

Chemisorption Determines the Photovoltage of a Ti/TiO₂/Au/Dye Internal Electron Emission Photovoltaic Cell

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The Ti/TiO₂/Au junction forms the basis of a promising new type of photovoltaic cell, provided that a light-harvesting antenna layer can be deposited on the thin gold film. We report that the electrical diode characteristics of the TiO₂/Au Schottky barrier deteriorate by deposition of a hydrophobic quantum dot film, Merbromin dye adsorption, or electron–hole photogeneration in TiO₂ under inert conditions. In the presence of oxygen and water vapor, the Schottky barrier characteristics and high photovoltage are recovered. The strong influence of the TiO₂ surface chemistry on the (photo)electrical characteristics of the solar cell is discussed on the basis of an existing microscopic model.

Introduction

Conventional photovoltaic cells based on high-quality crystalline or polycrystalline semiconductors combine high manufacturing costs with reasonable efficiencies, the latter being between one-third and one-half of the maximum obtainable efficiency of 33% of a one-band-gap device.¹ There is an extensive search for low-cost alternatives based on thin-film light-harvesting layers consisting of cheap semiconductor materials and/or easily processable organic molecules and polymers.^{2–5} Illustrative is the Grätzel cell that consists of a nanoparticulate TiO₂ layer on which a light-harvesting dye is adsorbed.⁶ This cell, invented in 1991, has now an efficiency of about 10% and is a credible competitor for commercial photovoltaic devices.

Recently, McFarland and Tang proposed a new and interesting working principle for a thin-film low-cost photovoltaic device.^{7,8} The device consists of an n-type TiO₂ layer (grown on Ti) on which a thin film of Au (15–50 nm) is electro-deposited or sputtered; a light-absorbing dye, i.e., Merbromin (or a monolayer of CdSe quantum dots⁸), is chemisorbed on the gold as an antenna layer (Figure 1E). Upon photoexcitation of the dye, electrons are injected through the thin gold film into the n-type TiO₂ layer and collected in the Ti contact. The photogenerated holes in the highest occupied molecular orbital (HOMO) of the dye are scavenged by electrons of the gold film. In such a way, a photovoltage is generated between the Au and Ti electrodes. McFarland and Tang propose that electron injection into the TiO₂ occurs by ballistic transport *through* the gold film. The Ti/TiO₂/Au/Merbromin photovoltaic device shows a photovoltage of about 650 mV; the photocurrent is however low ($\mu\text{A}/\text{cm}^{-2}$), due to the fact that light is harvested by only a (sub)monolayer of dye molecules. The Schottky barrier at the TiO₂/Au interface is essential for irreversible electron injection into the TiO₂ layer. The barrier height determines the maximum photovoltage that can be obtained with this cell.

We deposited CdSe nanocrystals as an antenna layer on top of the TiO₂/Au interface and discovered that the diode current–

voltage (I – V) characteristics typical for the Schottky barrier changed readily into a nonrectifying ohmic contact. Related to this, we observed that gold layers with a nominal thickness between 15 and 50 nm do not form uniform films on the TiO₂ surface, but interconnected gold patches are formed with a considerable fraction of the TiO₂ surface exposed (Figures 1C and 1D). These results suggest that the chemistry at the TiO₂ surface determines the electrical characteristics of the TiO₂/Au interface. We, therefore, have investigated the electrical characteristics of the Ti/TiO₂/Au device and the Ti/TiO₂/Au/Merbromin solar cell in detail, changing the surface chemistry by operating these devices under ambient, inert gases, and mixtures of water vapor and oxygen. In this letter, we report that water and oxygen chemisorbed on the TiO₂ surface are essential for Schottky barrier characteristics and for a reasonable photovoltage of the device. Reductive or oxidative desorption of these species, displacement by competitive adsorption of the Merbromin dye, or deposition of a quantum dot antenna layer has a strong negative effect on the photovoltage. A higher cell efficiency can only be obtained if the Ti/TiO₂/Au device is combined with a light-harvesting antenna system that maintains the peculiar chemistry at the TiO₂ surface.

