



Cobalt-doped Titanium Dioxide Photochemical Fuel Cell for Wastewater Purification

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Authors' contributions

This work was carried out by all the authors' collaborations. Authors AMH, JW, MJN, KPM and YXG designed the study, performed the experiments, and wrote the first draft of the manuscript. Authors YXG and YL performed the photochemical analysis and did literature searches. YXG managed the project. All authors read and approved the final manuscript.

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ABSTRACT

In this work, a photovoltaic electrochemical fuel cell consisting of a cobalt-titanate (CoTiO₃) anode and a platinum (Pt) cathode was utilized for the decomposition of environmentally hazardous materials in wastewater. The CoTiO₃ nanotubes (NTs) were prepared through electrochemical oxidation of pure titanium (Ti) strips. The titanium dioxide (TiO₂) nanotubes were doped with a cobalt salt via electrospinning followed by annealing to form CoTiO₃. The addition of cobalt to the TiO₂ NTs was tested to observe if

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photochemical catalytic properties increased in the presence of ultraviolet and visible light. The increases in photochemical catalytic properties were validated by comparing the measured electric potential differences (ΔE) between the CoTiO_3 test samples, and the TiO_2 control samples. It is concluded that the cobalt doped anode greatly increases the response of the fuel cell system to visible light stimulus. This allows for greater utility generation capacity and faster photochemical catalytic reaction at the anode surface. The application of cobalt doped titanium dioxide anodes in photovoltaic electrochemical fuel cells increases the photoelectric energy conversion efficiency and waste decomposition rate. There is potential to scale the system up for practical applications.

Keywords: Nanotube; doping; photoelectrochemical fuel cell; electricity generation; open circuit voltage measurement; wastewater purification.

1. INTRODUCTION

There is an increasing interest in researching the energy and environmental sustainability of the world. The demands of global energy needs and climate change are pushing new developments of producing alternative energy. Environmental sustainability is an issue that has been in the forefront of the global energy combat. Integrating environmental consciousness in all aspects of the public and private sectors has bred life for projects that utilize renewable alternative resources. Utility generation through methods that exploit solar, wind, and water options has evolved over the decades to become viable options to fossil fuel dependencies. One such innovation is the application of energy generation from wastewater recycling. The utilization of sunlight irradiation (ultra-violet light) for water purification has been a science that dates back to the early 1900s. As access to ultraviolet light further developed and became cost effective, initiative to pursue utility generation from such technologies was cultivated.

The use of photochemical catalysis for electricity and hydrogen production from waste and renewable sources is expected to play an important role in energy generation and environment cleaning. Research in the area of bio-photochemical fuel cells and systems has been performed. The ability to generate energy from waste and wastewater under the irradiation of solar rays, while cleaning the water for reuse and recycle has been a strong incentive to develop this technology. Although photo-biological process for hydrogen production has been studied for a long time [1-7], there are many problems remaining to be solved. For example, the efficiency of energy conversion is very low because the performance of the electrode is not good enough. Studies have shown that both the quantum efficiency and the hydrogen generation rate of bio-photochemical fuel cells can be increased by using new materials such as semiconducting oxides [8-11]. The advantages of using nanomaterials [12,13] especially nanoparticles have been investigated. Nanoparticles have much higher surface areas than bulk materials. Nevertheless, the agglomeration of particles is a challenging problem to be solved in order to keep the high surface area of the electrode. There are two ways to potentially resolve the agglomeration issue based on the studies of nanostructured energy conversion materials [14,15]. The first way is to control nanoscale phases growing out-of-the-plane along some preferential directions to form nanoscale fractals or dendrites, which prevents the agglomeration of nanoparticles on substrates. The other method is to use nanoporous substrates or templates because they can confine the growth of nanocrystals either inside the wall of the nanopores or on the surface of the substrates to prevent the agglomeration of nanoparticles. In our earlier work

