# PHOTODARKENING IN TELLURIUM-MODIFIED TITANIUM DIOXIDE NANOCRYSTALS

by

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A senior thesis submitted to the faculty of

Brigham Young University

in partial fulfillment of the requirements for the degree of

Bachelor of Science

Department of Physics and Astronomy

Brigham Young University

August 2008

BRIGHAM YOUNG UNIVERSITY

DEPARTMENT APPROVAL

of a senior thesis submitted by

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This thesis has been reviewed by the research advisor, research coordinator, and department chair and has been found to be satisfactory.

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ABSTRACT

# PHOTODARKENING IN TELLURIUM-MODIFIED TITANIUM DIOXIDE NANOCRYSTALS

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We have synthesized titanium dioxide nanocrystals that have been modified by addition of tellurium. After annealing, these nanocrystals become photosensitive, changing color from white to dark red when exposed to light. This change is stable, but reversible upon annealing. Te also causes a change in structure from rutile to anatase. The properties of these nanocrystals are explored.

# ACKNOWLEDGMENTS

I would like to thank Dr. Hess for his guidance and support as an advisor and Ian James for providing the TEM images. I would also like to thank the BYU Physics department and the Office of Research and Creative Activies for providing financial support.

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# Chapter 1

# Introduction

## 1.1 Titanium dioxide as a photocatalyst

The compound titanium dioxide ($TiO_2$) has been studied extensively and used commercially for several decades. One of the most important properties of $TiO_2$ is that it is a photocatalyst. Photocatalysis in $TiO_2$ is activated when exposed to ultraviolet light. Uses of photoexcited $TiO_2$ include breaking down pollutants in water and production of hydrogen gas by water splitting [1].

There are advantages to $TiO_2$ in nanoparticle form. The increased surface-to-volume ratio can result in an increase in the rate of the photocatalysis, as this effect occurs at the surface. They can also be used to produce electricity, and have application in solar cells [2].

A major drawback of $TiO_2$ use in solar hydrogen production is the limited absorption spectrum. $TiO_2$ has a band gap of approximately 3.5 eV, which corresponds to the absorption of light of about 350 nm, in the ultraviolet range, with essentially no absorption of light in the visible range. As only a small fraction of the solar spectrum reaching the earth's surface lies in the ultraviolet range, unmodified $TiO_2$

nanocrystals are unable to take full advantage of the solar radiation. There is much potential benefit in finding methods to increase the absorption of visible light in these nanocrystals. Some success has been found by doping $TiO_2$ with various elements, including carbon [3], nitrogen [4], and sulfur [5].

## 1.2 Tellurium modified nanocrystals

We have experimented with modifying $TiO_2$ nanocrystals with chalcogenides. We found that adding tellurium to the synthesis resulted in a powder that was photosensitive. The powder undergoes a change in color from off-white to reddish-brown when exposed to light. This change in color is stable, but is reversible upon annealing. To our knowledge, photodarkening like this has not been observed in doped $TiO_2$ or Te compounds. However, it has long been known that certain selenium-based glasses do exhibit photodarkening [6], [7]. We believe that there may be a similar underlying mechanism behind both these effects, and that they occur on the surface of the nanocrystals.

