



Photoresponse of Nanocomposite Titanium Dioxide with Transitional Metal Doping

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Authors' contributions

This work was carried out in collaboration between the two authors. Author SWL managed the experimental process, did the literature searches and wrote the draft of the manuscript. Author YXG designed the study, did the experiments and analyzed the data. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/ACRI/2016/23736

Editor(s):

(1) Sivakumar Manickam, Department of Chemical and Environmental Engineering, The University of Nottingham Malaysia Campus, Malaysia.

Reviewers:

(1) A. Ayeshamariam, Khadir Mohideen College, India.

(2) Rachid Masrour, Cady Ayyed University, Morocco.

Complete Peer review History: <http://sciencedomain.org/review-history/12931>

Original Research Article

Received 19th December 2015

Accepted 2nd January 2016

Published 9th January 2016

ABSTRACT

Photoelectrochemical fuel cells consisting of pure TiO₂ and doped TiO₂ with transitional metals, Ni, Cu, Fe, or Co, were made to decompose environmentally hazardous material and to generate electricity by capturing solar irradiations. The titanium dioxide porous structure was developed through electrochemical oxidation of pure Ti sheet in the solution with ethylene glycol, and ammonium fluoride. Four different solutions containing nickel (II) chloride, copper sulfate, iron (III) nitrate, and cobalt (II) acetate tetrahydrate were used to dope the TiO₂ nanostructure. The morphology of the nanostructure was analyzed by scanning electron microscopy. The environmentally hazardous material, car coolant, was studied for the photochemical reaction. It is found that all of the specimens are able to generate potential differences between two electrodes with different magnitudes. Co doped TiO₂ nanostructure is the only sample that can harvest the visible light energy. It is concluded that TiO₂ and the doped materials have the ability to generate electricity and to decompose environmentally hazardous materials.

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Keywords: Photoelectrochemical fuel cell; porous titanium dioxide; doped with transition metals; open circuit potential measurement; decomposing environmentally hazardous material.

1. INTRODUCTION

Limited natural resources and environmental pollutions are two of the major challenges to the human population. Utilizing renewable alternative resources has attracted peoples' attentions in the recent years. Energy generated through the methods that converts solar, wind, water, and also geothermal heating have become viable options to fossil fuel dependencies. The global energy needs are the driving force of new development in clean fuel technologies. Specifically, photoelectrochemical fuel cells can be used to harvest solar energy by generating electricity and decomposing the environmentally hazardous material [1-3].

The uses of photochemical fuel cells for clean energy production have been around for many years [4-10]. However there are still many problems remaining such as the low efficiency of the photocatalytic reactions [9]. The problems come from the low performance rate of the photosensitive anode. Many of the researchers have made significant efforts on searching new material to make a more effective anode. Over the years, various materials have been researched to solve this problem. Titanium Dioxide has drawn much attention due to its photoresponsive properties. Some of the research had shown that titanium oxide particles provide a relatively high quantum efficiency and hydrogen generation rate [11-13]. It has been shown that such particulate materials are able to decompose organic compounds, generate electricity, and produce hydrogen simultaneously under sun irradiations [14]. These properties can be attributed to the high surface area of TiO₂ nanostructures. With higher surface area comes the ability to support a greater photocatalytic reaction [15,16]. This approach has been considered as a comparatively simple and economical way for clean fuel production.

Although the famous photocatalysts such as TiO₂ and ZnO were still the main objects in this research area, many other important compounds are gaining more attentions in recent studies. Apart from the famous photocatalysts, many other doped semiconductors have some excellent photocatalytic properties. The band gap of the semiconductors is an important factor in affecting the photocatalytic properties [16-19].

The doping can effectively change the band gap to achieve better photocatalytic properties [20,21]. Moreover, due to its band gap energy, TiO₂ utilizes only a very small fraction of the solar spectrum and thus doping with transition metals has been implemented to extend the light absorption to the visible light region [22-25].

In this paper we will present work on the implementation of transitional metal such as Ni, Cu, Fe, and Co as a stimulating photocatalyst agent for the increased efficiency of TiO₂ nanostructure in fuel cell anode use. Renewable energy such as solar power is becoming a growing necessity as the world population increases. With the implementation of photovoltaic electrochemical fuel cells, two fundamental dilemmas will be undertaken: the global energy shortage and wastewater filtration. This research aims at providing preliminary insight to the use of transitional metal doped TiO₂ as a fuel cell anode that promotes photocatalytic reactions when excited by ultraviolet and visible light. Results of the electric potential difference measured from the open circuit voltage of the photovoltaic electrochemical fuel cell will be compared between each specimens. The potential difference between the electros indicates the occurrence of a photocatalytic reaction, which provides the evidence of energy generation and water filtration.