[16,17], anodic titanium dioxide nanotube membrane was processed and used as the template to make bio-photochemical fuel cell anode with high surface area. To prepare such a TiO_2 photosensitive anode which is able to generate electron under irradiation, and decompose biomass, pure Ti has been electrochemically oxidized in fluorine ion containing solutions to generate regularly aligned nanotubes. The generated nanoporous array with high surface areas was doped with a transition metal oxide, cobalt oxide to form the anode. Cobalt oxide is used due to its sensitivity to visible light. The un-oxidized Ti substrate was kept to establish the electron collecting path. A high efficiency cathode of pure platinum was used in the fuel cell. Through both experimental and theoretical studies, how nanoporous structures with high electrochemically active surface areas are obtained through controlled electrochemical processing is unveiled. It is shown that the photoelectron oxidation current density of the nanoporous material increases as compared with that of the bulk electrode with similar chemical compositions. Whether the doping enhances the photoelectron chemical oxidation of biodegradable fluids at the nanoporous electrode or not was also investigated. All these fundamental studies help evaluate the performances of the bio-photochemical fuel cell in view of electricity generation from biomass under solar rays, hydrogen production, noxious gas decomposition, and clean water regeneration.

Photovoltaic electrochemical fuel cells are a technology that utilizes sunlight to invoke photochemical catalytic reactions that both filter waste in water and generate electricity. While the application of electrochemical fuel cells for utility generation has been around for the past century, implementation on an efficient scale has been lacking. The root cause stems from the ineffective function of the photosensitive anode in the fuel cell. Over the years various materials have been researched to solve this problem, with titanium dioxide (TiO_2) taking the forefront. It is understood that TiO_2 has relatively respectable photosensitive properties when compared to its previous counterparts. These properties can be attributed to the high surface area of nanotube (NT) growth during electrochemical oxidation [18]. With higher surface area comes the ability to support a greater photochemical catalytic reaction. This attribute makes TiO_2 ideal when implemented in an electrochemical fuel cell. Further increasing the photochemical catalytic sensitivity of TiO_2 to react more efficiently to both ultraviolet and visible light will pose to advance this technology to a more implementable stage.

In this paper, we will present work on the implementation of cobalt as a stimulating photo catalyst agent for the increased efficiency of TiO_2 NTs in fuel cell anode use. Wastewater filtration is becoming a growing necessity as the world population increases. The removal of inorganic hazardous waste from our wastewater will further support the health of our struggling ecosystems. With the implementation of photovoltaic electrochemical fuel cells, two fundamental dilemmas will be undertaken: the global energy shortage and wastewater filtration. The research aims at providing insight into the use of cobalt-titanate (CoTiO_3) as a fuel cell anode that promotes photochemical catalytic reactions when excited by ultraviolet and visible light. With the occurrence of a photochemical catalytic reaction from exposure both light spectra comes the evidence of energy generation, and wastewater filtration. Results of the electric potential difference measured from the open circuit voltage of the photovoltaic electrochemical fuel cell will be compared between CoTiO_3 and TiO_2 anodes.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1 Preparation of Nanotubes and Doping

TiO₂ nanotube structured arrays were developed via electrochemical oxidation of pure titanium strips. Titanium strips were purchased from McMaster.com. Two different solutions were used as electrolytes in the oxidation process. First solution is alkaline-based, consisting of NH₄F, ethylene glycol, and deionized water. A total of two TiO₂ NT samples were developed using the first solution. One of which will be doped with cobalt in a later process, while the other sample will serve as the control specimen. The second solution is acid-based, consisting of hydrofluoric acid, ethylene glycol, and deionized water. The excess of hydrogen ions in the solution could potentially improve the conductivity of TiO₂.

