



Low Dimensional Oxide and Silicon Nanostructures for Promoting Photoelectrochemical Energy Conversion

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Authors' contributions

This work was carried out in collaboration between all the authors. Authors KH and DR did the lab tests and wrote the first draft of the paper. Author RNG performed the statistical analysis. Author KRA provided technical consulting. Author YXG designed the study. All authors read and approved the final manuscript.

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ABSTRACT

Electrospun titanium dioxide nanofibers can be applied to the surface of titanium dioxide nanotube photoanode to create a multiple component catalyst anode. The electrospinning process was found as a simple way to create the titanium oxide nanofibers with varying diameters ranging from 50 to 500 nm when polyvinylpyrrolidone (PVP) was used as the precursor for making the composite titanium oxide nanofiber with high surface area while perserving the intrinsic semiconductor properties of TiO₂. Photoelectrochemical decomposition of ethanol was tested on the composite photoanode. Different nanostructured photoanodes including silicon nanowire anode were designed and tested to determine which photocatalyst had the fastest response time. The effect of ethanol fuel concentration on the photovoltaic response of the photoanode was also studied.

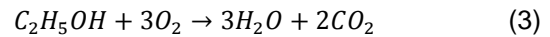
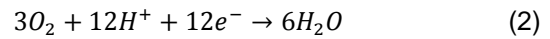
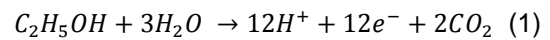
Keywords: Nanostructure; electrospun titanium dioxide nanofibers; composite photoanode; photovoltaic responses; ethanol fuel; fuel concentration effect.

1. INTRODUCTION

With the increase of environmental pollutants arising from biomass wastes and the diminishing of fossil fuel resources, the photoelectrochemical (PEC) process has gained more interest within recent years [1-6]. The use of photoelectrochemical cells first became popular before the 1960s [2], when it was discovered that this system could create renewable hydrogen by splitting water using solar radiation. However, splitting water was considered inefficient and needed an outside bias to run the oxidation process. With the recent ease of creating nanocrystalline semiconductors along with the rising concern over the impact of environmental pollutants there has been a reemergence of attention toward the PEC process [3]. Unlike the traditional photovoltaic conversion of solar power, the PEC process can simultaneously decompose biomass waste and be used as a clean source of energy [4]. The utilization of clean energy generation, converting solar energy into electrical current, over fossil fuel dependency is important to create a sustainable solution to multiple problems.

A photoelectrochemical cell is comprised of three primary components which include an anode, a cathode, and the electrolyte. The anode or photoanode is usually made up of an n-type semiconductor containing the photocatalyst nanostructure. Titanium Dioxide is considered one of the best photocatalysts to be used as an anode due to it being environmentally friendly, having a low cost, and having excellent photostability [2,5]. The structure of TiO₂ nanotubes gives a boost in the photocatalytic oxidation process due to its greater surface area [6]. When UV irradiation is applied onto the photoanode an electron-hole pair is created and the oxidation of biomass waste is started. The cathode is made of a material, usually a noble metal Pt or Pd, which enables the transfer of electrons from the electron-hole creation. The cathode attracts the hydrogen ions created at the anode and reduces them to form molecular hydrogen where it is recombined with oxygen to create water molecules. The electrolyte consists of the biomass waste and is important in increasing electrical conductivity [7,8]. For the purpose of this paper, ethanol was used as the electrolyte which has the following oxidation process at the anode, reduction process at the

cathode and overall redox reaction respectively [8]:



Electro-spun titanium dioxide nanofibers can be applied to TiO₂ nanotube photoanodes to create a multi-catalyst anode. The electrospinning process is considered as one of the simplest ways to create nanofibers of varying diameters ranging from 50 to 500 nm [9]. Titanium, when combined with a polyvinylpyrrolidone (PVP) composite, creates a nanofiber with high surface area while containing the intrinsic semiconductor properties of titanium dioxide.