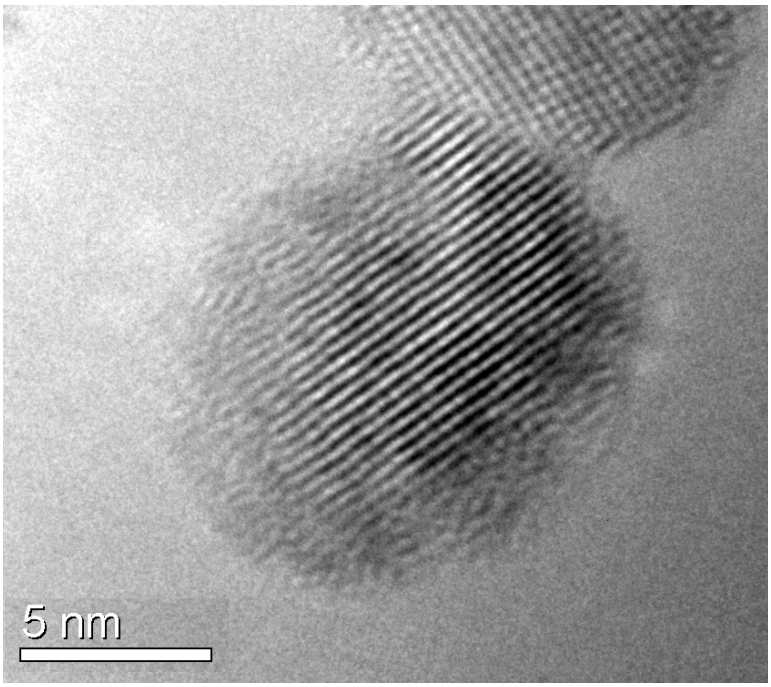


**Figure 1.1** A TEM image of a Te-modified $TiO_2$ nanocrystal

# Chapter 2

# Synthesis

We modified a hydrothermal synthesis to create the $TiO_2$ nanocrystals. The original synthesis is as follows. $TiCl_4$ was first added to a sufficient quantity of water at 0 °C for the hydrolysis reaction of $TiCl_4$ to $TiOCl_2$ using a significant amount of stirring. During the hydrolysis process, a large amount of HCl gas was released. After stirring for 2 hours, a transparent solution of 2.0 M $TiOCl_2$ was formed. The synthesis continued by the mixing $TiOCl_2$ solution with water, diluting it to 0.62 M, and heating it in a pressure vessel at 180 °C. After approximately two minutes, the clear solution quickly turned milky white. The solution was heated at 180 °C for 30 minutes. This process resulted in $TiO_2$ nanocrystals of purely rutile phase [8].

In the modified synthesis, we prepared a precursor by mixing Te powder, sodium borohydride, and water, and stirred for 4 hours. The synthesis proceeded as with the unmodified synthesis, with the Te precursor added to the $TiOCl_2$ solution before heating. After heating for 30 minutes, we used a centrifuge to separate the nanocrystals from the liquid, and then poured out the liquid. The precipitate had a purple color. At that point, there was no apparent photosensitivity. After allowing the powder to dry for about a day, we annealed the powder in air for 2 hours, at various temper-

atures ranging from 200 °C to 800 °C. The resulting powder was off-white in color, but underwent photodarkening when exposed to light, becoming reddish brown. This procedure was also done with both S and Se in place of Te. These samples did not show any photosensitivity.

# Chapter 3

# Characterization

## 3.1 X-ray Photoelectron Spectroscopy

The XPS data (Figure 3.1) show that there is a significant presence of oxygen, titanium, and tellurium in the modified nanocrystals. As expected, there is only titanium and oxygen present in the unmodified nanocrystals. Data collected from the samples synthesized with S and Se do not show any significant presence of either S or Se after annealing. Only the Te samples had been modified.

## 3.2 X-ray Diffraction

The data collected from x-ray diffraction show that the nanocrystals are in the rutile phase, anatase phase, or a mixture, and that it varies depending on composition and annealing temperature. As seen in Figure 3.2, the Te-modified nanocrystals that were annealed at 500 °C have broader peaks at different locations than those annealed at 800 °C. The broadening of the peak indicates smaller nanocrystals, and the location of the peaks matches that of the anatase phase of $TiO_2$. These are the nanocrystals