The pure titanium (Ti) sheet with a thickness of 0.1 mm was used as the starting material for preparation of self-organized TiO₂ nanotube arrays. Ammonium fluoride (NH₄F) was purchased from Alfa Aesar. A solution containing 5 wt% NH₄F + 90 wt% ethylene glycol and rest de-ionized water was made. This solution was used as the electrolyte for the electrochemical oxidation of the titanium sheet to generate nanotube arrays. It was also found that another electrolyte with glycerol as the solvent can be used to make titanium oxide nanostructures with high quality. These organic solvents resulted in a more uniform dissolution process and helped the titanium oxide to self-organize into more regularly shaped nanotubes. We used the NH₅F₂ and ethylene glycol solution before. It is a near neutral or weak acidic electrolyte [19]. The power supply for the electrochemical oxidation of the titanium was a regulated direct current power source. The processing parameters were kept as follows. The voltage used was 10 to 50 V. Processing time was 30 min to 2 h. The solution was kept at ambient temperature of 25°C. We also made another electrolyte containing 5% hydrogen fluoride (HF) + 95% ethylene glycol + 5% water by weight. This solution also worked well for processing titanium dioxide nanotube arrays. The titanium dioxide nanotube specimens were heat treated at 450°C to convert the amorphous structure to the anatase crystal structure as shown in [20].

2.2 Doping Titanium Nanotubes with Co

The TiO₂ samples were doped with cobalt through a combined process of electro-spinning and annealing. The reason behind this procedure is that standard TiO₂ NT is only sensitive to UV light spectrum. Therefore, by doping the NT with cobalt, we are hoping to broaden the light spectrum that the NT will be sensitive to and improve the overall efficiency of the photoelectrochemical (PEC) fuel cell. The mechanism for increased light absorption in Co-doped semiconductors is due to the increase in oxygen defects. For example, different concentration of cobalt-doped cerium oxide nanoparticles (NPs) were prepared by adding various concentrations of cobalt chloride to cerium nitrate [21]. Upon cobalt doping, the increase in oxygen defects localized between the Ce4f and O2p energy levels was confirmed.

A cobalt salt mixture was prepared using cobalt acetate tetrahydrate. In Fig. 1, an electromagnetic field was generated by a DC power supply of 15,000 V between the needle of our syringe containing the cobalt salt mixture and a metal plate. A syringe pump pumped out the cobalt salt mixture at a steady rate of 0.01 ml/min. The cobalt salt mixture travels along the electromagnetic field lines towards the target TiO₂ NT specimen. Cobalt salt was

deposited into the TiO₂ pores. The process is continued until 60% of the specimen's length is completely coated on both sides.

Next, all prepared samples are placed in a crucible and heat treated. Initially, they are annealed at the 400°C for 3 hours to dry and decompose the oxide coating on the specimens. Afterwards, temperature of the furnace is increased to 450°C for an hour. At 450°C, the once amorphous structure of the TiO₂ is now converted into a crystalline structure.