The novel approach in this work is to create titanium dioxide nanofibers setting on vertically aligned titanium dioxide nanotubes to obtain high active surface area. As a comparison, the effects of using silicon nanowires (SiNW) as a substrate will also be studied in this paper. SiNWs create a porous background for electrodeposited silver to be placed upon. Silver has a plasmonic effect which allows free electrons to oscillate on the surface of the metal when exposed to light [10]. This plasmonic effect allows Silver to be used as a photocatalyst. Silicon can also be easily etched which creates another photocatalyst. The porous SiNWs enhances the phonon scattering about the interfaces of the nanowires due to its high anti reflectivity causing higher absorption efficiency [11,12].

The functionality of a PEC cell is driven by many factors. Although titanium oxide nanotubes are the primary interest in this field of research, the purpose of this paper is to determine what nanostructured photocatalyst anodes, as well as varying concentration levels, effect the response time of the PEC reaction when exposed to UV irradiation. Over a short period of UV irradiation exposure, the response time influences how much the potential difference changes between the anode and cathode. Creating multi-catalyst anodes using doping techniques, electrospinning applications, and electrodeposition methods change the photocatalytic properties. Varying the concentration of the fuel by lowering the energy density present in the electrolyte also

affects the response time of the photoanode. By inspecting the various response times, we can determine which photoanodes are more efficient.

2. EXPERIMENTAL

2.1 Materials and Equipment

Titanium was cut into four (4) strips with dimensions 40 mm in length, 5 mm in width, and 1 mm in thickness as the starting material. Silicon nanowire bulk was cut into three (3) strips with dimensions 20 mm in length, 5 mm in width, and 1 mm thick. After preparing the strips, described later in the paper, the eight strips tested were the pure Titanium baseline, un-heat treated TiO₂ nanotubes, heat treated TiO₂ nanotubes, Cobalt doped TiO₂ nanotubes, heat treated electro-spun PVP nanofiber on top of TiO₂ nanotube, Silicon nanowire bulk, electrodeposited Silver nanoparticle on Si, etched electrodeposited Silver nanoparticle on Si. The power supplies used were a RSR model HY5003 DC power supply and a Hewlett Packard E3615A DC power supply. A CH Instruments 440C electrochemical analyzer connected to a laptop was used to record the potential difference between the anode and cathode of the photoelectrochemical fuel cell. A UVL-21 UV light source with the following specs (4 W, 365 nm, 16 Amps, 115V ~ 60Hz). A 3 mL plastic transfer pipette was used when moving small volumes of liquids. An OHAUS centi-o-gram model 311 was used to weigh chemicals and compounds for the mixtures needed. A 20 mL syringe and a Fusion 100 syringe pump was used for the electrospinning process. Ethanol with varying concentrations of 96%, 50%, and 25% were used as the electrolyte in the testing of the fuel cells.

2.2 Preparation of TiO₂ Nanotube Photoanode

Three (3) of the titanium strips were put through the oxidation process to create nanotubes on the surface. The strips were placed into an electrolyte solution containing 90% ethylene glycol (EG), 7.5% water (H₂O), and 2.5% ammonium fluoride (NH₄F) by weight. The titanium strips acted as an anode and platinum was used as a cathode. The direct current (DC) power supply delivered 50 volts between the anode and cathode for 2 hours to allow for the oxidation process to take place. The strips were then rinsed with water and

allowed to air dry. This process was completed for each of the three strips.

2.3 Preparation of Cobalt Doped and Heat Treated TiO₂ Nanotube

One of the oxidized TiO₂ strips was placed into a cobalt acetate tetrahydrate ($C_4H_6CoO_4 \cdot 4H_2O$) solution for 20 seconds. This process is for creating a cobalt – titanium doped composite. This doped strip, as well as one of the oxidized nanotube strips were then placed into a crucible set at 500°C for 2 hours for the crystallization process to be complete.

