure 6.9). From the slope of the I-V curve at \( V_{oc} \), series resistance is also large. Ethanol has the lowest slope and also the lowest short circuit current. In our group’s study of solvent effects on the efficiency of DSSCs,\textsuperscript{15,16} it was shown that interfacial charge transfer occurs with rates highest in iodide/triiodide electrolytes in acetonitrile while lowest in ethanol. The effect is that \( I_{sc} \) (acetonitrile) > \( I_{sc} \) (ethanol) however, \( V_{oc} \) (ethanol) > \( V_{oc} \) (acetonitrile). The higher Voc in ethanol may be due to lower standard reduction potential of \( \text{I}_3^-/\text{I}^- \) in ethanol. It was speculated that the solvent reorganization on the surface of the nanoparticles contributes a stabilizing energy to the electrons in the nanoparticles during transport.

![Fig. 6.8 Current-voltage curve of nanotube/betanin-based solar cells in various electrolyte solvents – acetonitrile (ACN), ethanol (EtOH), methoxypropionitrile (MPN).](image)

In the dark, a current generation \((I > 0)\) in the I-V curve (figure 6.9 for MPN), an indication of increased recombination. The sample in ethanol showed a diode-like behavior,
however, recombination currents arise early on. The results of dark current measurement are compared with nanoparticulate samples in MPN which shows the typical diode behavior and a defined onset of the saturation current.

![Current-voltage measurement of nanotube/betanin-based solar cells in the dark in various electrolyte solvents, methoxypropionitrile (MPN) and ethanol (EtOH), compared with nanoparticulate film (NP) in MPN.](image)

Fig. 6.9 Current-voltage measurement of nanotube/betanin-based solar cells in the dark in various electrolyte solvents, methoxypropionitrile (MPN) and ethanol (EtOH), compared with nanoparticulate film (NP) in MPN.

e. Diffuse reflectance

Another possible cause of the lower efficiency of the nanotube cells with betanin sensitizer is shown in the comparison of diffuse reflectance spectra between nanoparticulate P25 and nanotubular substrate (figure 6.10). The spectra on figure 6.10a were taken on unsensitized and betanin-sensitized P25 nanoparticulate film while the 6.10b shows the unsensitized and betanin-sensitized nanotubes. The difference in the diffuse reflectance spectra was taken and comparison showed that the adsorption on nanotubes resulted to a spectrum very similar to that
of betanin in water with a slight blue-shift of the peak absorption, 516 nm on nanotubes and 535 nm in aqueous solution. It also showed slight widening of the absorption peak. Figure 6.10c shows the comparison of the betanin in water, betanin adsorbed on nanotube, and betanin adsorbed on P25 nanoparticle. Adsorption of betanin on P25 showed a broader absorption band with a peak shifted to the blue (468 nm). This peak shows an increase in absorbance in the red wavelengths as well as in the blue. The ideal sensitizer should be able to harvest a wide range of the spectrum to be more efficient.

![Graphs showing diffuse reflectance of betanin adsorbed on P25 and nanotubular films.](image)

Fig. 6.10 Diffuse reflectance of a) betanin adsorbed on nanoparticulate P25 film b) betanin adsorbed on nanotubular film. The negative spectrum shows the difference Δ%R between the sensitized and unsensitized film.
Figure 6.10 shows that the adsorbed molecule’s absorbance changes and that various substrates can result in a different type of interaction. The narrower absorbance of betanin adsorbed on nanotubes results to lower light harvesting compared to P25 nanoparticles.

f. Other factors affecting device performance

An observation on the illuminated area after testing showed that in ethanol, the presence of a photodegraded spot can be seen as in figure 6.11. This is an indication that the betanin is not regenerated. This behavior has been seen in MPN electrolytes but only after after prolonged exposure and testing. This effect may be the reason for the very low $I_{sc}$ seen on cells with ethanol-based electrolytes. Electron donating $I^-$ may not be reducing betanin because mass transport in ethanol (viscosity = 1.07 cP) is more hampered than in nitriles (viscosity = 0.37 cP for ACN).\textsuperscript{17} Due to the low efficiencies seen during power conversion efficiency testing for the nanotube/betanin DSSC, the incident-photon-to-electron conversion efficiency (IPCE) was not done.

![Fig. 6.11 Image of a nanotube film sensitized with betanin after DSSC measurement, the light colored round spot (arrow)]
Conclusions

Betanin is a promising natural dye sensitizer for DSSCs showing comparable efficiency to N3 in nanoparticulate films. However for the titanium dioxide nanotube, the efficiencies of DSSC devices are low due to electrical shorts and high series resistance. The nanotube film surface contains microcracks that are pathways for electrical shorts between the electrolyte and the working electrode. These shunts were not healed with TiCl4 treatment. Variation of solvents used in device testing showed that acetonitrile and methoxypropionitrile behave similarly; ethanol, on the other hand, causes the betanin to degrade faster or not regenerate. Stabilization of charges hopping through the nanoparticles may be stronger in one solvent than others and this could be the main reason for the low efficiency in ethanol.

Acknowledgment We thank Dr. Rob Ronald for lending us the MPLC and the Berkman group at the Department of Chemistry for help with lyophilization.
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CHAPTER 7

Summary: The model of nanotube photoluminescence

7.1 Summary of results

Upon injection of an electron into titanium dioxide from an excited dye molecule, the electron can undergo: 1) charge collection – where the electrons are successfully collected in the electrode; 2) trapping and recombination – where the electron occupies a trap state and recombines with a nearby oxidized form of the electrolyte; 3) trapping and detrapping – whereupon trapped electrons are excited thermally back into the conduction band. The efficiency of charge collection, \( \eta_{cc} \), in a dye sensitized solar cell is expressed as:

\[
\eta_{cc} = \frac{\tau_t}{\tau_t + \tau_{cc}}
\]

where \( \tau_t \) is the time constant of electron trapping (equivalent to 1/rate of trapping) and \( \tau_{cc} \) is for charge collection.\(^1\) Thus the presence of deep electron traps greatly affects the overall efficiency of the device.

A major criticism on the dye sensitized solar cell device is that the photoanode – titanium dioxide – is composed of nanoparticles which require transport of electrons to be random and disordered. This gives rise to areas/regions in the material which are more susceptible to electron recombination into the electrolyte. It has therefore been postulated that the titanium dioxide in the form of nanotubes would provide a more efficient way to transport electrons from the injection site to the collecting electrode. In this study, we looked at the defect states in anatase titanium dioxide nanotubes and compared them with nanoparticles using photoluminescence (PL) spectroscopy in bulk and single particles in various environments.
We have found that nanoparticulate anatase PL is composed of a superposition of recombination from different trap states, an $e^-$ to an acceptor state (hole trap) which is in the green wavelengths, and an $h^+$ to a donor state (electron trap) on the red wavelengths. These conclusions were reached after the material exhibited selective PL quenching in different chemical environments. The luminescent traps are spatially isolated and the crystallographic orientation of the surfaces influences the type of emission observed. Hole traps arise due to the creation of oxygen vacancies while electron traps are present near or in 5-fold coordinated Ti. The 101 plane of anatase is composed of 5-fold and 6-fold coordinated Ti while the 001 plane consists only of 5-fold coordinated Ti, thus in nanoparticulate anatase which contains both planes, the PL spectrum is a composite of the two emissions, while nanosheet anatase exhibits more red emission.

Nanotube surfaces as characterized by electron backscatter diffraction were shown to be composed of planes (101), (110), and (100) – planes which grow (to some degree) along the c-direction of the unit cell. The nanotubes show weaker bulk PL than nanoparticulate/nanosheet anatase and the emission also has lower sensitivity to the contacting environment. There are two factors influencing the intensity of the PL in TiO$_2$ nanotubes, number of defects and transport of carriers where $I_{PL}$ is proportional to the number of defects but decreases as transport increases. We have shown that transport occurs in nanotubes through the PL peak shift from anatase to rutile emission in thin nanotube arrays where the anatase point of excitation is relatively close to the rutile boundary layer, and that grain boundaries impede transport resulting in a very bright luminescence.