Experimental Section

Polished titanium (99.6%) was anodized by a potential sweep from 0 to 50 V at a sweep rate of 5 mV/s in 0.5 M H₂SO₄, to grow a layer of n-type TiO₂. A gold layer was sputtered on top of the TiO₂ using an Emitech K-575X sputter coater, varying the nominal thickness between 15 and 50 nm. Electrical contact to the gold layer was achieved by a copper wire, gently touching the gold surface. “Annealed” samples were prepared by heating the Ti/TiO₂ sample for 1 h at 675 °C in air before the gold layer was deposited. For the attachment of the Merbromin dye (2,7-dibromo-5-(hydroxymercurio)-fluorescein, Sigma), the device was immersed in an aqueous solution of 5 mM Merbromin for 12 h. Subsequently, the device was rinsed with water, followed by drying in air for 2 h.⁷ For all electrical measure-

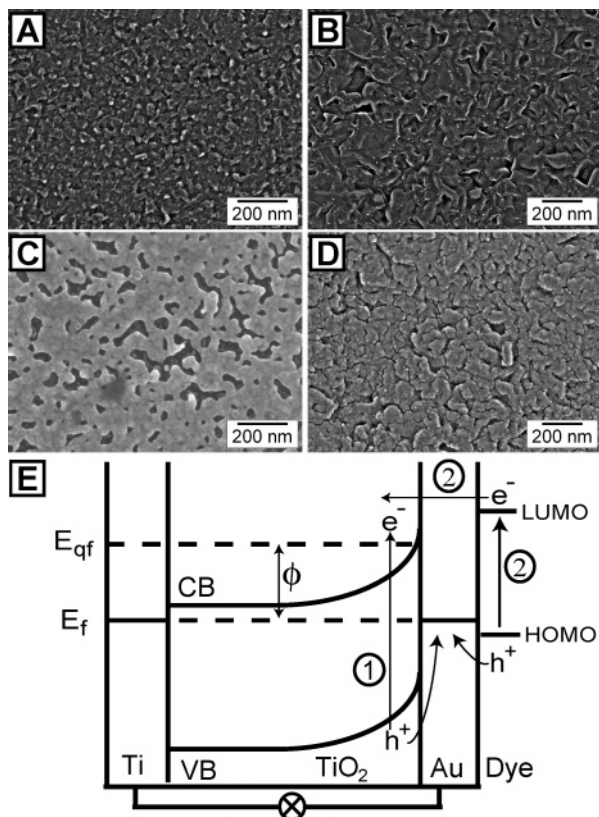


Figure 1. SEM images of (A) the bare TiO₂ surface, (B) the bare TiO₂ surface after annealing at 675 °C for 1 h, and the (C) nonannealed and (D) annealed TiO₂ surface covered with a 30 nm gold layer. (E) A representation of the band scheme of the Ti/TiO₂/Au device, where E_f is the Fermi level in the dark and E_{qf} the quasi-Fermi level under illumination. The difference ϕ between E_{qf} and E_f denotes the maximum obtainable photovoltage. Process 1 is the excitation of an electron from the valence band (VB) to the conduction band (CB) in the TiO₂. Process 2 is the internal electron emission process, where an electron is excited in the dye, ballistically transported through the gold layer, and injected into the CB of TiO₂. The created holes are transferred to the gold layer.

ments, an EG&G Princeton potentiostat was used, while illumination was done by a 75 W Xe discharge lamp (Oriol 6251). Sweep rates of the measured I - V characteristics were 10 mV/s, unless mentioned otherwise. Absorption spectra were measured using a double-beam Perkin-Elmer Lambda 16 UV/UV-vis spectrometer. Scanning electron microscopy (SEM) images (acceleration voltage 20 kV, beam spot 3 nm) and electron backscatter diffraction (EBSD) patterns were recorded with a Philips XL30-SFEG scanning electron microscope. X-ray diffraction (XRD) measurements were performed with a Philips PW 1729/3710 setup.