2.4 Preparation of Electrospun Titanium Dioxide Nanofiber Photosensitive Anode

In a beaker 0.75 grams of polyvinylpyrrolidone (C_6H_9NO), 8 mL 96% ethanol (C_2H_5OH), and 0.18 grams of titanium n-butoxide ($C_{16}H_{36}O_4Ti$) were initially mixed. Using a plastic pipette, 3 drops of vinegar and 3 drops of acetic acid were stirred into the mixture until all of the PVP powder was dissolved. Adding the acidic vinegar stabilizes the titanium n-butoxide since it decomposes in bases. This stirring process took approximately 5 minutes for the solution to be fully dissolved. The mixture was then put into a syringe and inserted into the syringe pump. The power supply was connected, the positive electrode connected to the tip of the syringe and the negative electrode connected to the collecting plate as seen in Fig. 1. The collecting plate was placed 12 cm away from the tip of the syringe. The voltage was set to 15 kV with the pump running at 0.05 mL/min. The un-heat treated TiO₂ nanotube strip was placed at the base of the collecting plate to allow for the nanofibers to evenly disperse across the strip. The strip was allowed to collect nanofibers for 20 minutes. The strip was fully covered in electro spun nanofibers and was then wrapped in foil and placed into a crucible and heat treated for 2 hours at 500°C. The electro spun TiO₂ nanotube strip, as well as the other titanium strips are shown in Fig. 2.

2.5 Preparation of Silicon Nanowire Array

Three strips roughly 20 mm in length, 5 mm in width, and 1 mm in thickness were cut using a diamond cutter from the silicon nanowire bulk. The control bulk silicon strip was cleaned with 5 mL hydrofluoric acid (HF) for 1 min. Two of the strips were then cleaned with 2.5 mL deionized

water and were then placed into 0.5 mL 0.6 M HNO_3 were silver (Ag) was electrodeposited to form a n-type doped nanofilm. One of the Ag electrodeposited strips was placed in 1:1 ratio bath of 0.2 M H_2O_2 and 4.8 M HF and was allowed to be etched for 60 min. The specimens are shown in Fig. 3.

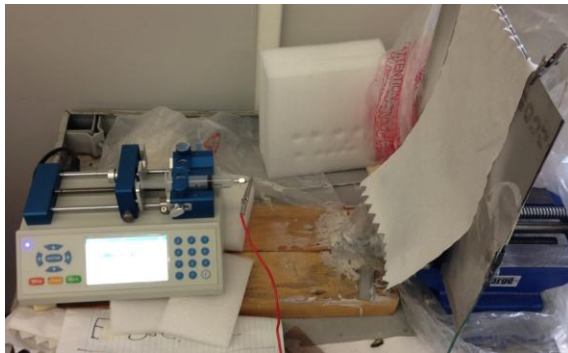


Fig. 1. Electrospinning pump and collector plate setup

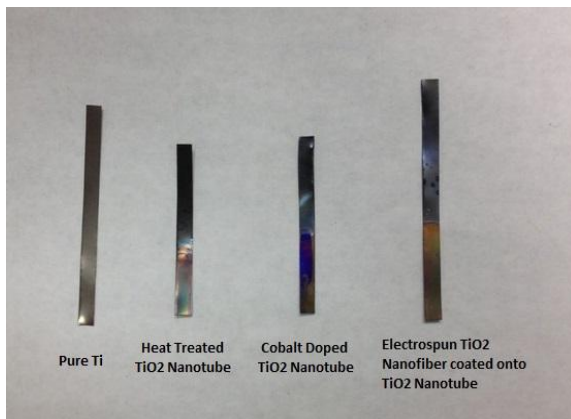


Fig. 2. Pure titanium and various titanium dioxide anodes used in the PEC fuel cell