The skewed peak of the mostly-green PL indicates the presence of more than one kind of trap state. Figure 7.1 show the fitting of gaussian peaks into the spectra with two peaks – a narrow distribution with peak in the green and a distribution peaking in the red.
Fig. 7.1 Fitting of gaussian curves for PL of nanotube films in a) argon, 2 peaks, b) air, 2 peaks, and c) ethanol, 3 peaks
From the numbers in Table 7.1, it was calculated that exposure to air quenches the red and green PL by less than 10%, while ethanol enhances the green PL by \(~20\%\) and quenches the red PL by \(~50\%\). The behavior of the film in ethanol is slightly similar to that in nanoparticulate anatase but the blue-shift of the peak position is not as great (\(~540\) nm against \(530\) nm in nanoparticles). However, the quenching in air is not as extreme as that in nanoparticles (10% against \(~90\%\) in nanoparticles) raising the question as to whether the traps are present but not accessible to the environment as some traps are known to bind \(O_2\) and ethanol (from Chapter 4). Another possible reason is that because the exposed crystal planes in nanotubes are different from nanoparticles, the defect type may be different.

Table 7.1 Characteristics of the fitted peaks in figure 7.1

<table>
<thead>
<tr>
<th></th>
<th>Center (nm)</th>
<th>Width (nm)</th>
<th>Height (arb. unit)</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NT Array</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Argon</td>
<td>566 (2.2 eV)</td>
<td>105.37</td>
<td>268.82</td>
<td>35500</td>
</tr>
<tr>
<td></td>
<td>679 (1.8 eV)</td>
<td>219.73</td>
<td>265.46</td>
<td>73105</td>
</tr>
<tr>
<td><strong>NT Array</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>564 (2.2 eV)</td>
<td>104.77</td>
<td>245.98</td>
<td>32300</td>
</tr>
<tr>
<td></td>
<td>674 (1.8 eV)</td>
<td>222.04</td>
<td>244.43</td>
<td>68021</td>
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<tr>
<td><strong>NT Array</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>427 (2.9 eV)</td>
<td>14.693</td>
<td>19.802</td>
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<td></td>
<td>542 (2.3 eV)</td>
<td>124.74</td>
<td>330.12</td>
<td>64683</td>
</tr>
<tr>
<td></td>
<td>644 (1.9 eV)</td>
<td>215.44</td>
<td>134.45</td>
<td>45498</td>
</tr>
<tr>
<td><strong>SNT Argon</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>557 (2.2 eV)</td>
<td>100.41</td>
<td>421.94</td>
<td>53100</td>
</tr>
<tr>
<td></td>
<td>670 (1.8 eV)</td>
<td>156.71</td>
<td>432.76</td>
<td>85000</td>
</tr>
</tbody>
</table>

Single nanotube PL showed that quenching with air is also less effective (compared to nanoparticle emission) with around 16% quenching and shows that although some traps are exposed or created upon dispersion into single particles, the amount of surface-oxygen-quenchable emitting traps is significantly less than nanoparticles. Bulk and single nanotube PL
showed that trap states present in nanotubes are similar to nanoparticles but with different proportions, and that the differences in morphology and crystallography affect the environmental sensitivity of these defect states.

In the model of nanoparticulate anatase photoluminescence emission, the following mechanisms were identified:

\[ e_{CB}^- + h_{tr}^+ \rightarrow h\nu_{PL(green)} \]

\[ h_{VB}^+ + e_{tr}^- \rightarrow h\nu_{PL(red)} \]

The nanoparticle emission is dominated by the red emission. In nanotubes, the green and red emissions were also seen but with different intensities. The assignment of these emissions are consistent with nanoparticles in that the green luminescence is related to hole traps and the red with electron traps. This is supported by evidence from vacuum annealing and spectroelectrochemistry experiments. An emission at 425 nm is also seen and is attributed to an exciton. If we apply the model of nanoparticle to nanotubes it will have the scheme shown in figure 7.2.

Fig. 7.2  Model of NP and single NT PL - if the emissions are a result of mobile and trapped charges recombination
The three types of emissions are: $I_{Ex}$ for recombination of excitons with binding energy of around 0.2 to 0.3 eV; $I_{eA}$ for recombination of an electron with an acceptor or hole trap at 2.2 eV; and $I_{hD}$ for the recombination of a hole with a donor or electron trap at 1.9 eV.

However for nanotube arrays, the data presented in Chapter 2 and 5, showing less environmental sensitivity and a power dependence of photoluminescence intensity, $I \propto P^k$, with $k \sim 1.5$, show that electrons and holes generated upon excitation are excitonic in nature. Although the emission energies are much lower than the bandgap, exciton binding energies range to about 1 eV in semiconductors and excitons can be weakly bound to defects. \textsuperscript{7,8}

In the model used in Chapter 5, the continuity equation included the generation of charges and recombination and trapping of charges in various radiative processes. However, in the case of anatase nanotubes, charge transport is significant and must be included in the calculation to account for the drastic difference in intensity.

![Diagram](image)

Fig. 7.3 A section of the nanotube showing the processes of generation($h\nu$), sink(PL), and transport ($J_n$)
Due to the complexity of solving the Boltzmann Transport Equation, the relation between I and P is determined through the balance equations. Consider the section of the nanotube in the excitation area as shown in figure 7.3, the electron continuity equation can be written as:

\[ \frac{\partial n}{\partial t} = -\nabla \cdot F_n + G_n - R_n \]  

(1)

where \( n(r,t) \) is the electron density, \( F_n \) is the electron flux, \( G_n \) is the optical generation, and \( R_n \) is the recombination (with a hole or a defect). Based on the tentative scheme in figure 7.2, the balance equation for the TiO\(_2\) nanotubes is:

\[ \frac{\partial n}{\partial t} = iL - an^2 - gnN_D - enN_A - \nabla \cdot F_n \]  

(2)

where \( i, a, g, \) and \( e \) are transition rates of the electron hole pair generation, exciton recombination, trapping of the electron, and mobile electron recombination with trapped hole processes, respectively; \( N_D \) and \( N_A \) are concentration of traps, and \( L \) is the laser intensity. The flux of electrons into the volume excited by the laser is the drift-diffusion equation

\[ J_n = J_{drift} + J_{diffusion} \]  

(3)

\[ J_n = q\mu_n nE + qD_n \nabla n \]  

(4)
where \( q \) is the charge, \( \mu_n \) is the mobility, \( E \) is the electric field, and \( D_n \) is the diffusion coefficient. Inserting this in the balance equation gives:

\[
\frac{\partial n}{\partial t} = iL - an^2 - gnD - enA - q\mu_n nE - qD_n \nabla n \tag{5}
\]

The drift term is neglected. The diffusion equation is more difficult to express into a form that will be easily evaluated. Further work with this equation will be done to model the power dependence data. Qualitatively, however, the diffusion term plays a big role in the nanotube array under the approximation of infinite slab and a gradient in concentration and flux of charges are always present – this decreases the intensity of the emission by decreasing amount of charges. However, for single nanotubes, at steady state the difference between the concentration at the excitation point and the point farthest to it will be lower, thus the driving force for diffusion is less compared to that in nanotube array.

7.2 Conclusions

Intraband defect states in anatase titanium dioxide nanotubes with \( E_g = 3.2 \) eV consist of a donor state and an acceptor state at 1.3 eV and 2.2 eV below the conduction band, respectively. Similar to nanoparticles, the emission with an energies peaking at 2.2 eV (green wavelengths) arise from recombination of mobile/shallow trap electron with an acceptor state while the emission at 1.9 eV (red wavelength) is from holes in the valence band recombining with electrons trapped in donor sites. However, in large nanotube arrays, the emissions exhibit an excitonic nature – that of a donor or acceptor bound exciton – with the same peak emission energies as the single nanotubes. These assignments were
supported by photoluminescence studies in electron scavenging and hole scavenging environments, spectroelectrochemistry, and vacuum annealing.

Transport in nanotubes contributes greatly to quenching of PL intensity. However, directional transport laterally between neighboring tubes is as significant as transport along the tube. This makes charge collection less efficient than initially supposed.

Comparison of the relative amounts of red and green emissions showed that nanotubes have higher ratio of green emission than nanoparticulate anatase, meaning higher relative number of hole traps than electron traps. Electron traps directly affect the collection efficiency of DSSCs. However, two issues were discovered that hinder the performance of nanotubes in a device: the occurrence of current shunts between electrolyte and electrode can be resolved by engineering; the more unexpected one is that charges generated behave in an exciton-like manner in nanotube arrays. To be able to collect electrons, efficient charge separation should occur. Although the DSSC sensitizer only injects electrons into TiO₂, it is possible that these electrons are stabilized by a corresponding positive charge (somewhere in the electrolyte). Creation of a surface result in a transition from exciton-like to free- to-bound emission – an interesting occurrence which can be studied further – could be one of the advantages of nanoparticulate anatase.