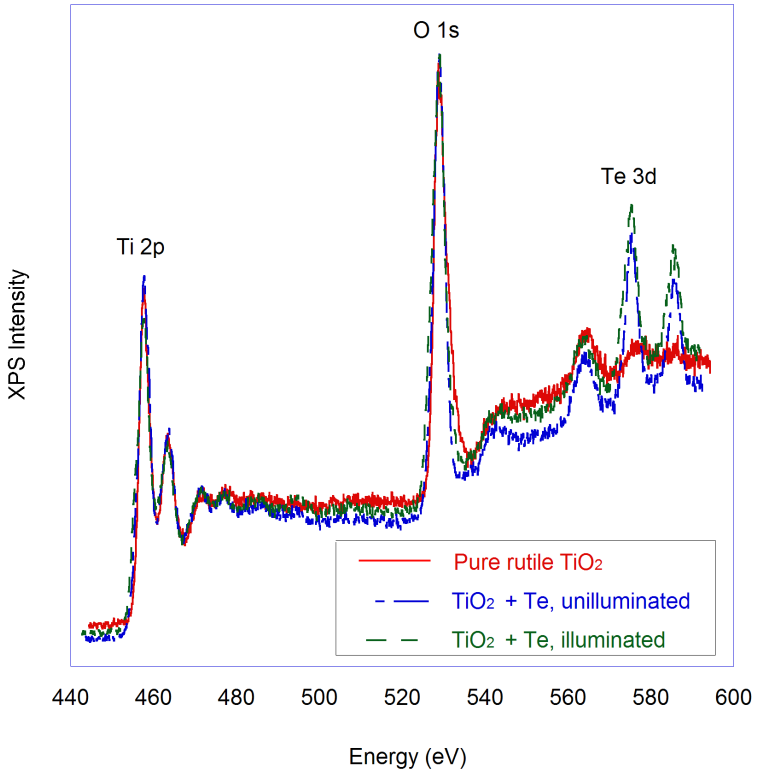


**Figure 3.1** XPS Data. Ti and O are present in all samples, and Te is also present in the Te-modified samples. There are no other elements with significant presence.

that exhibit the photodarkening effect. The size and location of the peaks for the higher temperature annealing indicates larger nanocrystals in the rutile phase of $TiO_2$. These nanocrystals do not show the photodarkening effect. The nanocrystals that are not modified with the described procedure all have rutile phase. It appears that the introduction of Te atoms to the nanocrystals changes the energy in such a way that anatase becomes the energetically favorable phase instead of rutile.

The Debye-Scherrer formula can be used to estimate the diameter of the nanocrystals from the width of the peaks in the x-ray diffraction data.

$$d \approx \frac{\lambda}{\Delta(2\theta)\cos\theta} \tag{3.1}$$

From this, we calculate that the photosensitive nanocrystals that are in the anatase phase have a diameter of about 6 - 10 nm, and the rutile phase nanocrystals, which are not photosensitive, have a diameter of approximately 30 nm.

## 3.3 Electron Spin Resonance

Electron spin resonance (ESR) measurements were taken on unmodified, modified/unilluminated and modified/illuminated nanocrystals. There was no difference in the ESR signal for Te-modified nanocrystals when comparing before and after photodarkening. However, when comparing the unmodified and modified nanocrystals, we found that the signal was reduced by a factor of four in the unmodified nanocrystals (See Figure 3.3). The reduction in ESR signal indicates a reduction in the number of unpaired electron spins. Since unpaired electrons are generally seen only on the surface of nanocrystals, this suggests that the tellurium modifies the surface of the nanocrystals and not the interior.

