Measuring the work function of TiO$_2$ nanotubes using illuminated electrostatic force microscopy

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Abstract. The varying nature of TiO$_2$ nanotube work function as a function of illumination wavelength has been determined using illuminated electrostatic force microscopy. The dark work function was found to be 4.902 eV, with the largest change in work function due to illumination being at 300 nm, which was higher than the work function for bulk TiO$_2$ (4.899 eV). The change in work function due to illumination arises from the flattening of the energy bands at the surface due to charge migration.

1. Introduction

It is a well known fact that solar energy has the potential to provide all of the Earth’s current power needs many times over, but the reason behind it not becoming a major industry as of yet is because of the difficulties in harnessing the power that is available. There are a huge variety of solar cells now being studied across the globe, including single-crystalline Si, dye-sensitized solar cells, quantum dot solar cells, polymer/organic cells, nanocrystal/nanostructure solar cells, multi-junction solar cells. Even within the latter of these streams of solar cell research there are several areas, including copper-indium-gallium-selenide (CIGS), gallium arsenide (GaAs) and gallium-indium-phosphide (GaInP$_2$) [1-4]. The research presented here has applications to nanostructure solar cells and multi-junction solar cells.

A problem associated with multi-junction solar cells is their loss of efficiency due to mis-aligned energy bands across the materials. As the electrons try to move through the device to produce the electrical current, they lose energy across the junctions between materials which results in them either falling back and recombining or only contributing a very small current, and thus the efficiency of the overall device is lowered. This research aims to look at how illuminated electrostatic force microscopy can be used as an aid for better material selection to help prevent this.

Titanium dioxide (TiO$_2$) is a relatively abundant, well-characterised material that has been used extensively for solar applications. It is commonly used as a photocatalytic material, both in experimental/research use for splitting water, and also as an end product for keeping windows or glass clean. By having TiO$_2$ in a nano-form, it allows us to build a theoretical multi-junction cell, as the nanotubes are formed on top of bulk TiO$_2$. These nanotubes are also currently being heavily studied for a great range of applications, but most importantly in relation to this research, they are one of the best materials at splitting water photocatalytically [2] – a process facilitated by a solar cell. It’s also useful to consider how the work function of the nanotubes will differ from the bulk material, as well as
whether they cause a shift in absorption of TiO$_2$ from the UV to the visible range of the electromagnetic spectrum.

2. Experimental

2.1. Sample Preparation
The titanium dioxide nanotubes were prepared by simultaneous anodisation and etching using a two-electrode electrochemical set-up, with electropolished titanium foil as the working electrode and a carbon rod as the counter/reference electrode, and non-aqueous electrolyte of 0.01% ammonium fluoride in glacial acetic acid. A bias of +40V was applied for 30 minutes. The sample was then washed with deionised water and dried under nitrogen. One side of the sample was then manually polished, and fixed to a manually polished sample puck using conductive carbon tape.

2.2. Illuminated Electrostatic Force Microscopy (iEFM)
The EFM measurements were taken on a Bruker MultiMode 8 microscope attached to a Nanoscope IV controller and an electronics extender module. The probes used for the measurements were Bruker SCM-PICs, with a force constant of 0.2 N m$^{-2}$ and a resonant frequency of approximately 13 kHz. These probes have pyramidal tips that are 13 µm in height. They are made of silicon and coated with PtIr, having a work function of 5.18 eV. The range of applied bias for the EFM was from -4V to +4V. The illumination came from a Bentham SSM150Xe xenon arc lamp with a typical output of 4 mW attached to a liquid light guide and a lens. This produced a light spot of approximately 1mm diameter on the sample. The wavelengths used in the experiments ranged from 200 – 700 nm.

3. Results and Discussion

3.1. SEM images

![SEM images](image)

**Figure 1** TiO$_2$ nanotubes seen at the surface of the sample. The figure on the right is a magnified version of the left figure. It gives a better indication of the size of the nanotubes, as they have an average diameter of 32nm.

The images above show that the nanotubes were formed on the surface of the TiO$_2$. Energy dispersive X-ray (EDX) analysis showed that the main components within the nanotubes were Ti (75%), O (20%) and F (5%). It is possible that N is also present, but the peak for N is hidden behind Ti in EDX. Both F- and N-doping are expected due to the ammonium fluoride in the synthesis.
3.2. Atomic Force Microscopy (AFM)

![AFM image of TiO$_2$ nanotubes formed by simultaneous etching and anodisation of TiO$_2$ foil.](image)

The nanotubes can be seen clearly in the AFM image in the form of round marks. They do not appear as rings due to tip convolution effects being greater than the diameter of the nanotubes (~32 nm).

3.3. iEFM Results

The work functions of the TiO$_2$ and the TiO$_2$ nanotubes were calculated by determining the contact potential difference between the tip and the sample. By knowing the work function of the tip (5.18 eV), the work function of the TiO$_2$ and the nanotubes can then be calculated using the equation:

$$\Delta V_{CPD} = \Phi_t - \Phi_s$$

where $\Delta V_{CPD}$ is the contact potential difference, and $\Phi_t$ and $\Phi_s$ are the work functions of the tip and the sample respectively. This was calculated to be 4.899 ± 0.02 eV for the bulk TiO$_2$.

The table below shows the calculated values for the TiO$_2$ nanotubes in the dark and under illumination:

**Table 1** Work function of TiO$_2$ nanotubes under illumination at wavelengths between 200 and 700 nm

| wavelength (nm) | work function (eV) |
|----------------|--------------------|
| Dark           | 4.902              |
| 200            | 4.877              |
| 250            | 4.877              |
| 300            | 4.871              |
| 350            | 4.882              |
| 400            | 4.889              |
| 450            | 4.892              |
| 500            | 4.893              |
| 550            | 4.900              |
| 600            | 4.906              |
| 650            | 4.904              |
| 700            | 4.905              |
The greatest change in work function occurs under illumination at 300 nm which coincides with the bandgap of TiO$_2$ being 3.2 eV. The decreased work function under illumination is due to the flattening of the energy bands at the surface as the electrons migrate into the bulk. Decreases in the work function seen at wavelengths greater than the band gap are due to surface states available on the TiO$_2$ nanotube surface as a result of fluorine and nitrogen doping. These produce trapped oxygen vacancies where electrons can migrate across the band gap in two stages via lower energy before migrating into the bulk.

4. Conclusion
We have shown that the work function of TiO$_2$ nanotubes can be measured using electrostatic force microscopy to be 4.902 eV. We have also shown that this work function varies depending on the wavelength of light that is illuminating the sample, with the greatest change in work function seen for an illuminating wavelength of 300 nm. This matches up with the expected change for TiO$_2$, which typically has the greatest photoresponse in the UV region due to its bandgap being 3.2 eV. The changes seen at higher wavelengths are due to the complex nature of the surface states commonly found on TiO$_2$. The relevance of these results is that by understanding how the work function changes under light, it will be possible to select more appropriate materials for multi-junction solar cells, thereby reducing energy loss.

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