7.3 Future work

The single nanoparticle PL results opened several areas for further study. The difference in spectrum shape of the array and the single particle suggest creation of defect states by the introduction of a surface. Further theoretical work can be done to determine the actual defect introduced. The presence of remote emissions on nanotubes is also interesting to explore further and see whether this technique can be used to track the propagation of an excitation in artificial photosynthetic systems.
To take the derived conclusions further, the best photoanode configuration is not nanotubes but nanowires – thick forest of well-aligned single-crystal nanowires. The single nanotube study has shown significant transport along the 001 plane. Exact values of mobilities on various planes of anatase is not yet available, however, oriented nanowires with 001 exposed surfaces would be a good starting point for future work. Several studies on TiO$_2$ nanowires have been done which gave almost 1D nanostructures in the anatase and rutile phase.$^{10,11,12,13}$ However, both dye loading and recombination are proportional to the length of the nanowire and in this architecture, compromises are still made. To address this, I propose a study on core-shell nanowires of TiO$_2$ and doped tin oxide. This can be done by growth of FTO nanowires and coating with TiO$_2$ through wet-chemistry processes or atomic layer deposition (as illustrated below).

![Core-shell nanowire of TiO$_2$ and FTO](image)

**Fig. 7.4 Core-shell nanowire of TiO$_2$ and FTO**

Nanotubes grown at 0 °C or ice-water bath temperatures show a very well ordered structure. These can be used as vessels for delivery systems or electrodes for intercalation devices.
Fig. 7.5 Well-aligned nanotubes
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APPENDIX A

EXPERIMENTAL DETAILS

1. Growing Titanium Dioxide Nanotubes

2. Photoluminescence Spectroscopy and Imaging

3. Device Assembly and Measurement

4. Spectroelectrochemistry
1. Growing Titanium Dioxide Nanotubes: Anodization and Sintering

1.1 Experimental Set-up and Results

Anodization is a process used to induce oxidation in metals by making them the anode in an electrochemical reaction. Titanium foils (Aldrich 99.7% 0.25mm thickness) cut to around 15mm x 30mm plates were polished with 2400 grit sandpaper for 3 minutes on each side to get a uniform clean surface. The foils were immersed in 18MΩ water with 10% Alconox and cleaned ultrasonically for 30 minutes. This is done once more with water and Alconox and twice more with only water. The same cleaning procedure was done for the platinum electrode (Alfa-Aesar Premion 99.99% Pt). The anodization electrolyte is prepared by dissolving NH₄F (Sigma Aldrich 99.99+% in Ethylene Glycol (JT Baker reagent grade) and adding 2% 18MΩ water. The ammonium fluoride does not dissolve easily in ethylene glycol, so the solution is stirred for 24 hours in a Nalgene beaker prior to use. The titanium foil is attached to the positive terminal of the DC power supply (HP Harrison 6205B) and the platinum to the negative (see figure A1.1a). At the start of anodization, bubbles will be generated on both electrodes so the alligator clips should be positioned to prevent the electrolyte from touching the steel and contaminating the anodization process. The current will be high in the beginning; however, as the oxide is formed it will decrease to almost zero (see figure A1.1b). The titanium will change color as it is anodized. If the set-up is contaminated with iron, the electrolyte will slowly become a golden brown/yellow color. The thickness of the nanotube film against the duration of anodization at 50 V in the electrolyt is shown in figure A1.2. Most of the anodization done in this study is at room temperature and using the electrolytes mentioned above, however anodization at around
273K and using an electrolyte composed of aqueous perchloric acid has also been done and morphologies of the resulting films are shown in figure A1.3.

Fig. A1.1 a) Anodization set-up b) Anodization current vs. time

Fig. A1.2 Nanotube length against anodization time at 50 V with the NH₄F and ethylene glycol electrolyte
After anodization, the nanotube films are sintered (usually) at 450°C for 3 h in a Barnstead Thermolyne 1400 muffle furnace.

Fig. A1.3 SEM images of the morphology of the samples anodized a) and b) at room temperature using perchloric acid as the electrolyte c) and d) at around 273 K with ammonium fluoride electrolyte
1.2 Simple calculation of the surface areas of nanotubes and mesoporous films

Considering the usual dimensions of the nanoparticles of anatase from TiO₂ vendors and nanotube films produced in the anodization of titanium mentioned in the earlier section, the maximum surface areas for a specified volume are calculated as follows:

For the nanotube:

\[ A_{wall} = 2\pi rh \]
\[ A_{face} = \pi r^2 \]

For nanoparticles:

\[ A_{sphere} = 4\pi r^2 \]
\[ V = \frac{4}{3}\pi r^3 \]

Assumptions:

Average external diameter of a nanotube = 100 nm
Average internal diameter of a nanotube = 60 nm
Length of the tube = 9 μm
Diameter of the nanoparticles = 10 nm

Thickness of the film = 9 μm

Surface area of one nanotube:

\[ S_{AN_T} = S_{ext} + S_{int} + S_{top} \]

\[ S_{AN_T} \approx 9 \times 10^6 \text{ nm}^2 \]

Surface area of one nanoparticle:

\[ S_{AN_P} \approx 1.2 \times 10^3 \text{ nm}^2 \]

NT sample dimension : 15 mm x 12 mm

\[ N_{NT} = \frac{A_{sample}}{S_{top}} \]

# nanotubes in sample = 5.7 x 10^9

NP sample dimension : 5 mm x 35 mm

\[ N_{NP} = \frac{V_{sample}}{V_{NP}} \]

# nanoparticles in sample = 3.8 x 10^{11}

NT total surface area:

\[ S_{A_{total}} = N_{NT} \times S_{AN_T} \]

\[ = 5.2 \times 10^{16} \text{ nm}^2 \text{ or } 5.2 \text{ cm}^2 \]

There are two sides so SA x 2 = SA total

NP total surface area:

\[ S_{A_{total}} = N_{NP} \times S_{AN_P} \]

\[ = 4.7 \times 10^{14} \text{ nm}^2 \text{ or } 4.7 \text{ cm}^2 \]

NT has 10% more surface area than NPs.
2. Photoluminescence Spectroscopy

2.1 Thin Film “Bulk” Photoluminescence

a. Experimental Set-up

The experimental set-up to measure the photoluminescence emission of thin films is shown in Figure A2.1. This is a backscattered configuration wherein the incoming laser excitation is approximately 45° incident to the film. The laser is focused into a line on the sample surface by a cylindrical lens. The collection lens is located 1 cm in front of the sample surface to collect the optimum signal. The collimated signal passes through a long pass or notch filter before being focused back into the entrance slit of the monochromator. This PL set-up is also referred to in this dissertation as the “bulk” photoluminescence set-up to distinguish it from the micro-photoluminescence set-up of single nanotubes and nanoparticle clusters.

b. Power measurement

Fig. A2.1 PL spectroscopy set-up for bulk measurements
The incident power of the 350.7nm excitation is measured by the Melles Griot bolometer after the cylindrical lens and shown in Table A2.1.