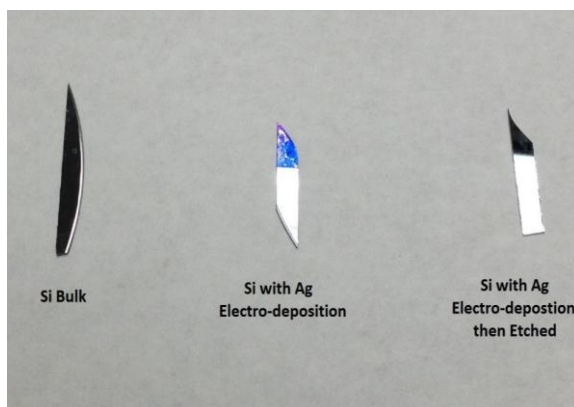


Fig. 3. Silicon anodes used in the PEC fuel cell

2.6 Photoelectrochemical (PEC) Fuel Cell Setup

Ethanol with varying concentrations, ranging from 96% to 25%, was used as the fuel for the PEC cell. The setup for the fuel cell is shown in Fig. 4, where the ethanol was placed in a small beaker and was set upon a CH Instruments stand. Originally 3 mL of 96% ethanol was placed into the beaker, then water was added and stirred to create uniform solutions with concentrations of 50% and 25%. The stand was placed over the beaker and had a slot for the photoanode and a slot for the Platinum cathode. The UVL-21 UV light source was used to start the oxidation and decomposition of the biomass waste. The anode and cathode were connected to the CH Instruments 440C electrochemical analyzer which was connected to a laptop. The analyzer recorded the open circuit voltage potential in volts with respect to time between the anode and cathode.

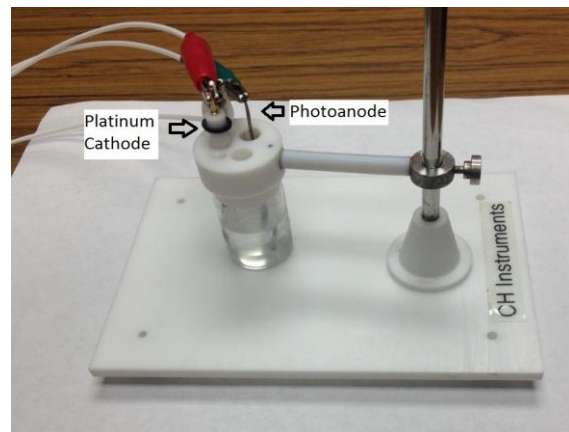


Fig. 4. PEC fuel cell setup with platinum cathode and photoanode.

3. RESULTS AND DISCUSSION

3.1 Surface Morphology of the Electrospun PVP Nanofiber and Etched Si Nanowire Structures

The electrospun PVP nanofibers and the etched electrodeposited silver were first viewed by the naked eye then inspected using a scanning electron microscope. The electrospun nanofiber anode has an orange color when observed with the naked eye. The surface of the nanofiber photoanode can be seen in Fig. 5. The image of the surface shows the chaotic array of nanofibers present on the anode. The nanofiber structures cover the original TiO_2 nanotubes on the surface

which decrease the amount of electrons that reach the cathode but increase the amount of holes, due to the increased surface area, which are used to decompose biomass waste faster. Even though the current is smaller with multi-catalyst anodes, the potential for increased photo degradation is presented.

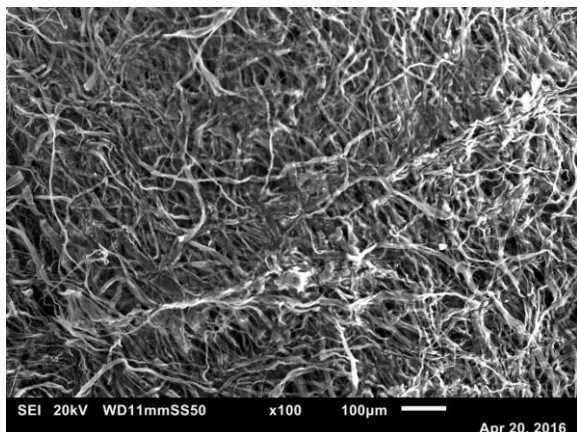


Fig. 5. SEM image of electrospun PVP nanofiber

When the silver electroplated silicon was observed with the naked eye, there was a blue color shown. The surface of the etched silver electroplated silicon anode can be seen in Fig. 6. From the SEM image, the silver nanoparticles can be seen scattered across the surface. The nanoparticles are much smaller than the nanofibers which allows for more photocatalysts to be placed onto the surface. The etching process produces another layer SiO_2 photocatalyst onto the surface. However, the etching process can remove some of the silver electroplating causing a decrease in voltage potential change.