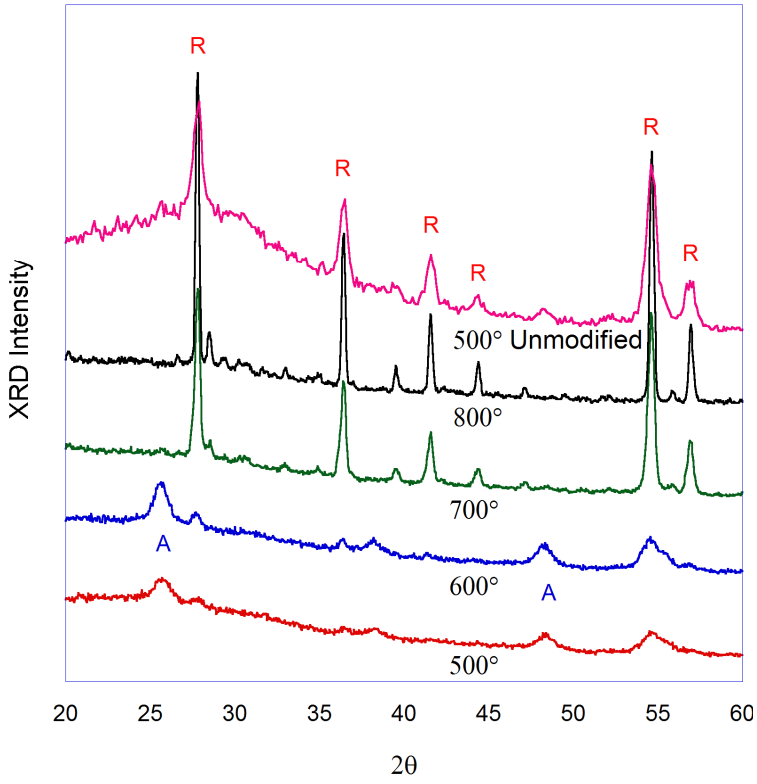


**Figure 3.2** X-ray Diffraction Data. We see that the modified nanocrystals annealed at temperatures 600 °C and below have anatase phase, while those annealed at 700 °C or 800 °C have rutile phase. The unmodified nanocrystals annealed at 500 °C also have rutile phase.

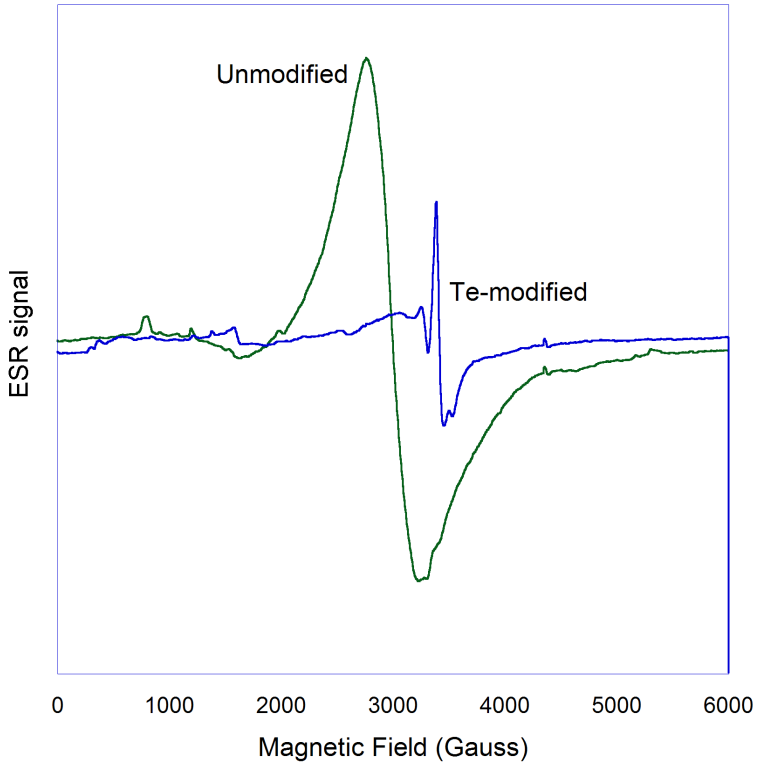


**Figure 3.3** ESR Data. The number of unpaired spins in the Te-modified nanocrystals is reduced by a factor of four.

# Chapter 4

# Optical Absorption Spectroscopy

## 4.1 Method

We used an integrating sphere to measure the absorption in these powders (See Figure 4.1). Light from a monochromator is sent into the integrating sphere, where it scatters from the sample. A photodiode is placed at an exit aperture to measure the intensity of the scattered light. The spectrum of the scattered light is very close to the spectrum of the lamp, but the ratio of the intensity measured with the sample in place relative to that measured with a blank slide of unpolished aluminum gives us a qualitative measure of the absorption spectrum of the powder.