<table>
<thead>
<tr>
<th>at laserhead (mW)</th>
<th>at sample plane w/o BP filter and obj</th>
<th>BP filter transmission</th>
<th>power with BP filter (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.5</td>
<td>0.23</td>
<td>0.805</td>
</tr>
<tr>
<td>15</td>
<td>6.1</td>
<td>0.23</td>
<td>1.403</td>
</tr>
<tr>
<td>20</td>
<td>8.27</td>
<td>0.23</td>
<td>1.9021</td>
</tr>
<tr>
<td>25</td>
<td>11.14</td>
<td>0.23</td>
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<tr>
<td>30</td>
<td>13.39</td>
<td>0.23</td>
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<td>35</td>
<td>16.01</td>
<td>0.23</td>
<td>3.6823</td>
</tr>
<tr>
<td>40</td>
<td>18.28</td>
<td>0.23</td>
<td>4.2044</td>
</tr>
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</table>

**c. Polarized Bulk PL Set-up**

The light exiting the laser is polarized vertically. The polarization vector is parallel to the surface. To study the effect of polarization on the nanotube photoluminescence, a half wave plate was placed before the 45° mirror. The PL was recorded in horizontally and vertically polarized excitations. The vertically polarized excitation (as mentioned earlier) hits parallel to the surface of the tubes while the horizontally polarized one has a component that in the direction of the axis of the tubes. Figure A2.2 shows the experimental set-up and the results of the polarized excitation PL emission.
2.2 Micro-Photoluminescence Spectroscopy

a. Micro-PL Spectroscopy and Imaging Set-up

To be able to have spatial as well as energetic information from the PL emission, a micro-PL set-up was built. It consists of an inverted microscope coupled to two detectors – a single monochromator spectrometer with a thermoelectrically cooled CCD (Acton and Spec-10) and a thermoelectrically cooled inter-line CCD with a focusing lens set (Andor Clara and...
Computar). Figure A2.3 shows the set-up and the location where filters can be inserted. At the top of the inverted microscope is the sample stage where various environments can be introduced.

![Fig. A2.3 Micro-PL spectroscopy and imaging set-up](image)

**b. Power Measurement using the micro-photoluminescence set-up at 100x magnification**

Figure A2.4a shows a schematic of the micro-photoluminescence set-up. The beam divergence after the focus point is so large that the bolometer (Melles Griot) is unable to get an accurate reading of the power of the beam after the 100x objective. Therefore, to measure the power incident on the sample, the power of the laser without the 350 nm bandpass filter (Thorlabs FGUV11) and the 100x objective (UPLSAPO) is measured and the transmittance of these two optical elements inserted in the calculation to get the final value for power. Figure A2.4b and c shows the absorbance of the band pass filter and transmittance of the objective respectively. Table A2.2 shows the calculated values of power.
Fig. A2.4 a) Experimental set-up of the micro-PL b) UV-Vis absorbance of the 350 nm band pass filter c) Transmittance of the 100x objective
c. Diameter of the beam spot after 100x objective

Dilute (< 1% by weight) aqueous silver nitrate was dropped on a thin anatase film. The film was then exposed to the UV laser focused by the 100x objective. The Ag\(^+\) is converted into Ag (dark spot). The dark spot was then observed with regular microscope illumination and the graduation of the color/darkness of the film. The image is converted into a distribution on intensity and the spot registers as a plateau (see figure A2.5). The measured spot is larger than the actual focused beam area because the silver nitrate tended to bleed through the film.

<table>
<thead>
<tr>
<th>at laser head (mW)</th>
<th>at sample plane w/o BP filter and obj</th>
<th>BP filter transmission</th>
<th>power with BP filter</th>
<th>100x transmission</th>
<th>power at sample with BP filter and 100x obj (mW)</th>
<th>Power density (mW/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
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<td>0.45</td>
<td>0.056925</td>
<td>1.50E+06</td>
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<tr>
<td>15</td>
<td>1</td>
<td>0.23</td>
<td>0.23</td>
<td>0.45</td>
<td>0.1035</td>
<td>2.72E+06</td>
</tr>
<tr>
<td>20</td>
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<td>0.23</td>
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<td>4.17E+06</td>
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<tr>
<td>25</td>
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<td>0.23</td>
<td>0.4692</td>
<td>0.45</td>
<td>0.21114</td>
<td>5.55E+06</td>
</tr>
<tr>
<td>30</td>
<td>2.46</td>
<td>0.23</td>
<td>0.5658</td>
<td>0.45</td>
<td>0.25451</td>
<td>6.70E+06</td>
</tr>
<tr>
<td>35</td>
<td>2.96</td>
<td>0.23</td>
<td>0.6808</td>
<td>0.45</td>
<td>0.30535</td>
<td>8.06E+06</td>
</tr>
<tr>
<td>40</td>
<td>3.35</td>
<td>0.23</td>
<td>0.7705</td>
<td>0.45</td>
<td>0.346725</td>
<td>9.12E+06</td>
</tr>
<tr>
<td>50</td>
<td>4.35</td>
<td>0.23</td>
<td>1.0005</td>
<td>0.45</td>
<td>0.450225</td>
<td>1.18E+07</td>
</tr>
<tr>
<td>60</td>
<td>5.35</td>
<td>0.23</td>
<td>1.2905</td>
<td>0.45</td>
<td>0.553725</td>
<td>1.46E+07</td>
</tr>
</tbody>
</table>
d. Fabrication of the Quartz Grid for Correlated SEM and PL

Optical images cannot resolve the features of a single nanotube. To be able to correlate the photoluminescence data with the actual morphology of the nanotube, scanning electron microscopes should be used. However, the image in an SEM may not exactly look like the optical so a system to correlate the two images should be created. The photoluminescence measurements in titanium dioxide are done using a UV laser excitation which limits the substrate to quartz. The quartz cover slips are 19 x 19 mm with 0.17 mm thickness from ChemGlass. Since there are no commercially available quartz grids, a lithographic technique was used to create one (see figure A2.6). First a mask was designed and printed into an ordinary transparency. A positive resist was then spin coated into a quartz cover slip (previously cleaned with a 5-step cleaning process – acetone > isopropanol > DI water > acetone > isopropanol >
dried with N₂). The mask is patterned through contact UV lithography and developed. A thin layer of gold was sputtered. The remaining photoresist was removed by acetone. A few seconds to a minute immersed in acetone while sonication removes most of the resists, however prolonged ultrasonic cleaning strips the gold from the quartz. The quartz grid is washed in water and air-dried prior to spin-coating with dispersed nanoparticles/nanotubes.

![Figure A2.6 Correlated PL and SEM grid showing the gold pattern on the quartz cover slip](image)

**e. Quantum Efficiency of the Andor Clara Interline CCD and Transmission of the Different Filters**

The following spectra show the performance of the CCD and filters used in the micro-PL imaging. Figure A2.7 shows the QE of the Andor inter-line CCD showing the peak QE of 60%
at 500 nm. The Transmission of the 510 nm (teal) bandpass filter is maximum at around 72% and that 610 nm is fully transmitting at around 650 nm (figure 2.8).

Fig. A2.7 Quantum Efficiency of the Andor Clara Interline CCD
2.3 Calibrating the Spectrometer

The Photoluminescence emission measurements were taken using an ACTON SpectraPro 2300i single monochromator coupled to a thermoelectrically-cooled Spec-10 CCD detector. The response of the detector was determined using an Oriel standard lamp (Model #63358) according to the set-up given with the instrument. The high-reflector used was MgO powder deposited on a stainless steel plate upon burning magnesium. The result is shown in Figure A2.9. The correction factor is around 1 within 500 to 800 nm, however, between 400 to 500 nm showed some variation. Another method used is the use of secondary standards given in the paper by Gardecki et al. Here, the correction factor from 400 to 500 nm is around 0.8 to 1.25, see figure A2.10.
The spectrometer and the detector readings are not significantly different from the standards and thus it is considered calibrated.
REFERENCE:

1. Gardecki, J.A.; Maroncelli, M. Set of Secondary Emission Standards for Calibration of the 
   Spectral Responsivity in Emission Spectroscopy *Applied Spectroscopy* **1998** 52 (9), 1179
3. **Assembly and Performance Measurement of the DSSC**

![Diagram](image)

**Fig. A3.1** a) Power conversion efficiency set-up  b) Typical current-voltage plot of a solar cell

Here is a general procedure on the assembly and measurement of DSSCs. Variations to the materials and steps may be done and will be specified in the experimental section of the papers/chapters. The nanotube array film on titanium is the photoanode side of the DSSC. The cathode is made by dropping 6 drops of 2.5 mM hexachloroplatinate(IV) (H$_2$PtCl$_6$ from Acros Organics) in 2-propanol (Fisher Scientific reagent grade) on the conductive side of the TEC 8 FTO glass (Hartford) and heating at 400 °C in the muffle furnace for 30 minutes followed by rinsing with 18 MΩ water. The redox electrolyte was made by dissolving LiI and iodine in solvents such as methoxypropionitrile (MPN from Fluka) or as specified in the experimental section of the paper. The sensitizing solution is made up of N3 (cis-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II), Solaronix) dissolved in ethanol or betanin (extracted from beets following the reference given in chapter 6) in 18 MΩ water. Drops of the electrolyte are put on the sensitized titanium dioxide and the Pt coated electrode is pressed on to the anode.
and held by metal clips. Prior to putting the electrolyte, an option to seal the solar cell can be done by putting JB-Industro-Weld on the edge of the two sides and holding these steady for 24 hours for the glue to set. When sealing, it is important to first drill holes on the side of the FTO to provide access for filling the electrolyte.