Results

Structure of the TiO₂ Film. For a complete understanding of the observed phenomena described below, insight into the structure of the TiO₂/Au interface on a microscopic scale is required. A SEM image of the bare as-prepared TiO₂ surface (Figure 1A) reveals a rough topography. The sensitivities of XRD and EBSD were not sufficient to determine the crystal structure of this TiO₂ film. When the TiO₂ sample was annealed, the morphology of the TiO₂ surface changed remarkably (Figure 1B). From both XRD and EBSD measurements, it could be concluded that the annealed TiO₂ layer has a rutile structure with a crystal size of 50–60 nm (using Scherrer's equation). Furthermore, annealing led to a color change of an initial blue

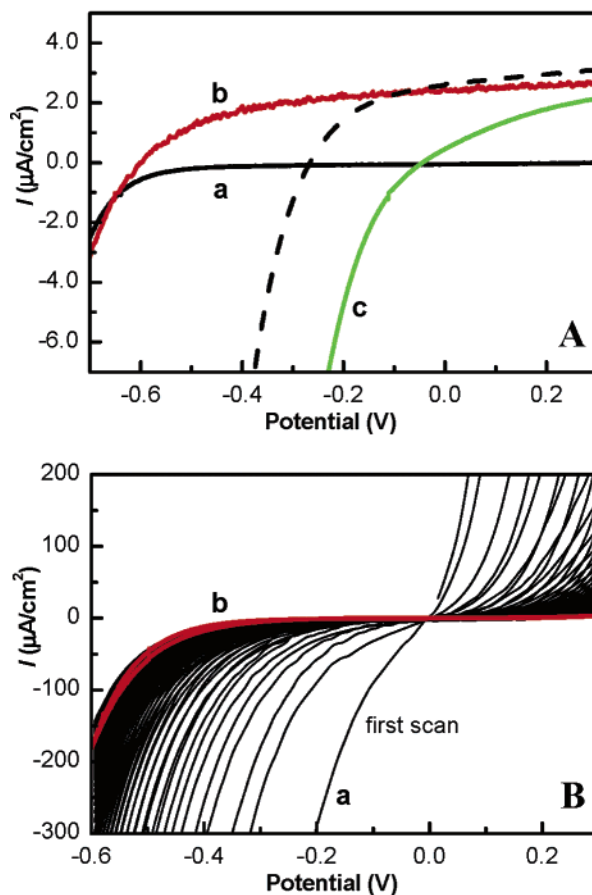


Figure 2. (A) I - V characteristics of a Ti/TiO₂/Au (30 nm) device in the dark (a, in black), under illumination (10 mW/cm²) in ambient conditions (b, in red), and in a closed cell (c, in green), which was also measured for an annealed Ti/TiO₂/Au (30 nm) device (dashed curve) (B) Dark I - V characteristics of a Ti/TiO₂/Au (20 nm) device before (b, in red) and after (a, in black) UV illumination, in a closed cell filled with argon. The first 50 scans are indicated.

to an eventual gray-yellow TiO₂ film, indicating that bulk defects in the nonannealed TiO₂ layer were removed.^{9,10} SEM images of the TiO₂ film covered with a 30 nm (nominal thickness) gold layer show that an interconnected network of gold islands forms (Figures 1C and 1D), leaving a significant amount of the TiO₂ surface exposed.