Using this method, we measured the absorption of the pure $TiO_2$ and the Te-modified nanocrystals (annealed at 500 °C) before and after photodarkening. We were also able to determine how this photodarkening effect depends on the wavelength of light that the nanocrystals are exposed to. An unexposed sample was placed in the sphere, and a spectrum is measured. This served as a reference spectrum. The sample was then exposed to a specific wavelength of light for a set amount of time, after which another spectrum is measured. By comparing these spectra to the reference data, we

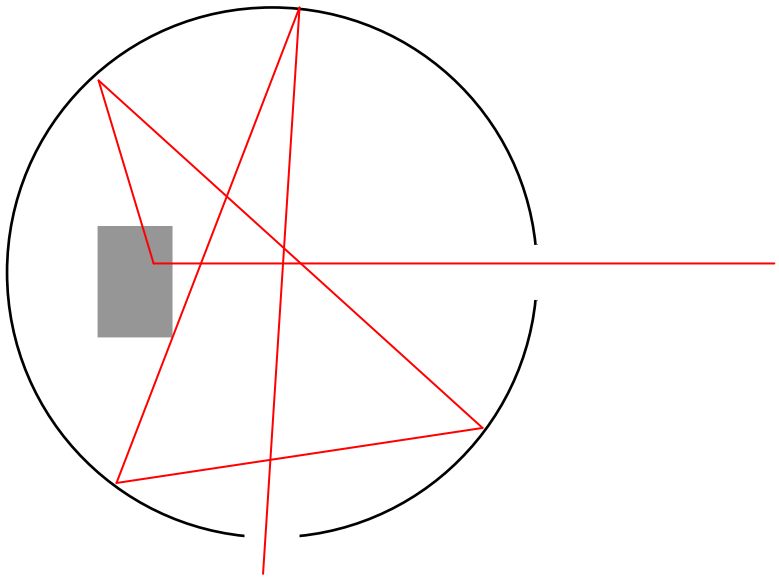

**Figure 4.1** A sketch of the integrating sphere used to measure optical absorption. The ratio of scattered light with a sample relative to scattered light without a sample gives a measure of the absorption spectrum of the powder.

could see the increase in absorption as the nanocrystals were exposed to various wavelengths of light.

## 4.2 Results

The absorption spectroscopy measurements show that the Te-modified nanocrystals have increased absorption between 400 and 700 nm relative to the unmodified nanocrystals. Figure 4.2 shows the absorption spectrum for the unmodified nanocrystals and the Te-modified nanocrystals. Both have an absorption peak around 350 nm, but the Te-modified nanocrystals have a broad peak in the band gap of $TiO_2$.

In order to determine what wavelength of light would activate this photodarkening, we exposed the sample to a certain wavelength and then measured the absorption spectrum. This process was repeated until there was no change in the spectrum. The