The efficiency of dye sensitized solar cell devices were measured using a Xenon arc lamp (connected to an Ealing power supply) as the source of illumination. This set-up is shown in figure A3.1a. The light passes through a 400 nm long pass and an 800 nm short pass filters to reject the UV and NIR. A Melles Griot Broadband Power/Energy Meter (13PEM001) was used to calibrate the light intensity to 13 mW. The illumination area is 0.126 cm² thus the corresponding illumination density or irradiance is 103.45 mW/cm². The platinum electrode is connected to the positive (red) terminal while the TiO₂ is connected to the negative (black). The connectors were plugged into the Keithley 2400 Source Meter and a voltage was stepped from 0 to 800 mV in 10 mV intervals. The current output was measured and the I-V curve plotted to determine the maximum power output of the solar cell. Figure A3.1b shows the typical I-V curve of a solar cell.

The power conversion efficiency is calculated by

\[ P_m = V_m \times I_m \]

\[ \eta = \frac{P_m}{P \times A} \]

\[ FF = \frac{P_m}{V_{oc} \times I_{sc}} \]
where $P_m$, $V_m$, and $I_m$ are the maximum power, voltage, and current given by the solar cell, $P$ is the input light in $W/m^2$ and $A$ is the area of the solar cell.

The Incident-Photon-to-Electron Conversion efficiency is measured using the Fluorimeter (Photon Technologies Inc) monochromatic light source instead of the Xenon Lamp. The photocurrent is measured for each wavelength step and recorded. It is then compared to the lamp profile and the percent of electrons gathered is divided by the supplied photons.

$$Quantum\ Yield, \ \Phi = \frac{\#\ of\ electrons,n}{\#\ of\ photons,N}$$

$$\Phi = \frac{en}{eN} = \frac{en/s}{eN/s} = \frac{I\ (amp)}{eN/s}$$

$$\Phi = \frac{I(amp)/cm^2}{eN/s/cm^2}$$

Incident Power:

$$P = Nh\nu$$

$$P\ \left(\frac{Watt}{cm^2} \ or \ \frac{Joules}{sec\ cm^2}\right) = Nh\frac{c}{\lambda}$$

$$P\ \left(\frac{J}{s\ cm^2}\right) = \left(\frac{N}{s\ cm^2}\right)(6.62 \times 10^{-34}\ Js) \times \frac{3 \times 10^8\ m/s}{\lambda(nm) \times 10^{-9}\ m}$$

$$\frac{N}{s\ cm^2} = \frac{P\ \left(\frac{J}{s\ cm^2} \ or \ \frac{W}{cm^2}\right) \times \lambda(nm)}{(6.62 \times 10^{-17}) \times 3}$$
\[
\frac{N}{s \ cm^2} = \frac{\text{Power} \left( \frac{W}{cm^2} \right) \times \lambda(nm) \times 10^{17}}{19.86}
\]

\[
\Phi = \frac{I_{sc} \left( \frac{amp}{cm^2} \right) \times 19.86}{e \times P \left( \frac{W}{cm^2} \right) \times \lambda(nm) \times 10^{17}}
\]

\[
= \frac{I_{sc} \left( \frac{amp}{cm^2} \right) \times 19.86}{1.6 \times 10^{-19} \times P \left( \frac{W}{cm^2} \right) \times \lambda(nm) \times 10^{17}}
\]

\[
= \frac{I_{sc} \left( \frac{amp}{cm^2} \right)}{P \left( \frac{W}{cm^2} \right)} \times \frac{1240}{\lambda(nm)}
\]

\[
\text{IPCE} (%) = \frac{I_{sc} \left( \frac{amp}{cm^2} \right)}{P \left( \frac{W}{cm^2} \right)} \times \frac{1240}{\lambda(nm)} \times 100
\]
4. Spectroelectrochemistry

Because photoluminescence observes electronic states, the application of bias is a useful tool in understanding the nature of the charge carriers and traps involved in the emission. Figure A4.1 shows the spectroelectrochemistry set-up used in the experiments. A 10mm x 50mm quartz cuvette was used as the reaction chamber, a platinum wire was used as the counter electrode, silver wire for the reference electrode, and the voltage was supplied by the Keithley 2400. The silver wire was used in conjunction with the non-aqueous electrolyte (NaClO₄ in acetonitrile) and standardized with ferrocene/ferrocenium Fe(C₅H₅)₂ / [Fe(C₅H₅)₂]+ reference.

Fig. A4.1 Spectroelectrochemistry set-up

Fig. A4.2 Plot of the photoluminescence with Voltage on one axis and wavelength on the other.
The following spectra show the results of spectroelectrochemistry of titanium dioxide nanotube film on titanium substrate in a 0.1M NaClO₄ in acetonitrile electrolyte.

Figure A4.2 show the Matlab plot of the photoluminescence spectra in various applied voltages. The PL showed no significant shifts at low voltages ~ 2.0 to -5.0V versus silver electrode. At 2.2V a spectrum shift to the green and an increase in the 425 nm peak is observed, this change is reversible and the spectrum is seen to go back to the original one when the applied voltage is decreased. On reversing the bias, at -5.2V, the spectrum undergoes a shift to the blue with a seemingly P25-like emission, however, the 425 nm peak is much more intense. These are seen in more detail from the series of spectra in figure A4.3.

Fig. A4.3 The development of the spectrum as the applied voltage is varied a) positive bias b) negative bias.
From the high negative bias and upon decrease of the applied voltage, the spectrum switches from the one in figure A4.3b to the intense PL in Figure A4.4a. This change is irreversible and variation of the applied voltage after this point does not affect the PL intensity or shape. The PL becomes a function of time, where initially, it increases but after reaching peak intensity proceeds to dim at an exponential rate (see figs. A4.4b and c).

Fig. A4.4 a) PL before (black-lower intensity) and after (red-higher intensity) switching the large bias off. PL shows a definite trend when plotted with time in b, against that plotted with applied voltage in c.
The shape of the resulting emission after the large bias is removed (figure A4.4a) is similar in shape as the initial nanotube PL and PL after vacuum annealing. This means that the defect site responsible for this intraband PL is the same.

Fig. A4.5 Development of the intensity of the two major peaks in nanotube PL – 425 nm and 525-550 nm in a) positive bias b) negative bias. The PL intensity is plotted against applied voltage and the current flowing between the working electrode and the counter electrode is also plotted.
Figure A4.5 shows that current flow upon application of negative voltages and starts to exponentially rise at ~ -4V. At this potential, the electrolyte is not only polarized but already participating in charge transport. The kinetics of the recombination depends on the concentration of the mobile component. The polarization of the electrolyte stabilizes the charges on the surface of the nanotube and prevents from participating in the photoluminescence relaxation. Upon release of the field, these electrons become part of the mobile electron concentration and resulting to the increase in PL intensity.

Fig. A4.6 The effect of applied bias and electrolyte polarization on the band structure of TiO$_2$ and the charges participating in the PL relaxation with no applied bias. 4.33V is the workfunction of titanium and 4.93 V is the conduction band level of anatase with respect to vacuum level. Energies are $E_C$ = conduction band, $E_F$= Fermi level, $E_V$ = Valence band, and $E_d$ = defect state. The ions are Na$^+$ and ClO$_4^-$ in acetonitrile.
APPENDIX B

CHARACTERIZATION

1. Photoluminescence Spectroscopy
2. Raman Spectroscopy
3. Diffuse Reflectance Spectroscopy
4. Scanning Electron Microscopy and Electron Backscatter Diffraction
1. Photoluminescence Spectroscopy

1.1 Introduction

Photoluminescence (PL) is a spontaneous emission of radiation as a means of relaxation from an excited state to a lower lying state. Figure B1.1 shows the Jablonski diagram of the PL process. The difference of PL from other forms of luminescence is the use of light as the source of excitation. Because the emissions have the energy of the electronic transitions, PL is an effective method in electrical characterization. Thus, the PL signal is a characteristic of the material. However, PL is limited only to observation of radiative events and can only identify defects and impurities that are optically active. Additionally, the emission is usually of longer wavelengths than the excitation. This is because upon excitation, the relaxation process to energies within $k_B T$ of the lowest available state is much faster than recombination. This difference is called the Stoke’s shift.