Electrical Characteristics of As-Deposited Ti/TiO₂/Au Devices. Current-voltage characteristics of the as-deposited devices were measured in the dark and under illumination of the full spectrum of a Xe discharge lamp (including UV radiation). The Ti/TiO₂/Au (30 nm) device showed typical rectifying behavior under ambient conditions in the dark (Figure 2A). Under illumination, a stable photovoltage (V_{oc}) of 600 mV was observed. However, when the same sample was placed in a closed cell (filled with air) and illuminated in the same way, the rectifying behavior deteriorated; the photovoltage decreased to 50 mV. After 1 h of exposure to ambient conditions, the sample regained the initial properties (not shown). An even more significant deterioration of a Ti/TiO₂/Au (20 nm) device was observed when the device was illuminated in a closed cell filled with dry argon (Figure 2B). Directly after illumination for 1 min (10 mW/cm²), nearly ohmic behavior of the junction was observed in the first few scans. A similar effect was observed when an assembly of CdSe quantum dots was drop-casted on top of the cell. This was followed by a gradual recovery of the sample during the successive scans in the dark. After 50 scans at a sweep rate of 50 mV/s (33 min), the current-voltage

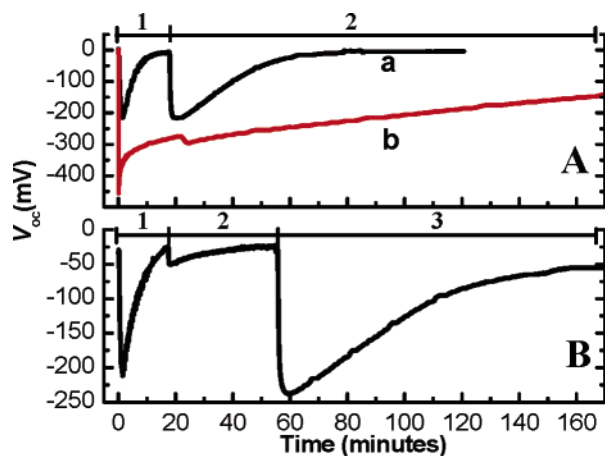


Figure 3. Evolution of V_{oc} over time of a Ti/TiO₂/Au (30 nm) device (a, in black) and an annealed Ti/TiO₂/Au (30 nm) device (b, in red) under UV illumination at 10 mW/cm². Measurements were performed in a closed cell, under a flow of (A) argon (section 1), followed by argon with water (section 2), and (B) argon (section 1), followed by a flow of oxygen (section 2) and oxygen with water (section 3).

characteristics were similar to the ones before illumination, i.e., recovery of the diode characteristics.

These results suggest that water and/or oxygen adsorbed at the TiO₂ surface of the device determine the electrical characteristics. The effects of chemisorbed water and oxygen species on the electrical characteristics of metal oxide semiconductors have been used for the design of gas sensors.¹¹ To gain more detailed information about these effects in the present case, the photovoltage of a Ti/TiO₂/Au (30 nm) device exposed to a variety of gas mixtures was measured over time (Figure 3). A photovoltage of 210 mV is measured immediately after the start of illumination in an inert argon atmosphere; however, the photovoltage vanishes within 20 min. A fast recovery of the photovoltage to 210 mV is observed under a wet argon flow followed by a slow deterioration. If a flow of pure oxygen is applied, then only a small increase in the photovoltage is observed (Figure 3B, section 2). Subsequent addition of water to the flow of oxygen (Figure 3B, section 3) results in a considerable increase in the photovoltage, to a value near 250 mV, again followed by a slow decrease. It should be noted that all devices showed a stable photovoltage of 600–700 mV under ambient conditions (Figure 2A). From these results, we conclude that the combination of inert atmosphere and UV radiation causes a degradation of the Schottky barrier of the TiO₂/Au interface; the Schottky barrier can be recovered by exposure to both oxygen and water.

Electrical Characterization of Annealed Samples. The optoelectrical properties of annealed Ti/TiO₂/Au devices were also investigated. Remarkably, the maximum obtainable photovoltage from annealed devices in ambient conditions was 350–450 mV (not shown), which is considerably lower than with a nonannealed sample (650 mV). We do not have a reasonable explanation for this reproducible effect. In a closed cell filled with air, rectifying behavior is still observed, although the photovoltage decreased to 270 mV (Figure 2A, dashed curve). The evolution of the photovoltage under a flow of Argon is depicted by the red curve in Figure 3A. The photovoltage reaches 450 mV at the start of illumination and slowly decreases with prolonged illumination. Addition of water to the flow of argon after 25 min causes a small temporal increase in the photovoltage. A comparison between the results obtained with the annealed and nonannealed devices shows that the annealed

TiO₂/Au junction is somewhat less sensitive to chemical changes at the TiO₂ surface induced by UV light.