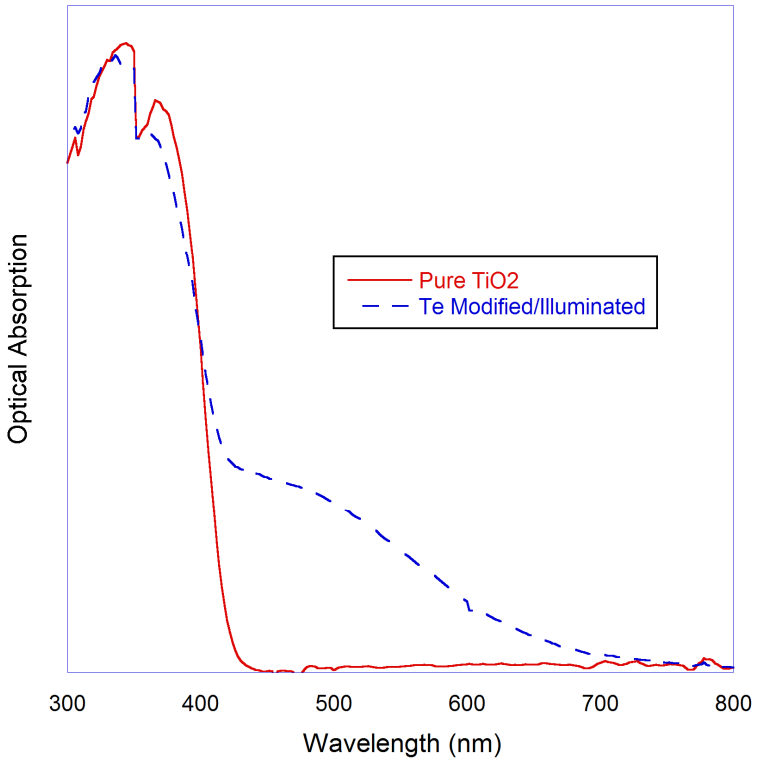


**Figure 4.2** Absorption spectrum for Te-modified and unmodified $TiO_2$ nanocrystals. The Te-modified nanocrystals have increased absorption in the visible spectrum.

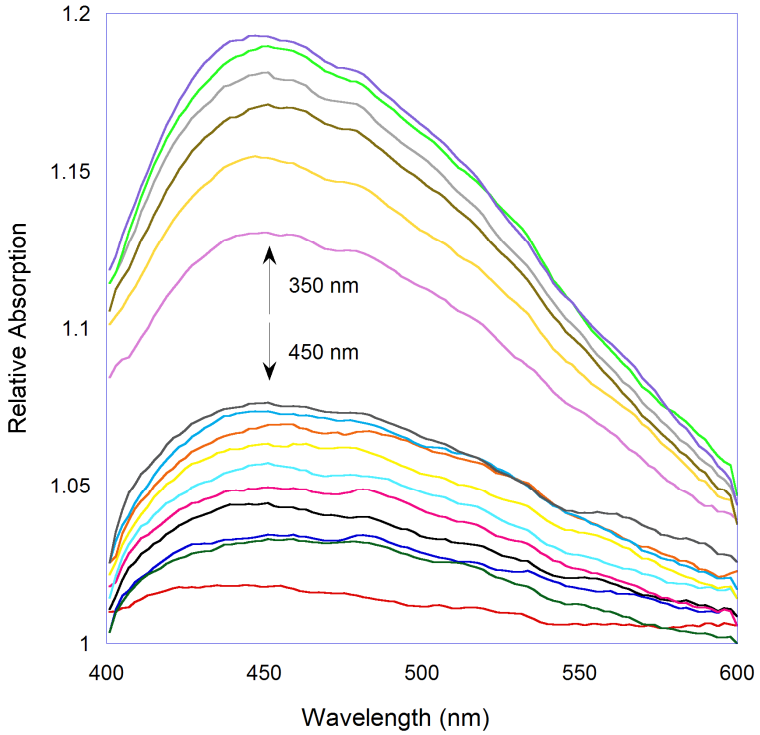


**Figure 4.3** The absorption spectrum changing as photodarkening occurs. Photodarkening due to exposure to 450 nm light saturates, and further photodarkening occurs upon exposure to 350 nm light.

sample was then exposed to a shorter wavelength of light, and the process repeated. Figure 4.3 shows the results of this experiment. We found that exposure to 550 nm light for 400 seconds resulted in increased absorption and subsequent exposure to 450 nm light for 400 seconds increased the absorption further. At that point, photodarkening saturates, with no further change from light at that wavelength. Further exposing the powder to 350 nm light caused a much more rapid and dramatic increase in absorption. The absorption peak is centered around 450 nm. This result suggests that there is a distribution of energy barriers for the photodarkening to occur. The lower energy photons cause slight photodarkening. As the photon energy approaches the absorption edge of $TiO_2$, the rate of photodarkening increases dramatically.

# Chapter 5

# Summary

In summary, we have discovered a synthesis for $TiO_2$ nanocrystals modified by Te that are photosensitive. We know that the Te modification changes the structure of the nanocrystals, and that the photodarkening effect is destroyed when the nanocrystals are annealed at a temperature 700 °C or above.

We do not yet know what the mechanism responsible for the photodarkening is. We are working on ab initio molecular dynamics simulation to model these nanocrystals. This should provide some further insight into this unusual behavior. Better understanding of this phenomenon could have potential use in the development of $TiO_2$ based photovoltaics and other applications.

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