As a prerequisite to PL emission, the material should be excited with light of sufficient energy for the electron to go to the excited state. In molecules the choice of excitation...
wavelength depends on the absorption maximum while in semiconductors, the excitation is chosen to have energy greater than the bandgap.

There are two types of luminescence – fluorescence and phosphorescence, however, in this research the emissions are taken in steady state and will just be referred to as photoluminescence.

1.2 Electronic properties of Anatase

Anatase is the crystal structure of interest in this research. Figure B1.2a shows the band diagram calculated by ab initio method from Ref. 1. In figure B1.2b, the Brillouin zone of anatase is shown, taken from Ref 2 and the directions corresponding to the axes in k-space are indicated. The maximum of the valence band occurs at 0 eV while the minimum of the
conduction band is at 3.3 eV. Hence, anatase exhibits indirect band gap and its bandgap emission is forbidden.

PL can be considered as a surface technique because it originates near the surface of the material probed, however, this varies with the excitation and the material. The penetration depth, which is the inverse of the absorption coefficient of a monochromatic light, can be measured using the absorbance with a known concentration of material. However, it can also be back calculated from a Tauc Plot. Reference 3 published a Tauc plot of the anatase titanium dioxide nanotubes and from this, the absorption coefficient at the excitation wavelength was calculated as shown in the next paragraph.

Figure B1.3 shows an example of a Tauc plot, which is used to determine the location of the band edge of amorphous and nanocrystalline materials. This is a plot of $(\alpha \hbar \omega)^{1/2}$ against $\hbar \omega$ from the equation:
This equation was derived in Ref. 4 from the definition of the absorption coefficient, intensity, and assumption of a parabolic density of states. From Ref. 3, the y-intercept of the Tauc plot for TiO\textsubscript{2} nanotubes is 275 cm\textsuperscript{-1/2}eV\textsuperscript{1/2} at 3.5 eV (corresponding to 350 nm), thus \( \alpha = 21607 \text{ cm}^{-1} \) and using \( \delta_P = \frac{1}{\alpha} \), where \( \delta_P \) is the penetration depth and calculated to be 0.46 \( \mu \text{m} \).

### 1.3 Analysis of the PL Intensity

The intensity of the exciting light controls the density of photogenerated electrons and holes and the mechanism of the electron and hole recombination is affected by carrier density. As an example given in Ref. 5, the number of interface and impurity states is finite for a certain sample and recombination at these states saturate at higher excitation.

![Fig. B1.4 Relationship between the PL intensity and excitation power and the states that give rise to these emissions.](image)
From Ref. 5 and 6, the relation between the excitation intensity and the PL intensity can elucidate the distribution of surface states. Figure B1.4 shows the plot redrawn from the references. This plot is important in identifying the characteristics of the intra-band states.

1.4 Information from the PL Spectrum

In a perfect semiconductor crystal, translational symmetry causes splitting of discrete energy levels into bands. Disruption in the ordering of atoms by defects results in a discrete/localized state within the band gap. Figure B1.5 shows the effect of a vacancy in the

Fig. B1.5 Electronic states of a) a perfect crystal of NaCl and b) Effect of defects in the lattice on the intra-band states (Ref. 7)
band structure of a material. These intra-band states are charged and attract oppositely charged carriers and bound by Coulombic forces. The binding energies differ between these defect systems because their effective masses vary. The trapped carriers can radiatively recombine and the energy of emission is the energy of the defect level. Figure B1.6 shows the various recombination pathways within the bandgap.

Surface states also contribute to intra-band PL because of dangling bonds which lead to surface reconstructions and/or adsorption of impurities from the environment.

Because PL probes the electronic states of a material, the application of a bias in an electrochemical set-up can change the observed PL emission. This is called spectroelectrochemistry and when applied to intra-band PL can show the activity of the trap states. The nature of the carriers contributing to the emission can be determined.
REFERENCES:


2. Raman Spectroscopy

2.1 Introduction

Raman spectroscopy makes use of the inelastic scattering of light. It occurs with either a creation (Stokes) or annihilation (anti-Stokes) of an excitation from the crystal or phonons. Figure B2.1 shows a simple diagram of these processes; note that for the anti-Stokes process to be observed, the crystal should already be in an excited state. As opposed to absorption and emission, scattering occurs mainly through virtual intermediate electronic transitions.

![Fig. B2.1 Rayleigh and Raman scattering](image)

2.2 Raman Modes of Anatase

The Raman spectrum of anatase is usually composed of four well defined peaks. The 144 cm\(^{-1}\) E\(_g\), 399 cm\(^{-1}\) B\(_{1g}\), 513 cm\(^{-1}\) A\(_{1g}\), and the 639 cm\(^{-1}\) E\(_g\). The 144 cm\(^{-1}\) peak is very close to the laser line and is usually cut-off by the notch filter when using a single monochromator. A double monochromator solves this problem and this low frequency mode is observed.
2.3 Experimental Set-up

The Raman set-up used in this study is the SPEX Ramalog double monochromator system with a Photomultiplier Tube (PMT) detector; the layout is shown below in figure 2.3. The excitation laser passes through a holographic band pass filter. The scattered light is collected and passes through a polarization analyzer and then through a scrambler before going to the spectrometer.

Fig. B2.2 From T. Ohsaka, et al. (Ref 1), the displacements of the oxygen and titanium atoms are shown for each of the optical lattice vibrations of anatase
2.4 Calibrations

Shifts in the peak position are important information in Raman studies so it is necessary to know the accuracy of the wavenumbers given by the “double.” A calibration using the position of the Hg lines (with a mercury lamp) was done and showed a deviation from the literature value of 0.55 to 1.55 cm⁻¹. Because the double monochromator is composed of moving parts, it is also necessary to determine whether the peak position changes due to equipment motor backlash. It was found by repeating the measurement twice that a variation of 1.27 to 2.27 cm⁻¹ is the machine limitation. Figure B2.4 shows the spectra resulting from the measurements described.
Fig. B2.4 Frequency calibration of the double monochromator with a Hg lamp
REFERENCE:

3. Diffuse Reflectance Spectroscopy

3.1 Introduction

When light is incident into a material, it is either reflected, absorbed, or transmitted. Absorbance of light (in the UV-Visible region) occurs when the energy of the light is equal to that needed for an electronic transition. UV-Vis, therefore determines the bandgap of a semiconductor and the presence of states with energies just below the bandgap (bandtails), usually caused by defects.

3.2 Experimental Set-up

![Integrating Sphere](image)

Fig. B3.1 UV-Vis Diffuse reflectance using an integrating sphere

The diffuse reflectance spectrum was measured using a Perkin Elmer UV/Vis/NIR spectrometer with an integrating sphere. A Labsphere Spectralon (PTFE) and a Lambda Physik
aluminum mirror were used as reference reflectors. The specimen was set-up to reject the specular reflection leaving only the diffuse reflectance to be collected (figure 3.1).

3.3 UV-Vis Diffuse Reflectance of Anatase TiO₂ Nanotubes

Observations of the nanotubes with the naked eye showed that the nanotube film is blueish in color, while anatase films are white. This is also seen from the diffuse reflectance spectra of the two materials shown in Figure B3.2. The absorbance, however, of the two materials are comparable at 350 nm – which is the wavelength used to excite photoluminescence. The reflectance of nanotube samples range from 5 to 12% in various samples showing the inhomogeneity of the anodized nanotube film (figure B3.3).