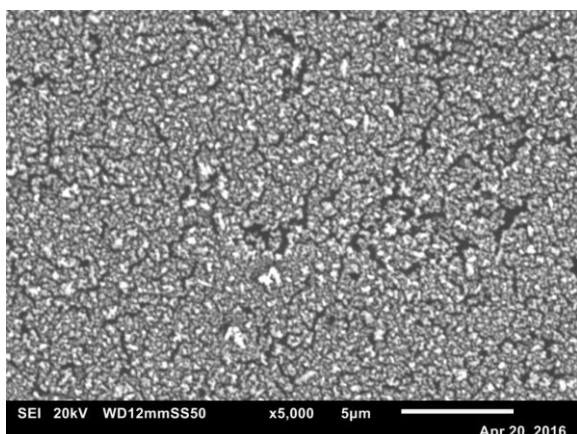


Fig. 6. SEM image of etched Ag electroplated Si

3.2 Photoresponse of Various Nanostructured Photocatalysts

For the photoelectrochemical process, Ethanol was used as the fuel in order to complete the redox reaction at the anode and cathode. The anodes were placed in the ethanol fuel mixture where the UVL-21 UV light source (4 W, 365 nm, 0.16 Amps, 115V ~ 60 Hz) was subsequently turned on and off. The duration of the ON/OFF processes were in the range from 10 to 20 seconds for each iteration. The CH Instruments 440C electrochemical analyzer recorded the potential difference (ΔE) in volts vs. time (t) in seconds. From the graphs that were constructed, the response time can be observed.

The first anode tested was the pure Titanium strip which was used as a baseline. The pure Titanium response to UV light can be seen in Fig. 7. When the UV light was turned on a linear decline in voltage potential was observed. When the concentration was 96% ethanol the voltage dropped about 0.516 mV/second and when the concentration was 50% the voltage drop was about 0.327 mV/second. This small change in voltage potential is due to the natural oxidation of the Ti strip. Since the amount of photocatalyst on the strip is small, the higher concentration helps in the redox reaction causing a higher potential increase. The next anode that was tested, as seen in Fig. 8, was the non-heat treated TiO_2 nanotube strip. When the anode was present in the 96% ethanol the voltage change was about 2.67 mV/second and had about 2.94 mV/second change in the 50% ethanol. Even though both of these strips are technically Titanium dioxide, the nanotube structure on the non-heat treated TiO_2 strip shows a drastic improvement in change of potential when compared to the pure Ti strip. The non-heat treated anode also shows how concentration plays a role in the response. One would expect to see a higher change in potential when the fuel is higher in concentration. However, the contrary was seen due to the decrease in energy density. The decrease in energy density allows the electrons to flow through the fuel more efficiently at a faster rate.

Next we tested the heat treated nanostructured photoanodes. The cobalt doped TiO_2 nanotube strip was the first of these heat treated anodes to be tested. From Fig. 9 the cyclic response behavior can be seen. When the UV light is turned on the response behavior can be described as [13]:

$$\Delta E = Ae^{-Bt} - E_0 \quad (4)$$

Where A and B are constants related to the excitation "On" cycle and E_0 is the equilibrium potential. Conversely, when the UV light is turned off and the recovery behavior is denoted as [13]:

$$\Delta E = E_0 - Ce^{-Dt} \quad (5)$$

Where C and D are constants related to the recovery "OFF" cycle and E_0 is the equilibrium potential. From the graph of the cobalt doped response it can be seen that with the allotted time that the UV light was turned on, the potential does not seem to reach an equilibrium. It can also be seen that the response from the ON cycle was faster than that of the OFF cycle causing the cycles to become more negative. This is due to the cobalt doping which caused the photoanode to become more sensitive to visible light. Fig. 10 shows the comparison of time response behavior for all of the heat treated TiO₂ nanotube anodes. The response was much faster than that of the cobalt doped strip. The time response of the heat treated TiO₂ nanotube anode in the 50% concentration was almost instant changing about 170 mV in potential difference, when compared to the slower 96% concentration potential difference change of about 131 mV. This again is due to a lower energy density of the lesser concentrated fuel causing the response time to be faster. When compared to the response behavior of the heat treated TiO₂ nanotube anode it has a much slower UV response time and smaller potential difference of 100 mV. The reduction in response potential and increase in response time is due to the multi-catalyst nanostructure present on the anode. It should be noted that none of the heat treated TiO₂ nanotube anodes have an instant recovery time but instead follow Equation (5).

Finally, we tested the silicon nanostructured arrays and can be seen in Fig. 11. The first anode used was the Si bulk strip. The pure Si bulk strip was not very photoresponsive but the response seen had an almost instant behavior. Both the silver electroplated and etched silver plated anodes showed a significant increase in potential change as well as an almost instant response time. When the UV light is turned on the Silver plated anode had an average photoresponse change in potential difference of 22.5 mV over a 0.5 second period and the etched silver plated anode had an average photoresponse change of 12 mV over a 0.6 second period. This quick response rate is due to

the plasmonic effect of the silver. The multi-catalyst etched Silver plated anode shows a smaller change in potential with a slightly longer response period. Unlike the Titanium based photoanodes the Si based anodes showed a linear recovery response when the UV light was turned off.

The photoresponse for the cobalt doped, heat treated TiO₂, electro-spun nanofiber, silver plated silicon, and etched silver plated silicon anodes during the excitation cycle in 25% ethanol can be seen in Fig. 12. From the results shown in this figure, the linear photoresponsive reaction can be seen from both of the silicon based anodes. The cobalt and PVP nanofiber anodes have the slowest response excitation times as can be seen in the slopes of the curves. The heat treated TiO₂ shows the largest potential difference when the UV light is turned on.

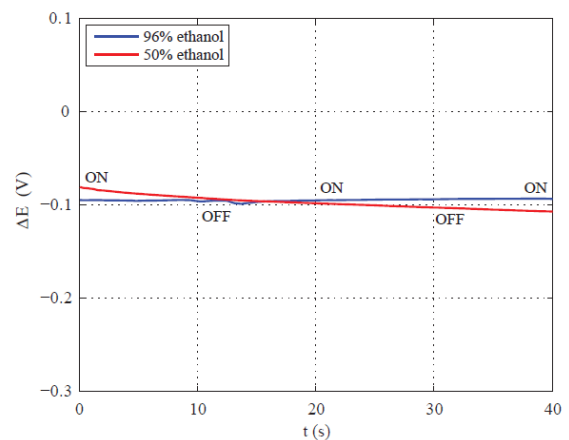


Fig. 7. Photoresponse of pure titanium with 96% and 50% concentrations of ethanol

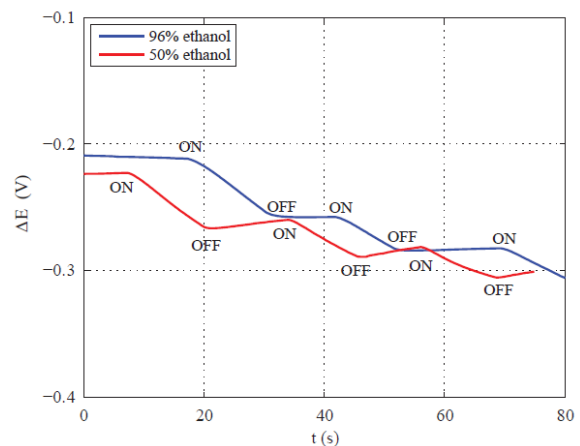


Fig. 8. Photoresponse of non-heat treated TiO₂ with 96% and 50% concentrations of ethanol