To explain the strong influence of the chemistry at the TiO₂ surface on the electrical characteristics of the Ti/TiO₂/Au device, we refer to the literature where perfect (single-crystal) rutile TiO₂ surfaces were considered. It is known that Ti³⁺ defect sites at the surface (which can be created by photoreduction of a Ti⁴⁺ site, Ti⁴⁺ + e⁻ → Ti³⁺, and oxidative removal of the oxygen anion by the holes^{10,12–16}) correspond to a band-gap state located at 0.5–0.8 eV below the conduction-band edge.^{16,17} We believe that an abundant presence of these defect levels at the surface can lead to a deterioration of the diode characteristics of the TiO₂/Au interface, leading to a decrease in the photovoltage. In addition, a recent paper showed the importance of hydroxyl groups (formed by the dissociation of water on Ti³⁺ sites) for the reoxidation of Ti³⁺ sites by (physisorbed) oxygen. A second adsorbed water layer can block this reaction, preventing the reoxidation of Ti³⁺ sites.¹⁷ We ascribe the above-mentioned water/oxygen dependency for the formation of a proper Schottky barrier at the TiO₂/Au interface to the UV creation of unfavorable Ti³⁺ defects, a process that can be reversed by chemisorption of water/oxygen. As mentioned earlier, the nonannealed sample has a very rough surface, whereas the annealed TiO₂ surface has a rutile, polycrystalline structure with less roughness. The observation that the annealed devices are less sensitive to chemical changes may be explained by the smaller microscopic area compared to the rough nonannealed TiO₂ surfaces (Figure 1). Furthermore, the nonannealed TiO₂ surface exposes more Ti^{4+/3+} sites with a nonideal oxygen coordination, which makes these sites more reactive. Our results seem to agree with the model proposed by Henderson et al.,¹⁷ which emphasizes that the combination of water and oxygen is required for the reoxidation of Ti³⁺ sites. The slow decrease in the photovoltage when an oxygen flow saturated with water is supplied may be explained by a second water layer adsorbed on the surface that blocks the Ti³⁺ reoxidation.¹⁷

Devices Sensitized with Merbromin. To investigate the effect of chemisorption of an antenna layer on the nonannealed Ti/TiO₂/Au (50 nm) device, Merbromin was attached to the TiO₂/Au interface as described in the Experimental Section. The *I*–*V* characteristics of such a device were measured in the dark and under illumination with visible light (Figure 4A). A cutoff filter was used to block UV radiation. We will now focus on the effects of the Merbromin chemisorption on the photocurrent and the Schottky barrier of the Ti/TiO₂/Au/Merbromin device. As expected, the photocurrent under illumination with visible light is greatly enhanced by Merbromin adsorption compared to a nonsensitized device, confirming electron injection by photoexcited Merbromin into the conduction band of TiO₂. More remarkably, the *I*–*V* curves of the sensitized device in the dark and under illumination are shifted compared to the curves of the nonsensitized device. Thus, chemisorption of Merbromin decreases the Schottky barrier height of the TiO₂/Au interface.

A photocurrent spectrum of a Merbromin-sensitized Ti/TiO₂/Au (20 nm) device was measured and is plotted together with the absorption spectrum of the same dye in solution and adsorbed on glass (Figure 4B). A clear broadening and red shift is observed for both the absorption spectrum of Merbromin adsorbed on glass and the photocurrent spectrum with respect to the dye in solution. An identical broadening and red shift were observed for the Merbromin adsorbed on gold (not shown), which McFarland et al. ascribed to electronic coupling of the dye with gold. Our results for the absorption spectrum of

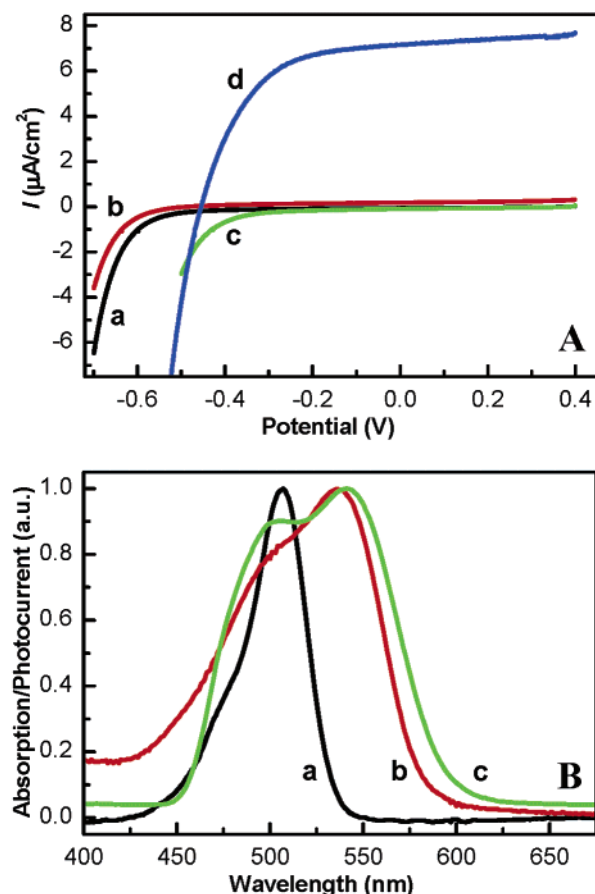


Figure 4. (A) I - V characteristics of a $\text{Ti}/\text{TiO}_2/\text{Au}$ (50 nm) device without dye in the dark (a, in black) and under illumination (b, in red) and with dye in the dark (c, in green) and under illumination (d, in blue). A cutoff filter ($T(\lambda < 450 \text{ nm}) = 0$) was placed between the light source and the device to block UV radiation (B) Absorption spectra of the Merbromin dye in solution (a, in black) and attached to glass (b, in red) and the photocurrent spectrum of a Merbromin-sensitized $\text{Ti}/\text{TiO}_2/\text{Au}$ (50 nm) device (c, in green). All spectra are normalized to the peak maximum.

Merbromin on glass point out that the observed red shift is not due to coupling with gold but due to intermolecular interactions between the dye molecules in the adsorbed layer. Hence, the photocurrent action spectrum in combination with the absorption spectrum of Merbromin on gold does not provide proof for the internal electron emission mechanism proposed earlier.⁷ On the basis of the results obtained in this study, direct electron injection from Merbromin close to the $\text{TiO}_2/\text{Au}/\text{air}$ three-phase contact across the bare TiO_2 surface cannot be excluded. It is worth

noting here that the carboxyl functionality of Merbromin can form a bond with a Ti surface atom.¹⁸

Conclusions

Nonannealed $\text{Ti}/\text{TiO}_2/\text{Au}$ junctions, which form the basis for a new type of solar cell, show a dramatic decrease in the height of the Schottky barrier by UV illumination under inert conditions. We ascribe this deterioration to the creation of Ti^{3+} sites at the TiO_2 surface. It was observed that the Schottky barrier and diode characteristics are recovered by exposure to a combination of water and oxygen. Devices where the TiO_2 layer was annealed showed a similar but less sensitive response to UV radiation. Remarkably, the maximum obtainable photovoltage was diminished by 200 mV with respect to the nonannealed devices. Sensitizing the nonannealed device with Merbromin was successful but caused a decrease in the Schottky barrier height. This shows that the electrical characteristics of the $\text{Ti}/\text{TiO}_2/\text{Au}/(\text{Merbromin})$ devices are very sensitive to the chemistry at the TiO_2/Au interface.

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