![Fig. B3.2 Comparison of the diffuse reflectance spectra of nanotube and nanoparticles or anatase showing similar reflectance/absorbance at 350 nm](image-url)
3.4 Diffuse Reflectance and Kubelka-Munk Transform

The diffuse reflectance spectrum can be analyzed using the Kubelka-Munk function to determine whether a material has direct or indirect band-gap. The KM function, $F(R\infty)$, relates to the optical characteristics through the following:

![Comparison of diffuse reflectance spectra of nanotube and showing variations in visible reflectance of various samples (A, B, and C) but similar reflectance/absorbance at 350 nm](image)

Fig. B3.3 Comparison of the diffuse reflectance spectra of nanotube and showing variations in visible reflectance of various samples (A, B, and C) but similar reflectance/absorbance at 350 nm
Where \( K \) is the absorption coefficient and \( S \) is the scattering coefficient

\[
K = 2\alpha
\]

\( S = \text{constant} \)

There are two relations that can be used to relate the KM function and the energy:

\[
\alpha^n = \text{Const} \left( h\nu - E_g \right)
\]

Or

\[
(\alpha h\nu)^n = \text{Const} \left( h\nu - E_g \right)
\]

Where \( n \) is given by

\[
n = \begin{cases} 
  2, & \text{for direct, allowed} \\
  2/3, & \text{for direct, forbidden} \\
  1/2, & \text{for indirect, allowed} \\
  1/3, & \text{for indirect, forbidden} 
\end{cases}
\]
The function \([F(R_{\infty})h\nu]^{1/3}\) is plotted against \((h\nu)\) and the \(E_g\) is found by extrapolating the linear part of the absorption edge to the x-axis (in eV). This resulted in a value of around 3.0 to 3.2 eV for the nanotubes (figure B3.4).

Fig. B3.4 a) The diffuse reflectance spectrum of TiO\(_2\) nanotubes b) Kubelka-Munk transform to determine the location of the band edge. It was seen to be \(E_g = 3.0-3.2\) eV, reported literature data 3.34eV (Mor et al., Solar Energy Materials & Solar Cells 90 (2006) 2011-2075)
REFERENCES:


4. Scanning Electron Microscopy and Electron Backscatter Diffraction

4.1 Theory

Scanning electron microscopes were used extensively to determine the morphology of the anodized films. Figure B4.1 shows an electron beam and the corresponding volume of the sample that the electrons will interact with and the depths of the sample which contribute to the various signal detected. Although the interaction volume depends on the parameters of the electron beam, secondary electron imaging and cathodoluminescence contain information about the surface, backscattered electrons in intermediate depths and x-rays for the bulk.

Fig. B4.1 Interaction volume of the sample bombarded with an electron beam, different signals come from different regions of the sample. The scale of the excitation volume is dependent on the electron beam parameters.
To determine the crystallographic texture, electron backscatter diffraction was used. When an energetic beam of electrons is incident on a crystal plane, diffraction occurs in accordance to Bragg’s law which results in the appearance of lines on a camera/phosphor detector (figure B4.2). This is called the electron backscatter diffraction patterns (EBSP) and is transformed into Hough space and indexed by a computer algorithm (details beyond the scope of this section). A library of indexes for crystals phases of various common materials is available and determination for a sample with a known composition and structure is fairly quick once a nice image has been recorded.

4.2 Experimental Set-up and Results

Scanning electron images at high magnification showed crystallites on the open end of the nanotubes. These crystals are around 100nm in width and are bipyramidal in shape. These grow on the region of disorder on the top surface of the nanotubes, which are composed of
incomplete, heavily etched or dissolved tubes. Due to the random order of the crystallites, EBSD patterns were difficult to obtain. However, at higher beam current ~23nA (accelerating voltage 30 Kv and beam spot of 3nm), diffraction patterns were seen from several crystal planes. Automatic indexing done by pattern recognition and phase identification through voting confirmed the crystallites to be anatase.

Due to the roughness of the open-end surface of the nanotube, no electron diffraction pattern was seen in several areas tested. Treatment of the surface is necessary. Gallium-ion milling, however, created amorphitization and caused curtaining, thus, diffraction patterns were also not observed for sectioned samples.

Fig. B4.3 Electron backscatter diffraction pattern from the nanotube wall, the interaction volume is around 10 nm.
Fracture surfaces, however, gave smooth continuous surfaces (figure B4.3). Although the angles with respect to the beam still vary, some tubes satisfy the condition for $20^\circ$ tilt with respect to the EBSD detector. These gave more than 3 diffraction lines suitable for pattern indexing.

Figure B4.4 shows an orientation map of a cluster of nanotubes. At 100kx magnification, the electron beam scans with a 10nm step size and a dwell time of 1.258 sec/point. The resulting image is a color-coded plot of the crystal planes comprising the wall of the nanotubes. In this figure, only the top shows a contiguous structure. The lower part shows areas where identifiable diffraction patterns were taken but do not show any structure. The black region is area where no consistent or clear pattern was seen.

The walls of the nanotubes are mostly (110) and (100). The (001) was not seen but planes close to this orientation can be seen on the uppermost of the map and corresponds to the tubes that are slightly rotated from the ordered nanotubes shown (figure B4.4). These tubes are presented to the electron beam from a slight axial direction. Because the sample is tilted $20^\circ$ with respect to the electron beam and $110^\circ$ from the EBSD detector, the area from the SEM image is smaller than the orientation map.
From this result, it can be see that the nanotube walls are composed mostly of planes that are parallel to the c-axis of the unit cell (figure B4.5). This means that the nanotube structure supports crystallization where the unit cell’s longer side is along the axis of the nanotubes.

Fig. B4.4 Orientation map of a cluster of nanotubes with the corresponding SEM image of the area scanned. The lower right is the legend of the colors and the crystal planes they represent.

Fig. B4.5 Anatase unit cell with the lattice parameters and the crystal planes that corresponds to the legend in figure B4.4.

\[ a = 3.7845\text{Å} \quad c = 9.5143\text{Å} \]
Figure B4.6 below illustrates the position of the unit cell on several points of the orientation map. It should be noted that the dimension of the areas corresponding to one crystallographic orientation is around 800 nm. Within the ‘green’ and the ‘blue’ regions, only small variations in orientation were seen. This signifies that grains in nanotubes can have dimensions in the hundreds of nanometers and these are aligned vertically on the tube walls.

Fig. B4.6 A part of the map of a cluster of nanotubes showing the orientation of the unit cell in the location indicated by the arrows.
REFERENCES:


APPENDIX C: The Mechanism of Formation of Titanium Dioxide Nanotubes by the Anodization of Titanium

Titanium dioxide (TiO\textsubscript{2}) is a wide bandgap semiconductor present in three polymorphs – rutile (3.0eV), anatase (3.2eV), and brookite.\textsuperscript{1} Rutile is stable in larger grains while the anatase phase is stable in microscopic grains.\textsuperscript{1}

The first report on the formation of nanoporous titania was published by Zwilling et al. (1999) after observing the structure upon subjecting a film to a dilute HF solution. In 2001, Grimes et al showed the formation of nanotubes by anodization of titanium films in an electrolyte containing HF.\textsuperscript{2} Since then several studies have been published on the relationship between the process parameters and the resulting structure (pore size, tube length, wall diameter, etc).

The reason for the growing interest in this material is that the ordered array of nanotubular TiO\textsubscript{2} can be used in many different applications. The electrical resistance of TiO\textsubscript{2} nanotubes varies greatly in the presence of any gas, which makes it a good sensor.\textsuperscript{3} Another important application is the use of TiO\textsubscript{2} nanotubes in dye-sensitized solar cells where the tubes provide a more direct charge percolation path (compared to nanoparticles) and improve the lifetime of the charge carriers.\textsuperscript{3} In addition to it having a wide-range of applications, another good characteristic of TiO\textsubscript{2} nanotubes is the uniformity and predictability of the structure. TiO\textsubscript{2} nanotubes will form, provided it is exposed to the correct growing conditions, and the structure will be comparable to literature. This type of growth is often referred to as self-organized and
although with respect to processing it is relatively simple, the mechanisms involved in the formation of the tubes is more complex.

TiO$_2$ nanotubes are formed when a film of high purity titanium metal is anodized in fluoride containing electrolytes with voltages ranging from 2V$^4$ to 65V$^5$ opposite a Pt counter electrode. There are several factors to consider, voltage applied (including ramp, pulsed, etc), surface of the titanium foil, viscosity of the electrolyte, composition of the electrolyte (amount of F$^-$, presence of NH$_4^+$ ions, amount of water), distance between the electrodes, and anodization time.

The structure of TiO$_2$ nanotubes is different from other nanotubes; they are open on the surface, thus you will see only an array of circular tube mouths when viewed from the top. The bottom is rounded and closed and packed similar to grains. To be able to illustrate more clearly, the nanotubes are like laboratory test tubes arranged as vertically as closely-packed as possible. Several papers have described the mechanism of formation of TiO$_2$ nanotubes as a combination of the following key processes: chemical dissolution and metal oxide formation.$^6,7,8$ However, the explanations did not cover all the aspects of tube formation, so for this paper, the key processes are broken down into smaller steps for clarity. These steps are oxide nucleation and growth, pore nucleation, pore growth, and tube growth.