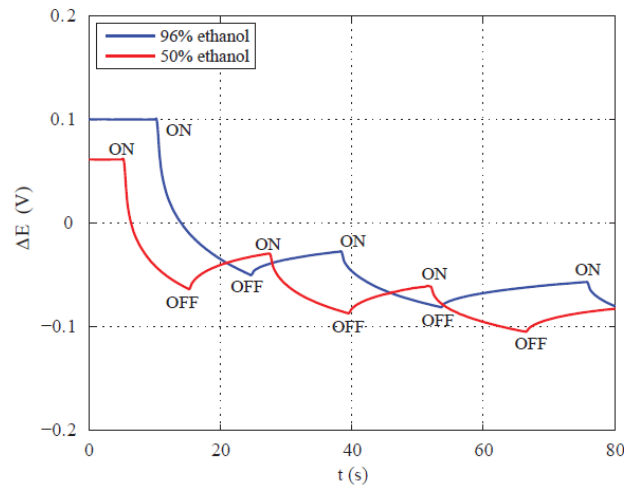


Fig. 9. Photoresponse of cobalt doped heat treated TiO₂ with 96% and 50% concentrations of ethanol

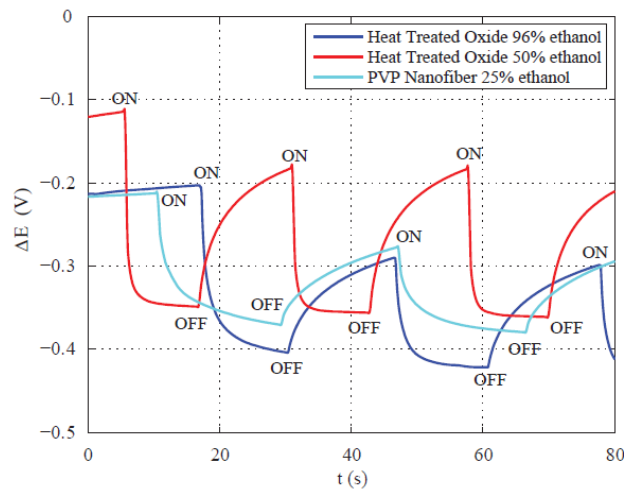


Fig. 10. Photoresponse comparison of heat treated TiO₂ and electrospun PVP nanofiber in varying ethanol concentrations

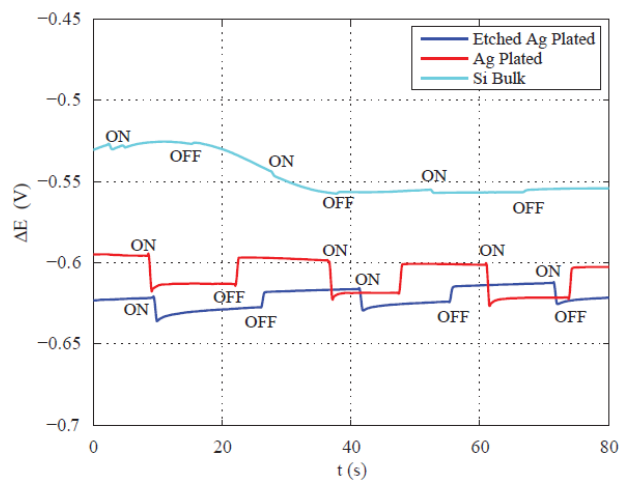


Fig. 11. Photoresponse of silicon nanowire, Ag electroplated Si, and etched Ag electroplated Si in 25% ethanol

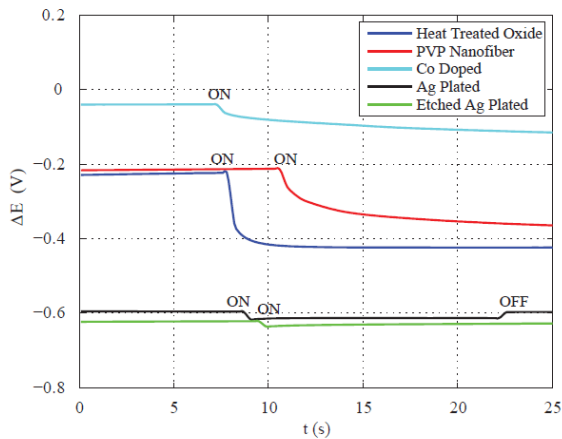


Fig. 12. Photoresponse of excitation period between different nanostructured anodes

Error analysis is considered as one of the most important parts in the work to give a better result and comparison and accuracy of the whole study. In order to perform such an analysis, repeated tests on typical photoanode were made. Fig. 13 shows the open circuit voltage measurement results of two runs on titanium dioxide nanostructured photoanode in 25% ethanol fuel. Obviously the data repeat very well for the two tests. Also, the comparisons with other peoples' studies reveal better performance of our photoanode. For example, Kaneko et al. [2,3] did the photosensitive response studies on titanium dioxide nanoparticles. But the response time is not reported. In view of the service time, nanoparticles easily fell down from surface of anode to the fuel solution. The service time for nanoparticle anode should be much shorter than that of the anode prepared in this work.

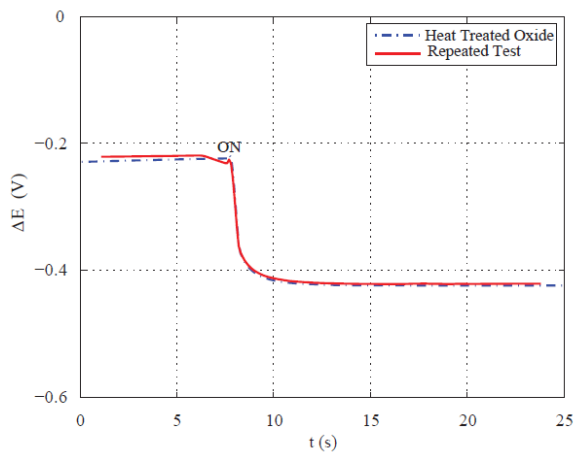


Fig. 13. Photosensitive results based on the repeated tests for the heat treated oxide specimens

4. CONCLUSIONS

The photoelectrochemical process of various photoanodes, including electro-spun PVP nanofibers and Silver plated Silicon nanowires, were subjected to UV irradiation and the response time was studied. The photoanodes provided a potential difference which lead to the decomposition of the biomass fuel.

Based off of the research completed, the heat treated TiO_2 photoanodes displayed the greatest potential difference when the UV light was applied. However, some of these anodes contained some of the slowest response times, namely the electro-spun PVP nanofiber. By electroplating the silicon with silver, the potential difference can be greatly increased.

The silver plated silicon anodes showed a fast response in both the excitement cycle and recovery period while having an overall potential difference similar to the cobalt doped TiO_2 photoanode. Even though the Ag plated silicon nanowires showed increased efficiency in recovery time, the heat treated TiO_2 photoanode showed the largest potential difference even though the response time was slightly slower. The larger potential difference is ideal when creating a sustainable energy source. The concentration of the fuel used directly impacts the photoresponse time. This can be primarily observed when the heat treated TiO_2 photoanode was tested in the 96% and 50% ethanol concentrations. The higher concentration fuels create longer response times due to the higher energy density.

Since it has been observed that silver plated silicon photoanodes can create energy efficiently as other photocatalysts, further research can be performed on the hydrogen production and decomposition rates of the fuel. The hydrogen production and decomposition rates can also be tested on the multi-catalyst PVP nanofiber anode. Since the nanofiber anode has a lower potential difference than the heat treated TiO_2 photoanode it should have an increased rate of decomposition. PEC fuel cells utilizing the nanofiber anode and primarily be used to decompose organic pollutants. As our future work, the nanofiber may be aligned regularly onto the substrate by innovative additive manufacturing processes such as 3D printing couple with the near-field electrospinning.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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