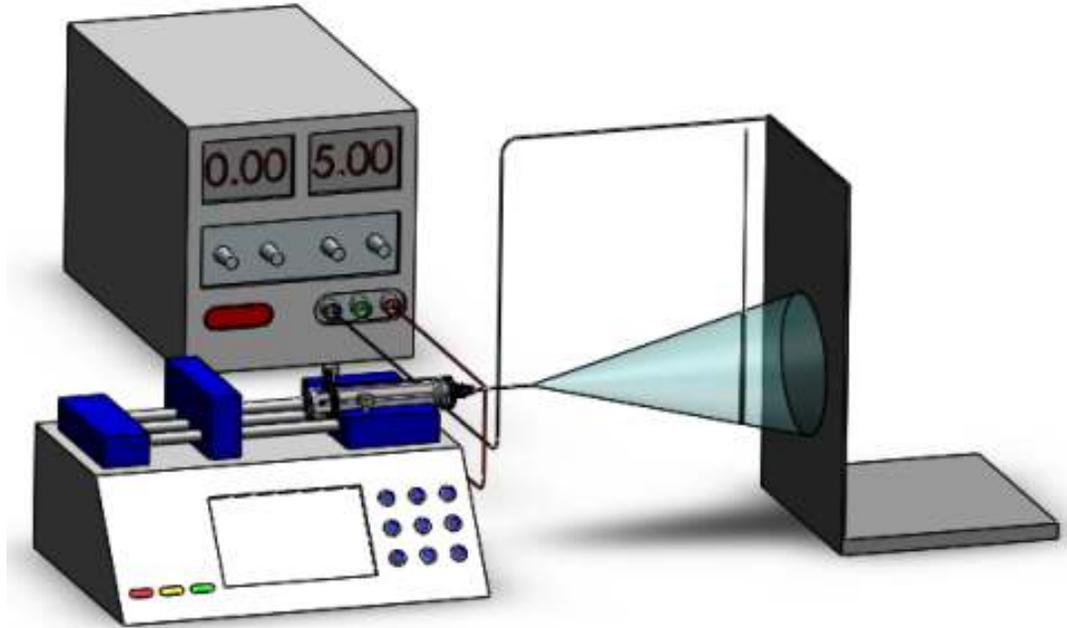


Fig. 1. Electrospinning Co-salt into nanotubes

2.3 Solutions for the Photovoltaic Electrochemical Fuel Cells

A total of six different fuels as listed in Table 1 were selected in the tests. Ethanol and methanol are standard fuel selections for chemical fuel cells. Both are quasi-renewable and commonly used in the industry as gasoline substitutes. They are not completely renewable because their production requires large amount of energy. In addition, ethanol is produced through fermentation of crops such as corn and sugarcane, making it less desirable economically due to its competition with food sources.

Table 1. Selected electrolytes for the photochemical fuel cells

Name	Concentration in vol.%	Chemical formula
Ethanol	95%	C ₂ H ₅ OH
Methanol	100%	CH ₃ OH
Car coolant	25%	C ₃ H ₈ O ₂
Hydrogen peroxide	3%	H ₂ O ₂
Ammonium nitrate	15%	NH ₄ NO ₃
Ethylene glycol	88%	HO-CH ₂ CH ₂ -OH

The rest of the fuels are selected from either organic or inorganic chemicals commonly found in wastewater. Ethylene glycol is used as antifreeze. It is highly toxic, acidic and corrosive. Propylene glycol is another chemical used as antifreeze. Hydrogen peroxide is used in the industrial production of paper and detergents. It is also used in medical and dental applications. Ammonium nitrate, on the other hand, is a type of agricultural fertilizer. In addition, it is also used to produce explosives because it is highly energetic, making ammonium nitrate both part of agricultural and industrial water.

3. RESULTS AND DISCUSSION

3.1 Fuel Cell Configuration and Structure of the Nanotube Anode

Fig. 2 shows the schematic of the fuel cell and the surface morphology of the anode with TiO_2 nanotube arrays. Fig. 2(a) illustrates the configuration of the fuel cell in the one-compartment form. The anode is made from the TiO_2 nanotube arrays on Ti. The cathode is Pt. The reference electrode used is Ag/AgCl. The main reaction at the cathode is hydrogen generation. Reactions at the anode and in the solutions cause the decomposition of the waste materials and generation of electrons. Electricity generated in the circuit was measured by an HP 34401A multimeter. Fig. 2(b) is a scanning electron microscopic (SEM) image showing the open end of the nanotubes. The outer diameter of the TiO_2 nanotubes is about 150 nm. The wall thickness is around 15 nm. Fig. 2(c) is a scanning electron microscopic (SEM) image showing the Co-doped nanotubes. There are some clusters of materials setting on the top end of the nanotubes, which were from the electrospinning materials. After heat treatment, the electrospun nanofibers shrank into these islands. The size of the CoO nano-sized clusters is about 30 nm. They are slightly bigger than the wall thickness of the nanotubes. That is why these clusters setting on the top ends of the nanotubes.

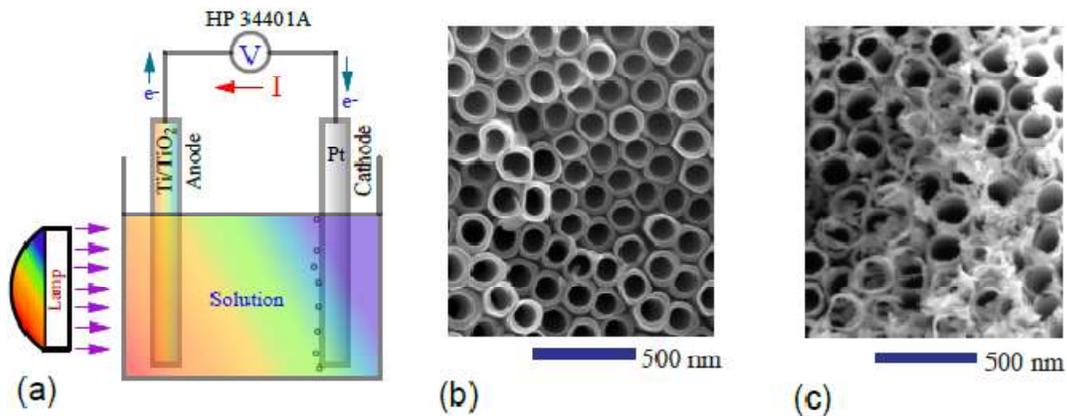


Fig. 2. Schematic of the fuel cell and the morphology of nanotubes: (a) a sketch of the fuel cell, (b) the image of TiO_2 nanotubes, (c) the image of Co-doped TiO_2 nanotubes

In order to confirm the composition of the nanostructures, energy dispersive X-ray (EDX) diffraction spectra are presented in Fig. 3(a) and (b). In Fig. 3(a), it can be seen that the main peaks are from titanium and oxygen. Due to the thin sputtered coating of gold on the surface of the specimen, the Au peaks are observed. It is noted that the signal from aluminum is due to the sample holder. It is made by aluminum and it is in a cylindrical disk

shape. That is why an Al peak is shown at the energy level of about 1.5 keV. Carbon residue is also found because of the conducting tape for fixing the specimen on the sample holder.

In Fig. 3(b), the two main peaks are from titanium and oxygen are observed, indicating that the nanotubes contain Ti and O. Similar to the results as shown in Fig. 3(a), the Au peaks, due to the sputtered gold on the surface of the specimen, were also observed. The Al signal from the aluminum sample holder was detected as well. An extra peak was observed which is due to the Co doping. This peak is located at 0.8 keV. Therefore, the results of EDX as shown in Fig. 3 validate the doping of Co towards the nanotubes.

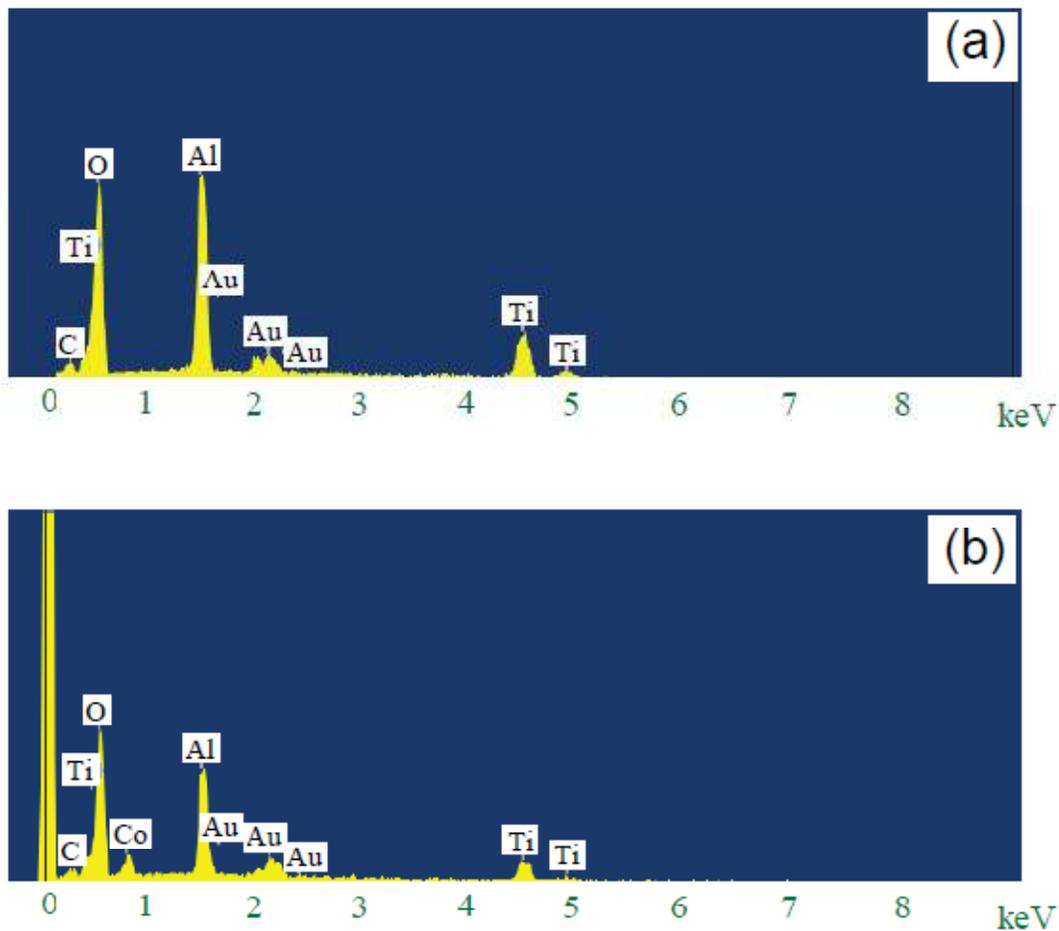


Fig. 3. Energy dispersive X-ray diffraction spectra of undoped and doped nanotubes: (a) TiO₂ nanotubes, (b) Co-doped TiO₂ nanotubes

3.2 UV Light Responses of the Doped and Undoped Anodes

The results presented here are based on the comparative studies of the two anodes (doped and undoped) to validate the function of Co in the nanotube. In addition, we also observed the difference in open circuit voltage when changing light sources excited the photochemical

catalytic specimens. Both ultraviolet and visible light spectra were utilized to excite the test samples in incremental on and off durations that lasted twenty seconds. Given that these fuel cell anodes behave as over damped systems, we allowed them enough exposure to the light sources to generate an ideal electric potential difference representative of normal function. In general, open loop circuit voltage in fuel cells is entirely dependent on the composition of the fuel source. If a solution has too little or too much oxygen, the output of the fuel cell will vary. Either the fuel cell will form hydrogen or water as a byproduct of the photochemical catalytic reaction on its surface, and hence generate an electric potential difference indicative of such. The following figures showcase the trails with the greatest electric potential difference between the experimental and control tests.

The photosensitive anodes with Co doping and without the doping were tested under the irradiation of the 326 nm ultraviolet light. The intensity of light power is about 1.3 W per centimeter square. The UV light source was set about 7.5 cm away from the fuel cell anodes. The open circuit voltage (potential difference between anode and cathode) of the fuel cell, ΔE , was recorded and plotted with time, t , in second. Fig. 4 shows the electric potential difference for the ultraviolet trial of the ethanol fuel source. This fuel source displayed the greatest difference between the CoTiO_3 specimen (represented in green) and the TiO_2 specimen (represented in orange). An average of 0.15V difference was recorded for the CoTiO_3 , while the TiO_2 only saw a difference of 0.0747V. These results were indicative of a 101% increase in ultraviolet light response. Furthermore, across the board the CoTiO_3 trails displayed and increased response to sensible light. It is understood that the annealing process that reformed the crystalline structure to include cobalt, shifted the light spectrum response of the specimen to react with increased sensitivity to visible light.

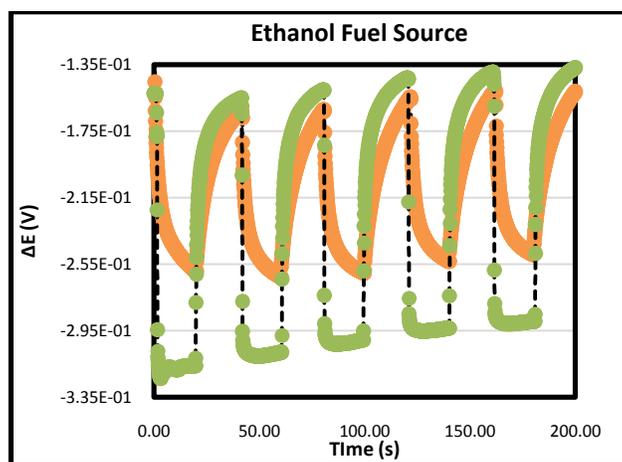


Fig. 4. Response of the nanotube in ethanol fuel under ultraviolet light

3.3 Visible Light Responses of the Doped and Undoped Anodes

It is meaningful to explore the response of the photoanode to the visible light source because only about 5% of the energy in the sunlight is from UV irradiation, while the majority is from the visible light. The following figure, Fig. 5, displays the experimental trial that witnessed the greatest reaction to visible light exposure.

Fig. 5 displays the electric potential difference of the open loop circuit voltage for the most promising visible light trail. When compared, the CoTiO_3 specimen saw a difference of 0.023 V from the on and off sequence, while the TiO_2 saw a difference of 0.004 V. These results were symbolic of a 475% increase to visible light response. Furthermore, the results of the six varying solutions suggest that the addition cobalt to the TiO_2 NTs greatly increased the response to visible and ultraviolet light spectrums.

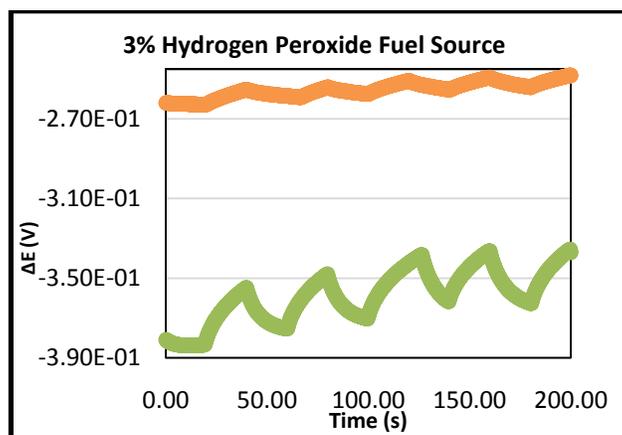


Fig. 5. Response of the nanotube in 3% hydrogen peroxide under visible light

3.4 Photochemical Catalysis Efficiency Comparison using Different Fuels

More results of the photovoltaic responses of the fuel cell using other waste materials are presented. Ammonium nitrate as the major content for fertilizers is considered as a hazardous material to biological species such as fish. In Fig. 6, the open circuit voltages of both undoped and doped anodes in the ammonium nitrate solution are given. As can be seen from the curves shown, ammonium nitrate can be an effective electrolyte or a fuel and the photochemical anodes in the solution show obvious responses under UV light stimulation. The data shown in Fig. 6(a) represent the responses of undoped titanium dioxide nanotubes. Under visible light, the nanotube has no adsorption as the titanium dioxide has an energy band gap of 3.2 eV, which corresponds to the UV light range. Under the 326 nm UV light shining, the nanotube anode shows very good response. In Fig. 6(b), the responses to both UV and visible light by the Co-doped titanium dioxide photosensitive anode are presented. It is found that the doped photochemical anode responds to both UV and visible light.

In addition to ammonium nitrate, another organic compound, methanol is used as the fuel as well, which shows nice photosensitive responses when the nanotubes are used as the anodes. Other organic materials such as ethylene glycol, propylene glycol in car coolant are also used as the fuels to test the photosensitivity of the undoped and doped anodes. Table 2 shows the results acquired from the tests on the anodes in the mentioned fuels. The efficiency of the light responses is used as the main parameter to evaluate the fuel cells with different waste materials as the fuels.

As seen from the results listed in the Table 2, the addition of cobalt to TiO_2 nanotubes has resulted in an increased response to the two light spectrums tested. All trails saw a positive

percent increase, with the most favorable showing a percent increase upwards of 400% in visible light and 100% in ultraviolet light. These results are indicative that cobalt increased the photochemical catalytic properties of the anode, and has increased the functionality of the fuel cell when it is exposed to visible light.

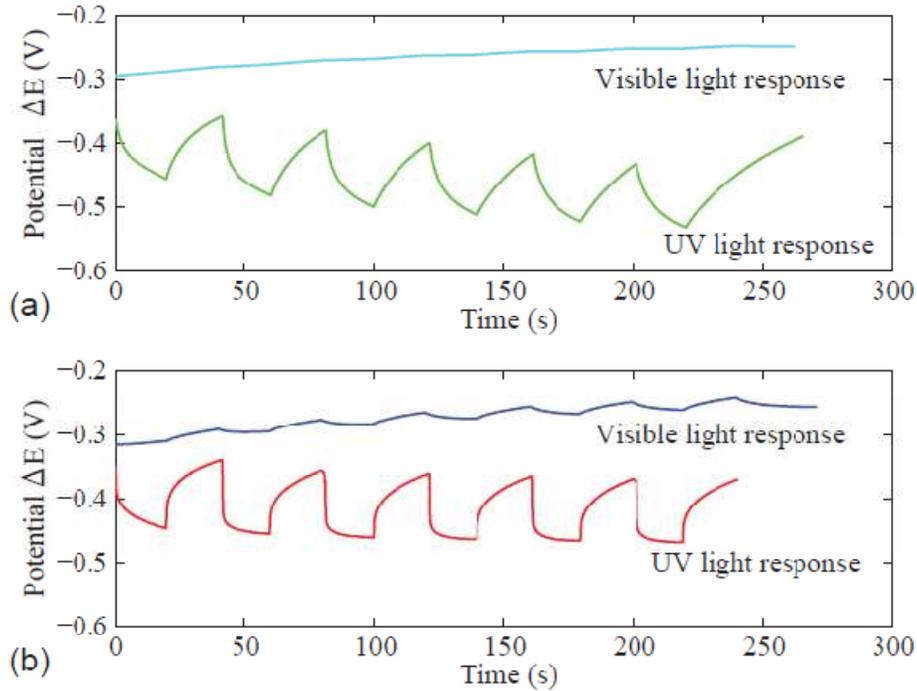


Fig. 6. Response of the nanotube anodes in 3% ammonium nitrate: (a) undoped titanium oxide nanotube anode, (b) Co-doped titanium oxide nanotube anode

Table 2. Experimental test results of the efficiency of different fuels

Fuel source	Ultra-violet light tests (percent increase in electric potential)	Visible light tests(percent increase in electric potential)
Ethanol	102.7%	<100%
Methanol	40.4%	25%
25% diluted car coolant	1.6%	350%
3% hydrogen peroxide	2.6%	475%
Ammonium nitrate	15.9%	<100%
Ethylene glycol	40.4%	<100%

5. CONCLUSION

The cobalt doped titanium dioxide nanotubes are sensitive to both UV light and visible light. It is better than the pure titanium oxide nanotube to serve as the photosensitive anode in photochemical fuel cells. As shown by the open circuit voltages of the photosensitive anodes under both UV and visible light irradiation. We also demonstrated the feasibility of decomposing the six materials including ethanol, methanol, ammonium nitrate, car coolant,

ethylene glycol, and hydrogen peroxide in wastewater. The preliminary results demonstrated that there are a number of practical applications for the photovoltaic electrochemical fuel cells. Harvesting solar energy, wastewater recycling, hydrogen production, and biofuel generation are just some of the modern day uses. Currently, the paper focuses on the most common application for photovoltaic electrochemical fuel cells in water treatment. A photovoltaic electrochemical fuel cell as using the nanotube anode is able to achieve chemical waste decomposition and energy generation at the same time. In modern wastewater recycling facilities, ultraviolet light is already being utilized to kill microorganisms. This process can be further expanded to generate electricity with the application of the CoTiO₃. As shown by the research in this paper, the implementation of the cobalt doped anode greatly increases the response of the six fuel cell systems to light stimulus. This allows for greater utility generation capacity and shorter photochemical catalytic reaction time on the anode surface than the undoped anode. Therefore, the application of cobalt doped titanium dioxide anodes in photovoltaic electrochemical fuel cells significantly increases the system's energy conversion efficiency. It is possible to scale the system up to a larger size and find practical applications in the future.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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