1. Oxide Nucleation and Growth

   An anodization cell is a typical two electrode electrochemical cell with the titanium foil attached to the positive electrode (anode) and a platinum counter electrode to the cathode. Upon switching the voltage, the following reaction takes place.$^7$
This is equation is the net of two electrolytic reactions, the anodic reaction of metallic Ti which results in Ti⁴⁺ and the reaction with water to form TiO₂ and release H⁺. This reaction forms a thin layer of barrier oxide. FESEM images of the surface of anodized foils after a 5s anodization time showed the surface to be composed of small round grains [6 Fig 3a]. Studies have been done correlating the appearance of the surface to the anodic polarization curve and the current density at the onset of formation of the oxide. These showed that the log current density increase as the potential is increased until the critical current density is achieved signaling the onset of passivation. This point correlated to the formation of the barrier layer from the SEM image. These data confirmed the formation of the barrier oxide layer, however, the actual mechanism of nucleation and the microstructure of this layer has not yet been fully explored. Similarly, another important but not yet clearly understood aspect is the growth of the barrier oxide and the state that this layer is in (with respect to stresses) because this plays a large role in the next step of tube formation.

One of the proposed stresses is a compressive stress that is induced by the volume expansion occurring during oxide layer formation:

\[
\sigma_{\text{vol}} = -\frac{(\partial V / V)Y(l - \nu)}{(1 + \nu)(1 - 2\nu)}
\]

where \(\partial V / V\) is the volumetric strain, \(Y\) is young’s modulus and \(\nu\) is Poisson’s ratio. Because of the applied anodization potential, the barrier oxide also experiences an electrostriction stress:
\[ \sigma_{es} = \gamma_{11} YE^2 \]

where \( \gamma_{11} \) is the electrostriction coefficient and \( E \) is the electric field. It has been described in Ref. 6 that the applied electric field causes the TiO\(_2\) to undergo polarization and the Ti-O bond becomes weaker. The electrostriction strain, which is dilatational, could have the same effect. Another important influence on the state of the barrier oxide under the applied potential is electrostatic or Maxwell stress expressed as:

\[ \sigma_{es} = -\frac{1}{2} \varepsilon_0 \varepsilon \varepsilon_0 \]

where \( \varepsilon_0 \) permittivity of free space, \( \varepsilon \) is the relative dielectric constant. Maxwell stress is said to exert a significant effect on the surface but only one part \((-\varepsilon^2\) of the tensor is given in the reference and the reason for assuming compressive stress only.

2. Pore Nucleation

The next step in nanotube formation is the pore nucleation. The barrier oxide layer, from SEM images presented in Refs. 6, 7, 8 is a relatively flat surface. However, due to the presence of the stresses mentioned above, this surface is unstable. A balance between the driving force to maintain the current structure and driving force for creation of new surfaces must exist. These driving forces are the surface energy which acts to maintain the surface flatness and the strain energies mentioned above which destabilizes the surface. From Ref. 6, pores nucleate because the polarized Ti-O bond is weak and easily dissociated. This is called field-assisted dissolution. In Ref. 7 the existence of these stresses is at equilibrium with the surface energy and it was proposed that a perturbation is necessary to actually initiate pore formation. The actual source of
the perturbation was not described, but this proposal addresses the observation that nanotubes form as an ordered array. The uniformity of the structure was not considered by the field-assisted dissolution proposal. The mechanism of pore nucleation based on perturbation considers a homogeneous barrier oxide layer, no localized stresses, to form uniformly spaced nanotubes. As stated in the section on oxide nucleation and growth, the state of stress of the barrier oxide layer may require further study to define the actual mechanism for pore nucleation. It is possible that within the barrier oxide, uniform localized stresses are present which could be sites for pore nucleation and a uniform array of nanotubes can be grown without external perturbation.

3. Pore Growth

The dissolution of the barrier oxide in the areas where the pores nucleate follows the reaction:\textsuperscript{7,8}

\[ \text{TiO}_2 + 6\text{HF} \rightarrow (\text{TiF}_6)^{2-} + 2\text{H}_2\text{O} + 2\text{H}^+ \]

This reaction together with the reaction to form TiO\textsubscript{2} from Ti metal and water result in accumulation of H\textsuperscript{+} as part of the product. Because of this the H\textsuperscript{+} concentration becomes non-uniform within the pore. A plot of the pH of the electrolyte inside the pore showed that the bottom is more acidic relative to the walls and that the etch rates are higher at the pore bottom than along the walls.\textsuperscript{9} In addition, the dissolution along the bottom of the pores is increased due to the mechanism of field-assisted dissolution described in earlier section. These conditions allow the pore to grow downward into the oxide layer while maintaining the thickness of the walls.
As the pore growth reaction is happening on the oxide-solution interface, the metal-oxide interface moves deeper and deeper into the metal as the oxygen-containing anions, $O^{2-}$ and $OH^-$, migrate through the oxide layer to the metal-oxide interface and react with the metal forming more and more layer of oxides. From SEM images, the thickness of the barrier layer appears to be uniform and approximately as thick as the nanotube walls. There were no quantitative studies done on this aspect in the referenced papers although this information could be used to determine the stress state of the barrier oxide. The thickness of the barrier layer at the pore bottom could signify the point where the driving forces of dissolution is in equilibrium with the stabilizing forces.

4. Wall Formation

Up to this point, the mechanisms given describe the formation of a surface filled with an array of uniformly sized pores. This section discusses the mechanism of formation of the tube walls. One mechanism proposed was the presence of un-anodized metallic portions between the pores where inter-pore voids start forming and growing together with the pores. This proposal lacks strength, although it may well be that inter-pore voids could form, the configuration suggested in Figure 5e of this paper does not agree with SEM images. In the proposal, the bottom of the voids are also protected by a barrier, however, SEM showed that the voids go through the oxide layer to the metal-oxide surface. The other mechanism presented in follows the point-defect model or vacancy condensation mechanism for alumina by D.D. MacDonald\textsuperscript{10} (Ref. 10) and explained as follows: When the oxide layer undergoes field-assisted dissolution, the Ti\textsuperscript{4+} diffuses into the solution leaving cation vacancies. These $V_{Ti}^{4-}$ are attracted to the anode and migrates toward the metal-oxide interface. Although not stated in the paper, the diffusion of
the titanium vacancy can also be driven by a concentration gradient where the inner portion of
the walls are rich in $V_{\text{Ti}}^{4-}$. Vacancies condense halfway between the walls of the tubes and at
points where three tubes meet because of high area disorder in those regions. Another reason for
the condensation of vacancies in these areas is that cation vacancies come from inside the pores,
so the midpoint between pores is the part where vacancies migrating inward would meet and in
regions bounded by three tubes, vacancies come from three sources. These are areas where the
rate of annihilation of vacancies is overcome by the rate of arrival of new vacancies, thus leading
to condensation of voids. In the paper it was mentioned that oxygen vacancies are also formed to
maintain charge neutrality, however, the behavior of this species was not described.

The mechanisms described above occur simultaneously during tube formation. The
nanotubes are growing towards the metal as more and more oxide layers are added and etched or
dissolved. If the current is high enough and the electrolyte does not get depleted of reactants, the
formation of nanotubes will continue until the titanium foil is consumed. The anodized TiO$_2$
nanotubes is initially amorphous and a high temperature anneal is required for it to crystallize.

The mechanisms described in sections 1 to 4 are mostly qualitative. Details are still not
yet fully understood and more experiments have to be done to confirm the proposed
mechanisms. The following questions remain for further study: What are the stresses acting on
the barrier oxide layer? How is it distributed in the surface? What is the structure of the barrier
layer? Is there evidence that vacancy condensation sites exhibit more disorder? What drives the
nucleation of pores? How do ions move through the solution and through the barrier oxide layer?
As mentioned earlier the anodization process of titanium foil to produce titanium dioxide
nanotubes is relatively simple but the mechanisms involved in their formation are complex and interesting.

Fig. C.1 Cartoon of the different steps in the formation of TiO$_2$ nanotubes.
REFERENCES:


