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Enhanced Photoelectrochemical Water Oxidation via Atomic Layer Deposition of TiO2 on Fluorine-Doped Tin Oxide Nanoparticle Films

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TiO2 is an exemplary semiconductor anode material for photoelectrochemical (PEC) water-splitting electrodes due to its functionality, long-term stability in corrosive environments, nontoxicity, and low cost. In this study, TiO2 photoanodes with enhanced photocurrent density were synthesized by atomic layer deposition (ALD) of TiO2 onto a porous, transparent, and conductive fluorine-doped tin oxide nanoparticle (nanoFTO) scaffold fabricated by solution processing. The simplicity and disordered nature of the nanoFTO nanostructure combined with the ultrathin conformal ALD TiO2 coatings offers advantages including decoupling charge carrier diffusion length from optical penetration depth, increased photon absorption probability through scattering, complimentary photon adsorption, and favorable interfaces for charge separation and transfer across the various junctions. In this report, we examine the effects of porosity of the nanOFTO scaffold and thickness of the TiO2 coating on PEC performance and achieve an optimal photocurrent of 0.7 mA cm^{-2} at 0 V vs. Ag/AgCl under 100 mW cm^{-2} AM 1.5 G irradiation in a 1 M KOH aqueous electrolyte. Furthermore, the fundamental mechanisms behind the improvements are characterized via cyclic voltammetry, incident photon-to-current efficiency, transient photocurrent spectroscopy, and electrochemical impedance spectroscopy and are contrasted with those of single crystal rutile TiO2 nanowires. The strategies employed in this work highlight the opportunities inherent to these types of heteronanostructures, where the lessons may be applied to improve the PEC conversion efficiencies of other promising semiconductors, such as hematite (α-Fe2O3) and other materials more sensitive to visible light.

1. Introduction

The direct use of sunlight as the electromotive force driving the electrolysis of water is a process known as photoelectrochemical (PEC) water splitting. Given the renewable nature and abundance of solar energy, this PEC process is considered to be the "holy grail" of achieving an economically sustainable and environmentally friendly hydrogen production system.[1] In addition, the storability of hydrogen fuels curbs the intermittency issues intrinsic to the sun's diurnal cycle. This PEC process is made possible when a semiconductor material[2] comes into contact with an aqueous electrolyte and causes a depletion region to be created within the semiconductor, forming the semiconductor-liquid junction (SCLJ). The corresponding band bending can drive the separation of photogenerated electrons and holes so that they may undergo the chemical reactions of water oxidation at the anode (oxygen evolution reaction, OER) and water reduction at the cathode (hydrogen evolution reaction, HER), respectively.[3, 4] The HER and OER reactions on the cathode and anode in an alkaline environment are shown in **Equation 1** and **Equation 2**, respectively.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{1}$$

$$4OH^- + 4h^+ \rightarrow O_2 + 2H_2O \tag{2}$$

One intrinsically n-type semiconductor material that meets the proper valence and conduction band edge position requirements for the OER is titanium dioxide (TiO_2). Since 1972,[5] TiO_2 has shown great potential as an exemplary PEC material since it consists of earth-abundant elements, is considered non-toxic, and it is highly stable in a variety of aqueous electrolytes.

Most of the recent approaches to optimizing PEC performance using TiO_2 have deviated from traditional photonic systems with planar morphologies and moved towards employing porous 3-dimensional (3D) nanostructures to enhance the functionality of the PEC devices. The large electrochemically active SCLJ surface area from a 3D porous electrode provides a large contact area between the electrolyte and the electrode, which enables the

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usage of a larger portion of the electrode materials to enhance the throughput of the

kinetically sluggish OER. Moreover, loading TiO_2 onto a 3D conductive scaffold can

decouple the required thickness for efficient light absorption from the minority charge carrier

diffusion length and thereby avoid significant recombination of the photogenerated

electron/hole pairs. Recent approaches have utilized various conductive 3D nanostructured

scaffolds, including Si nanowires[6], $TiSi_2$ nanonets[7], carbon nanotubes,[8] and even single

crystal rutile TiO_2 nanowires[9]to support TiO_2 for the synthesis of TiO_2 anodes. However,

many of these approaches suffer from the fact that the supporting scaffolds are expensive to

fabricate and may compete with TiO_2 for the absorption of photons.

　　　　To circumvent these problems, our nanostructuring approach utilizes solution-

processed transparent conductive oxide (TCO) nanoparticles as a 3D mesoporous scaffold

material. The TCO's wide bandgap makes the nanoparticles less likely to compete with the

photoactive semiconductor layer. Most recently, Peng *et al*. demonstrated the potential of this

approach for the synthesis of TiO_2 PEC electrodes by coating antimony-doped tin oxide

nanoparticles (nanoATO) with TiO_2 by atomic layer deposition (ALD).[10] In this study, we

demonstrate additional PEC performance enhancements achieved when solution-processed

fluorine-doped tin oxide nanoparticles (nanoFTO) are used as the porous TCO scaffold for

supporting ALD TiO_2 films. FTO is one of the most commonly used TCOs in optoelectronic

applications due to its thermal stability over a wide temperature window and is thus attractive

as a mesoporous scaffold. We characterized the TiO_2-coated nanoFTO photoanodes

(TiO_2/nanoFTO) by cyclic voltammetry, incident photon-to-current efficiency (IPCE) and

transient photocurrent analysis. Importantly, we find that despite the simplicity and disordered

nature of the TiO_2/nanoFTO core-shell nanostructure, an extremely effective PEC

photoelectrode is created due to the intrinsic benefits of using ultrathin TiO_2 core-shell

coatings and specific surface properties inherent to ALD TiO_2. Additional advantages

observed from this particular heterostructure included complimentary photon adsorption from

FTO and TiO_2 and a favorable interface for charge separation and transport.

2. Results & Discussion

2.1. Materials Synthesis and Characterization

The self-limiting cyclic layer-by-layer growth mode of ALD enables coating of high

aspect ratio nanostructures with angstrom-level thickness precision, conformality, and

uniformity. This makes ALD an ideal tool to maximize the performance of the TiO_2/nanoFTO

heteronanostructure studied herein. The concept behind using ALD to deposit TiO_2 thin films

over the nanoFTO scaffold to construct a

PEC photoanode is illustrated in **Figure 1**.

Given that the absorption coefficient of

polycrystalline TiO_2 for a 370 nm photon is

roughly 1.2 μm,[11] a colloidal nanoFTO film

with a total thickness of roughly 2 μm was

spin-coated onto a planar FTO glass substrate

in order to ensure ample absorption of

photons with energies larger than 3.0 eV

(bandgap of rutile TiO_2). The resulting

nanoFTO scaffold consists of a porous

Figure 1. Schematic diagram illustrating the light trapping and charge carrier separation mechanisms for the TiO_2/nanoFTO architecture, where a thin film of TiO_2 (orange) is coated over a conductive network of nanoFTO (green). On the left, a region is shown where the TiO_2 film causes some pores within the network to become closed, thus preventing an electrochemically active SCLJ from being within reach of photogenerated holes.

network of nanoparticles with diameters spanning 100-300 nm. It is expected that the disorder

of the nanoFTO scaffold will promote optical scattering effects within the bulk of the film,

thus enhancing the light harvesting efficiency of the TiO_2 coatings that serve as the principal

photoactive component for PEC water oxidation.

TiO_2 films with thicknesses ranging from 5-20 nm were deposited onto nanoFTO

substrates and their resulting chemical composition was characterized by X-ray photoelectron

spectroscopy (XPS). **Figure 2** shows XPS spectra of a 10nm TiO_2-coated nanoFTO

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(TiO$_2$(10nm)/nanoFTO) sample, which is also representative of the other samples in this study. The survey scan in Figure 2a shows TiO$_2$ with the presence of N (0.5 at%), C (13.1 at%), and Si (2.2 at%) contaminants. The N and C species can be attributed to the N$_2$ carrier gas used during ALD[12, 13] and adventitious carbon, respectively. The presence of small concentrations of Si is likely due to contamination from sample handling and is not expected to contribute to PEC performance. The lack of detection of Sn peaks indicates that a conformal coating of TiO$_2$ with minimal pinholes was achieved on near the surface of the nanoFTO network. Figure 2b displays the Ti 2p triplet region of the spectrum, whose Ti 2p$_{3/2}$ peak maximum near 538.4 eV confirms the presence of a Ti^{4+} oxidation state, which further confirmed the presence of TiO$_2$.[14] Similar spectra were observed with TiO$_2$/nanoFTO samples with different TiO$_2$ coating thicknesses of 5nm-20nm, which suggests that 5nm TiO$_2$ was able to conformally cover the nanoFTO substrates.

Figure 2. a) XPS survey spectrum and b) corresponding Ti 2p regional spectrum collected from a TiO$_2$(10nm)/nanoFTO sample.
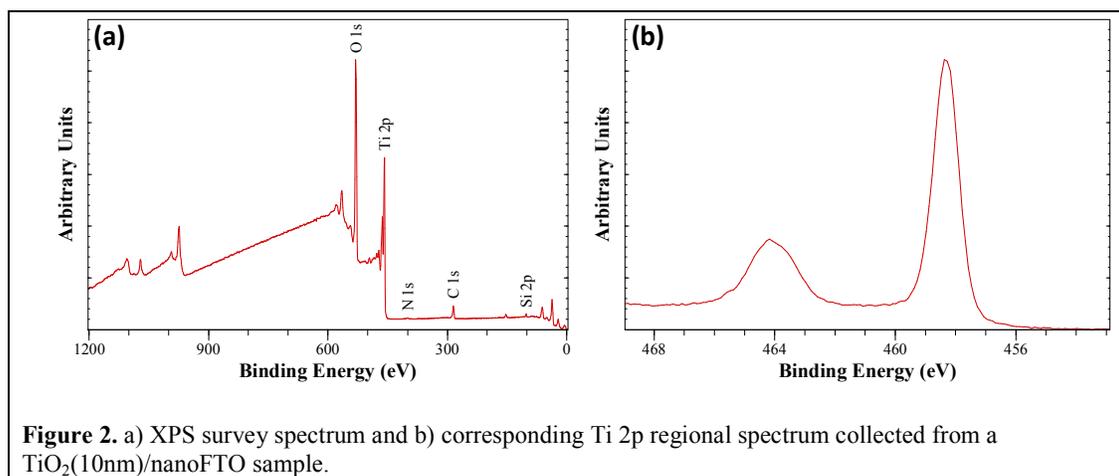
To analyze the crystal structure of TiO$_2$ ALD coatings onto the nanoFTO structure, Raman spectroscopy was performed on TiO$_2$/nanoFTO with various thicknesses of TiO$_2$. **Figure 3** shows the Raman spectra of nanoFTO (cassiterite crystalline phase) and nanoFTO coated with 5, 10, and 20 nm of TiO$_2$. All the TiO$_2$/nanoFTO samples show strong Raman modes near 242 cm^{-1}, 440 cm^{-1}, and 610 cm^{-1}, which are the three strongest Raman bands associated with the rutile polymorph of TiO$_2$.[15] As anatase TiO$_2$ is the usual polymorph at this

low growth temperature,[16] we attribute this preferential rutile formation to the underlying cassiterite lattice structure of the nanoFTO, which is from the rutile family and possesses similar lattice constants as rutile TiO_2. This is consistent with recent studies that show
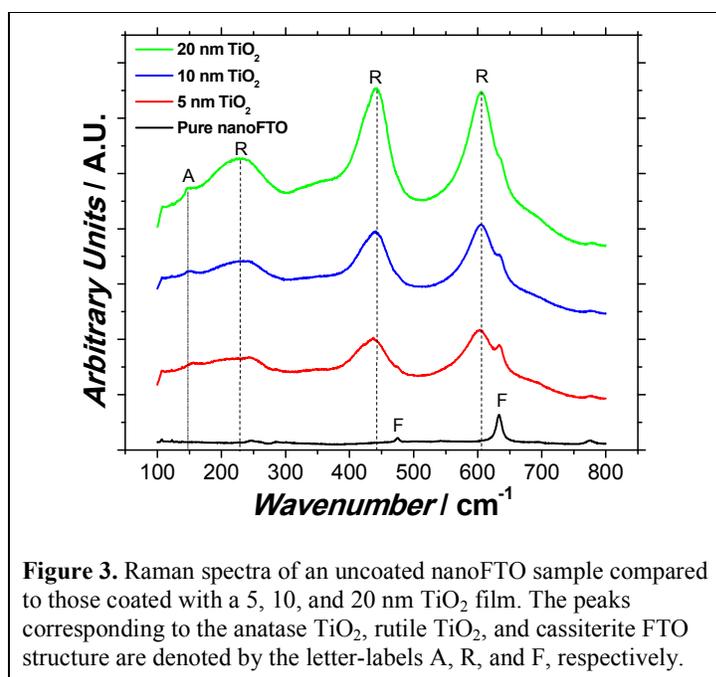
Figure 3. Raman spectra of an uncoated nanoFTO sample compared to those coated with a 5, 10, and 20 nm TiO_2 film. The peaks corresponding to the anatase TiO_2, rutile TiO_2, and cassiterite FTO structure are denoted by the letter-labels A, R, and F, respectively.

a preferential formation of rutile TiO_2 via ALD when deposited on rutile-like substrates at low growth temperatures.[10, 17, 18] Interestingly, as the film thickness increases, a small peak corresponding to the major anatase TiO_2 Raman band near 143 cm^{-1} starts to be detected, as shown by the TiO_2(20nm)/nanoFTO sample. This suggests that although our polycrystalline TiO_2 material consists mostly of the rutile phase, some TiO_2 crystals with the anatase phase might also be present in small concentrations.

Figure 4 contains scanning electron micrographs (SEMs) of TiO_2/nanoFTO samples as the TiO_2 coating thickness is increased. The plain-view SEMs in Figures 4a-c show the transition from the wide distribution of open pores (dark regions) provided by the uncoated nanoFTO scaffold (Figure 4a) to the sample with the thickest TiO_2 film (Figure 4c), where the density of visible pores has been drastically reduced. In contrast, the TiO_2(10nm)/nanoFTO sample displayed in Figure 4b shows an intermediate state where the smallest pores may have been filled but the larger pores remain. The cross-sectional perspective in Figure 4d, shows the larger pore channels through which the TiO_2(10nm)/nanoFTO photoelectrode maintained electrolyte accessibility throughout the depth of the nanostructure.

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Figure 4. Top-down SEM images displaying the evolution of topological porosity from a)
pristine/uncoated, b) 10 nm TiO_2, and c) 20 nm TiO_2 nanoFTO samples. The inset figures are the
regions on the samples under higher magnifications. d) Cross-sectional SEM image of a
TiO_2(10nm)/nanoFTO sample displaying pore channels inside of the film.
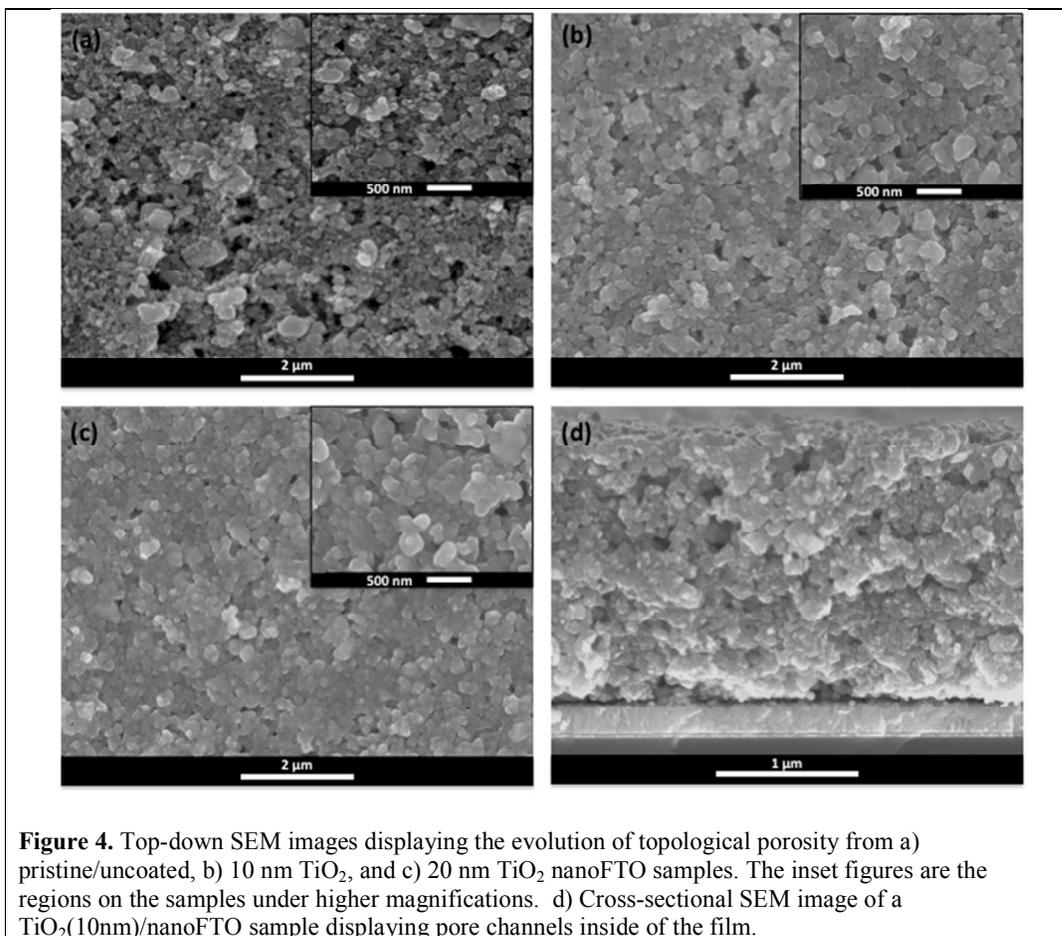
2.2. Photoelectrochemical Performance

2.2.1. Photocurrent Optimization

Figure 5 displays the photocurrent density (J) as a function of the applied potential

versus an Ag/AgCl (KCl sat') reference electrode ($E_{Ag/AgCl}$) and was obtained by performing

linear cyclic voltammetry scans on TiO_2/nanoFTO photoelectrodes with a range of TiO_2

thickness. The consistent diode-like shape (or fill factor) across all of the photocurrent

responses plotted in Figure 5a confirms the conformal coverage of the ALD TiO_2 coating over

the entire surface area of the underlying nanoFTO. In addition, the cathodic peak observed at

$E_{Ag/AgCl}$ = -0.9 V corresponds to the oxygen reduction reaction resulting from ineffective

purging of the recently evolved O_2 within the mesoporous nanostructure. Figure 5a shows that

the TiO_2(10 nm)/nanoFTO produces a photocurrent density of 0.7 mA/cm^2 at $E_{Ag/AgCl}$ = -0 V.

This is the maximum J observed among various TiO_2 film thicknesses and can henceforth be

considered to be the optimal thickness for this particular nanostructure. This value represents an almost fourfold enhancement over the recently reported values for planar ALD TiO_2/FTO and is even higher than the 0.58 mA/cm^2 photocurrent density value which was recently observed with nanoATO.[10] Figure 5b summarizes the J-$E_{Ag/AgCl}$ data in order to help to visualize the effect of thickness on photocurrent. At thicknesses less than 10 nm, there is a high surface area in contact with the electrolyte, allowing a large concentration of reactive sites to be available for the OER. However, there is not enough TiO_2 to absorb and convert an optimal number of photons, which is evidenced by the Incident Photon-to-Current Efficiency (IPCE) measurements presented in the following section. As the thickness increases to 10 nm, the smaller pores may begin to be filled (as shown in the SEM from Figure 4). However, any detrimental effects on PEC performance caused by a decrease in active surface area are likely outweighed by a boost in light absorption from the higher loading density of the photoactive TiO_2 coating (**Figure S3**). As the thickness of TiO_2 coatings becomes larger than 10 nm, the majority of the pores become filled which causes a sharp drop in photocurrent. The filling of larger pores reduces the active surface area and increases the hole transport lengths, counteracting the benefit of adding photoactive TiO_2. These competing contributions account for the leveling off of J. Thereafter, J is expected to continue to decrease as the last pores become filled in a manner similar to a previous study.[10] As for the stability of these samples, within the roughly 30 minute time period required for most experiments, no obvious degradation of the photocurrent is observed for any of the TiO_2/nanoFTO samples. Even more, the J-$E_{Ag/AgCl}$ curves from a TiO_2(10nm)/nanoFTO sample that had been stored in air and then retested periodically in 1 M KOH over the course of approximately 1 year displayed no significant signs of degradation (**Figure S4**).

Figure 5. a) Cyclic voltammograms taken at a sweep rate of 20 mV/s of TiO$_2$/nanoFTO samples with a range of TiO$_2$ thicknesses (colored lines) under ~ 1 sun of AM 1.5G irradiation and under dark condition (black line). b) Photocurrent densities measured at E$_{Ag/AgCl}$ = 0 V of TiO$_2$/nanoFTO samples as a function of TiO$_2$ thickness
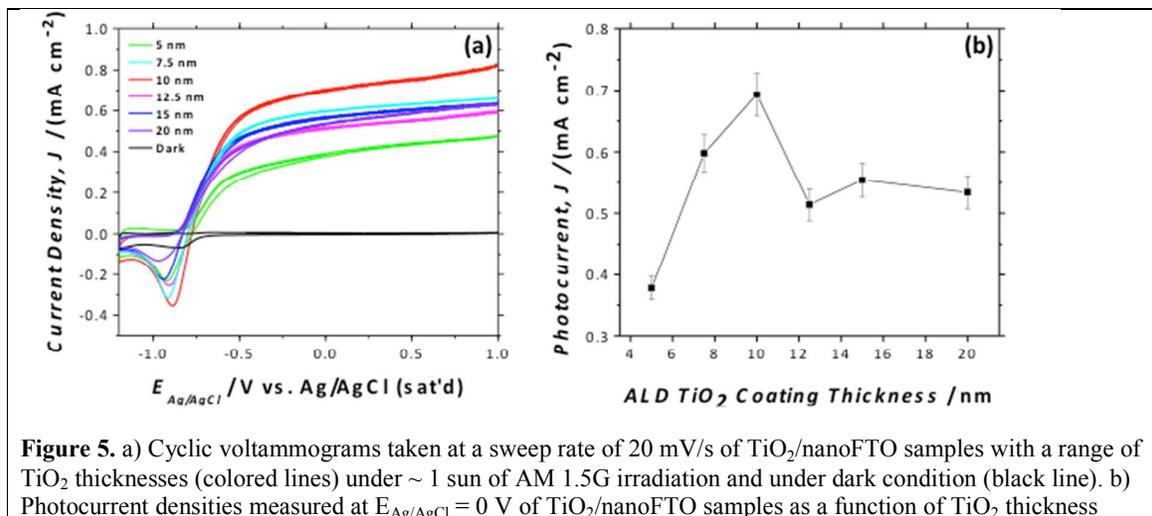
2.2.2. Incident Photon-to-Current Efficiency (IPCE)

IPCE measurements were conducted on the photoelectrodes to gain additional insight into the wavelength-dependent photon absorbance, carrier separation, charge transport, and interfacial charge transfer mechanisms related to the total photocurrents observed above. IPCE spectra of various samples and a schematic of the corresponding mechanisms are shown in **Figure 6**. The IPCE spectra displayed in Figure 6a were collected at E$_{Ag/AgCl}$=0, thus characterizing the mechanisms behind the photocurrents observed in Figure 5b. As expected from the data above, the TiO$_2$(10nm)/nanoFTO IPCE curve shows the highest overall efficiencies. The IPCE curve of TiO$_2$(7.5nm)/nanoFTO closely matched the IPCE behavior of the TiO$_2$(10nm)/nanoFTO sample at wavelengths (λ) less than 380 nm, but its values are smaller at wavelengths longer than 380 nm. The smaller IPCE at these longer wavelengths accounts for the lower total photocurrent performance of TiO$_2$(7.5nm)/nanoFTO in comparison with TiO$_2$(10nm)/nanoFTO (Figure 5a), despite the fact that the overall area under each IPCE curve is similar for both samples. This is because of a much higher weighting factor for photons near 400 nm in the simulated solar spectrum (AM 1.5 G) than the photons with shorter wavelengths deeper into the UV region.[19]

It is also important to note the relatively high IPCE efficiencies obtained for the higher energy UV photons (below 350 nm wavelengths) in all the TiO$_2$/nanoFTO electrodes. For

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other reported TiO_2-based nanostructured photoelectrodes, the IPCE values peak and then

decrease dramatically as the wavelengths decrease.[17, 20] As an example, we confirmed this

behavior for 1.8um TiO_2 nanowires (NWs) on planar FTO glass, which show IPCE values

that peak around 380 nm and decrease sharply at shorter wavelengths (**Figure S1**). This is due

to a larger recombination ratio for photoelectrons excited by shorter wavelength, which tend

to be generated near the tips of the nanowires and thus have a high probability of recombining

as they are transported throughout the micrometer-long NWs. However, such behavior is not

the case here for the TiO_2-coated nanoFTO electrodes; the high IPCE values are sustained

down to a wavelength of 300 nm. We attribute this efficient behavior to the unique ALD

TiO_2/nanoFTO hetero-nanostructure.

The underlying nanoFTO support plays several roles here. First, the high electron

conductivity of the FTO nanoparticles decreases the transport time needed for electrons to

reach the collecting electrode. When this is combined with the short distance that holes

photogenerated within the thin TiO_2 coating need to travel before reaching the SCLJ, the high

electron conductivity decreases the recombination rate of the electron-hole pairs. This is

especially important for the electron-hole pairs that are generated from high-energy photons,

since they will be absorbed near the top surface of the electrode due to their large absorption

cross-section.[17, 20] Second, nanoFTO will transmit or scatter photons with energy smaller than

3.5eV. Although this means that it will not compete with TiO_2 for the absorption of photons

with energies between 3.0-3.5 eV, the absorbance of such photons within thin TiO_2 coatings

(≤ 20 nm) is normally very small. However, due to the 3D morphology of the nanoFTO

scaffold, the probability that the TiO_2 coating will absorb these photons will be dramatically

increased as they scatter and propagate through the tortuous pathway inside the TiO_2-coated

FTO nanoparticles. Third, the IPCE spectrum of nanoFTO without ALD coating indicates

that the nanoFTO support will absorb photons with energies greater than 3.5 eV ($\lambda < 350$ nm)

and convert them into useful electron-hole pairs. Based on the respective positions of the

conduction and valence band edges of FTO and TiO_2, a type II heterojunction is formed

between FTO and TiO_2 that promotes charge transport across the semiconductor junction in

the desired directions for the OER.[21] The approximately 40% IPCE values imply that the

nanoFTO is not only absorbing a large number of the incident photons with $\lambda < 350$ nm, but is

also helping to separate the photogenerated carriers efficiently at the heterojuncion with TiO_2.

We postulate that an additional reason for this rapid charge separation may be due to the

reported intermixing of the electronic structure of FTO and TiO_2 near the heterojunction,

which may cause a small potential distribution to be felt near this interface.[22] In addition, it is

possible that the complete depletion of the ultrathin TiO_2 coating at $E_{Ag/AgCl} = 0$ may cause the

total width of any depletion layer ($W_{D,Total} = W_{D,FTO} + W_{D,TiO2}$) to extend a small distance into

the nanoFTO structure. The strength of the electric field (amount of band bending) within

TiO_2 is expected to be small due to the ultrathin dimensions of the ALD TiO_2 coatings.[23]

Although there have been reports of small scale band bending inducing the photooxidation of

water on TiO_2,[24] we ascribe most of the charge separation within our ALD TiO_2 films to their

long diffusion lengths (10-100 nm)[25-27] by which they will reach the SCLJ and become

rapidly scavenged by the OH^-/O_2 redox-driven free energy gradient on the surface.[28] On the

other hand, within the nanoFTO, the formation of the depletion layer might provide the

electric field required to efficiently separate the photogenerated charges (Figure 6b). This kind

of extension of the depletion layer into the underlying TCO material has been reported for

anatase TiO_2 thin films on tin-doped indium oxide.[29] In summary, the combined effects of

these above-mentioned mechanisms help to produce the unique IPCE behavior of these ALD

TiO_2/nanoFTO nanostructured photoanodes.

Figure 6. a) IPCE spectra of nanoFTO with and without ALD TiO$_2$ coating samples collected at E$_{Ag/AgCl}$ =0 with 1 Sun AM 1.5 illumination; b) Schematic band diagram depicting the heterojunction at the interface between a nanometer FTO particle and TiO$_2$. The band bending between TiO$_2$ and FTO heterojunction favors the separation and transport of photogenerated charges.

2.2.3. Characterization of Recombination Mechanisms

To help further understand the charge transfer mechanisms of the TiO$_2$/nanoFTO samples, we analyzed their transient photocurrent behavior from chopped illumination and contrasted it with the performance of a sample of hydrothermally-grown rutile TiO$_2$NW/FTO with similar photocurrents (**Figure 7**). The measurement of these non-steady state photocurrents can be used to study recombination mechanisms since the characteristic relaxation time for minority carriers trapped in surface states or accumulated near the surface is slow enough to be detected experimentally.[30]

Figure 7a shows the similar levels of total photocurrent performance for both of these samples under chopped illumination as well as a saturation of photocurrent transient effects as a function of additional negative bias. Since the photocurrent transient effects are more pronounced near the onset of photocurrent, we chose to compare their transient behavior during an amperometric scan conducted at a constant potential of $E_{Ag/AgCl}$ = -0.8V. This low band-bending region is expected to highlight the recombination due to the accumulation of holes and surface states, and not be subject to the effect of photon flux.[31] The symmetry of the anodic and cathodic transients observed for each sample indicated that both samples suffered

from these recombination mechanisms. However, the drastically larger transient peak current feature observed from the TiO_2 NW sample indicates a loss of a significantly higher fraction of photogenerated charges[32] than the ALD TiO_2/nanoFTO sample. The dramatic difference in charge transfer mechanisms between TiO_2/nanoFTO and rutile NWs is also highlighted by their different impedance response under EIS, whose Nyquist plot shows an additional charge transfer (semicircular) feature at low frequencies only for the rutile NWs (**Figure S2**). This indicates that the surface of the ALD TiO_2 allows more facile charge transfer across the SCLJ.[33, 34]

In highly alkaline 1 M KOH, two possibilities have been previously proposed as explanations for the faster surface hydroxide-driven reaction kinetics[35] observed on certain rutile TiO_2 materials. The two possibilities are i) the presence of multiple rutile crystal facets, and ii) a higher concentration of oxygen vacancies on the film's surface.[36] Both of these are possible given the polycrystalline and defective growth mechanism inherent to ALD. However, a more intriguing possibility is the generation of more peroxide (H_2O_2) species generated only near the surface[31] which serve as hole scavengers[37] and thus accelerate the OER.[32] Given the slightly more negative redox potential for OH^-/H_2O_2 than OER,[21] such peroxides could be generated more easily if "hot holes" reached the surface before having time to relax down to the valence band edge by thermalization. However, assuming that the thermalization time is just under 100 ps for n-TiO_2[38] and that the hole transit time through a full depletion layer is less than 40 ps,[21] it may be possible that the efficient collection and utilization of the deep UV photons by the TiO_2/nanoFTO photoelectrodes could be yielding such behavior. This may be even more likely for the nanoFTO system, given the ultrathin nature of the ALD TiO_2 films that would result in even shorter theoretical hole transit times. Although the feasibility of such behavior is still under some debate, there have been some reports claiming that it can be sustained across the SCLJ using oxide-covered metallic electrodes.[39, 40]
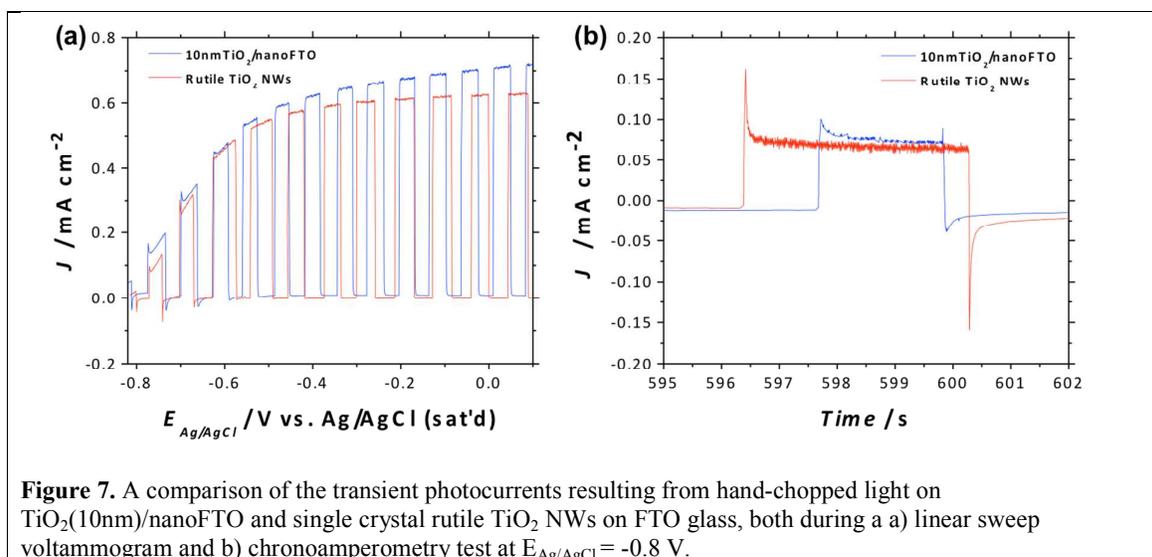
Figure 7. A comparison of the transient photocurrents resulting from hand-chopped light on TiO_2(10nm)/nanoFTO and single crystal rutile TiO_2 NWs on FTO glass, both during a a) linear sweep voltammogram and b) chronoamperometry test at $E_{Ag/AgCl}$ = -0.8 V.

3. Conclusion

We have shown that the ALD TiO_2/nanoFTO nanostructure resulted in a photoanode with impressive light harvesting efficiency for the photooxidation of water. In particular, the high IPCE efficiencies of TiO_2/nanoFTO throughout their materials' respective absorption regions provide insights for future development of tandem heteronanostructures for applications in PEC conversion and solar cells. Moreover, the photocurrent transient behavior indicates charge transfer mechanisms on the surface of these nanostructures is extremely efficient and could be a property inherent to these ultrathin ALD films. Given the large junction area that is responsible for the photocurrent enhancement, future work should be done to characterize the specific electronic properties and chemical bonding structure near the interface between the ALD TiO_2 and the nanoFTO, as it is possible that the *d* orbital occupancy has been modified near this transition metal oxide interface.[22] We expect that future applications could exploit the beneficial effects observed herein to further improve the PEC conversion efficiencies of other promising materials such as hematite (α-Fe_2O_3).

4. Experimental Methods

Synthesis of nanoFTO-coated Substrates

FTO nanopowder (3 g, Keeling and Walker, 0.1 - 0.3 microns, BET surface area 10-15 m^2) was added to 200 proof ethanol (10 mL) to make a suspension of nanoFTO as discussed previously.[41] The application of nanoFTO onto 12 mm x 50 mm FTO-coated Soda lime glass (Hartford Glass, 15 ohm/sq) was accomplished by spin-coating the nanoFTO suspension according to earlier procedures.[10, 42] Finally, the approximately 2μm thick layer of nanoFTO was sintered at 450 °C for 2 hours before the ALD process.

Atomic Layer Deposition (ALD)

The TiO_2 films were deposited on the nanoFTO-coated substrates described above by a "homemade" hot-wall viscous flow ALD reactor operated at 300 °C. The reactor was kept at process pressure of 1.42 Torr under a constant 300 sccm flow of UHP nitrogen (Airgas Inc.) as a carrier and purging gas. $TiCl_4$ and deionized H_2O were used as the metal precursor and the co-reactant, respectively, for the TiO_2 ALD process. All precursors were held at the temperature of ~ 40 °C. The time sequence of the recipe used was 1.5/5 and 1.5/5 s for the $TiCl_4$ dose/purge and H_2O dose/purge, respectively. Prior to growth, substrates were blown dry with UHP nitrogen before loading them into the ALD chamber. During each growth run, p-type Si (100) substrates covered with a native oxide layer were placed along the length of the reactor as the control samples to monitor the film thickness. Film thickness was measured by using a J.A. Woollam M-88 Variable Angle Spectroscopic Ellipsometer at scan angles ranging from 65-75° and a polarizer angle of 20°. These thicknesses corresponded to the thickness of the films deposited on the nanoFTO glass substrates since the growth rate has been shown to be the same on Si as on FTO ([43]). 5, 7.5, 10, 12.5, 15, and 20 nm TiO_2 films were deposited using 120, 171, 225, 270, 318, and 410 ALD cycles, respectively. The measured growth rate was approximately 0.5 Å per cycle.

Material Characterization

The chemical compositions of TiO_2 films were characterized by X-ray photoelectron

spectroscopy (XPS) using a Kratos Analytical Axis Ultra equipped with a monochromated Al

K-α x-ray source operated at an emission current of 10 mA with an accelerating voltage of 15

kV. Pass energies of 20 eV and 160 eV were used for regional and survey scans, respectively.

The step sizes were 0.1 eV and 1 eV for the regional and survey scans, respectively. All XPS

spectra were processed with CasaXPS software, and were calibrated to an adventitious carbon

peak near 284.6 eV. The crystallinity of the films was characterized by Raman spectroscopy

via an Horiba Jobin Yvon LabRam ARAMIS Raman microscope with a 633 nm He/Ne laser.

The morphologies of samples were imaged using an FEI XL30 Scanning Electron Microscope

(SEM) under a high-resolution mode with electron beam energy of 15 kV. Lastly, optical

measurements from the TiO2/nanoFTO nanostructure was collected at UNC-Chapel Hill

using a Cary 5000 UV-Vis spectrometer with the DRA-2500 internal integrating sphere

accessory. Using a planar FTO sample as the blank for reference, reflectance and

transmittance data were measured in order to calculate the amount of absorption plus

scattering (that couldn't be accounted for by the integrated sphere) taking place in our

samples according to the formula $100 - T - R = A + S$, where T is the total transmittance, R is

the total reflectance, A is the absorption, and S is the unaccounted scattered light.

PEC Performance Characterization

All electrical connections were made by scratching the ALD film to expose part of the

underlying FTO surface. The scratched region was then rubbed with InGa eutectic metal

(Sigma-Aldrich, 495425) in order to ensure an ohmic contact with low resistance between the

FTO coating on the glass and the flattened end of a bare Cu wire used as the electrode lead.

This contact region was then sealed with a nonconductive epoxy (Hysol 9460, Loctitte) and

left to cure for at least two hours. In order to isolate all non-semiconductor (inactive)

components from the electrolyte, the rest of the length copper wire was fed through a quartz

glass tube (Ace Glass, O.D. 6mm) and the active planar PEC area was defined by covering all

inactive regions of each sample with the same nonconductive epoxy resin. Electrochemical

activity was measured using a Bio-Logic SP-200 potentiostat. An Oriel 150 W Xe Arc lamp

with an AM 1.5 G filter was used as the light source with the calibrated power of 100 mWcm^{-2} on the sample surface. All measurements were performed with a 1 M KOH electrolyte and

under a constant flow of Ar as the sparging gas, via a standard three-electrode configuration

with a Pt mesh as the counter electrode and an Ag/AgCl (saturated in KCl) reference electrode

(0.198 V vs. standard hydrogen electrode). To measure the basic photoresponse, cyclic

voltammetry (CV) scans were taken at a voltage sweep rate of 20 mV/s. The photocurrent

density was then obtained by dividing the photocurrent by the photoactive area of the

electrode, which was measured through scale-marked photos via Image-J. The

electrochemical impedance spectroscopy (EIS) measurements were performed under both

dark and light conditions. The amplitude of the sinusoidal voltage was 10 mV and it was

applied across a frequency range from 1 MHz to 1 mHz. Mott-Schottky analyses were derived

from the EIS measurements at the frequency of 1 kHz. The incident photon-to-current

efficiency (IPCE) data was collected at 0 V vs. Ag/AgCl using a customized Newport-Oriel

system powered by a 300 W Xe (Ozone-free) lamp equipped with a Cornerstone 130 1/8 M

Monochromator. The irradiance was measured with a power meter (Newport 1918-R)

adjusted to the calibrated photoresponse of a standard silicon photodetector.

Rutile TiO$_2$ Nanowire Synthesis

The hydrothermal synthesis procedure of TiO$_2$ nanowires on a FTO glass substrate is similar

as the literature report. The reaction solution was made by mixing 5 ml concentrated HCl

(ACS, ~37%,) with 5 ml de-ionized (DI) water, followed by addition of 0.16 ml of titanium

butoxide (Reagent Grade, Sigma Aldrich). The solution was stirred for 10 min before

transferred into a hydrothermal autoclave reactor, which has a volume of 20 ml. A cleaned

FTO glass substrate, which was sonicated in soap water, DI water, ethanol, and DI water

sequentially, was then leaned against the wall of the Teflon lined autoclave with the FTO

coated surface facing downwards. The sealed autoclave was then transferred into a furnace

and sit in the furnace for 2h at 200 °C. After the reaction, DI water was used to cool down the

autoclave to room temperature before open it. Then the FTO substrate coated with uniform

pale white film of TiO_2 nanowire (NW) was recovered and rinsed thoroughly by DI water,

and dried in air. The synthesized TiO_2NW/FTO samples were then annealed in air at 500 °C

for 2h before assembled into a testable electrode.

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Notes and References:

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