2. EXPERIMENTAL METHODS AND MATERIALS

2.1 Materials and Instruments

Pure titanium (Ti) sheets with dimension of 50 mm*5 mm*0.1 mm was used as the starting material for making the TiO₂ nanostructure. Solution of Ethylene Glycol 90%, H₂O 7.5% and NH₄F 2.5% were prepared to be the electrolyte for the electrochemical oxidation of the titanium sheets. Previous studies show that there are many types of organic or inorganic compounds that can be used as electrolytes to construct titanium oxide nanoparticles. For example, Mackay et al. found that neutral NaF solutions can thicker the wall of the TiO₂ nanotubes [26] and Narayanan et al. showed that TiO₂ networks can be obtained in the Na₂SO₄ + NaF electrolyte [27]. The purpose of using NH₄F and Ethylene Glycol solution is to let titanium oxide dissolves more uniformly in near neutral or weak base

solutions than in acids. That allows the titanium oxide film to generate holes like structures and eventually form the self-organized nanotube structures.

Total of five (5) titanium strips are prepared through the oxidation processes in the electrolyte with a power supply. The power supply for the electrochemical oxidation of the titanium is a regulated DC power source, model HY5003 (0–50 V, 0–3 A). To observe the surface structures of the specimen a scanning electron microscope, Jeol JSM-6010PLUS/LA Analytical Scanning Electron Microscope, was used. The ultraviolet lamp, UVL-21 (365 nm UV, 4 W, 0.16 A), was used as a power source to simulate the solar irradiation. A CHI 440C electrochemical workstation was used to monitor the waste material decomposition process by measuring the open circuit voltage of the fuel cell. Car coolant was chosen to perform the photoelectrochemical decomposition test. It is considered as an environmentally hazardous compound that can cause harmful effects to animals and plants. The reason for choosing a coolant for study is that automobile radiator flushing generates a lot of diluted coolant solution. The major composition for the antifreeze and cooling function in the original product is ethylene glycol, which is poisonous. A solution with 90% of ethylene glycol was also prepared for visible light test. Four (4) different solutions containing Nickel(II) chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), Copper Sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), Iron(III) nitrate ($\text{Fe}(\text{NO}_3)_3$), and Cobalt(II) acetate tetrahydrate ($\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$) were prepared for the doping processes. All of the solutions were made with 1 M in concentration.

2.2 Develop of Titanium Nanostructure

The 0.1 mm thick titanium (Ti) sheet was cut into 50 mm*5 mm*0.1 mm in dimension. A total of five (5) titanium sheets were prepared through same electrochemical oxidation processes. The titanium strip was immersed into the electrolyte with 2.5% NH_4F (Ammonium fluoride) + 90% Ethylene Glycol + 7.5% water in weight. A two-electrode cell was used for the electrochemical oxidation of Ti at room temperature. The titanium strip was used as anode in the cell, and platinum was used as cathode. The process was monitored by CHI 440C electrochemical station. The titanium strip underwent the electrochemical reaction for 1000 seconds with the uses of CHI 440C electrochemical station to monitor the processes. The titanium strip was then put under

voltage of 50.0 V to be oxidized for about 2 hours. This allows the holes on the titanium strip to broaden. After the electrochemical processes, the strips are rinsed with water and air dried. The surface of the anode was completely covered by TiO_2 nanoparticles and nano-sized holes. The same procedures are repeated five (5) times to produce total of five titanium oxide specimens.

2.3 Doping and Heat Treatment

After the electrochemical reaction, the specimens were dipped into different solutions to begin the doping process. First titanium strip was dipped into Nickel (Ni) ion solution, which was made with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. Second specimen was doped with solution that consist Copper (Cu) ion, which was made with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Third strip was doped with Iron (Fe) ion solution, which is made with $\text{Fe}(\text{NO}_3)_3$. Fourth titanium strip was prepared with Cobalt (Co) salt solution, which was made with $\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$. Then all of the specimens were air dried (Fig. 1). Next, the specimens were put into a crucible and heat treated (Fig. 2). This process is to allow the TiO_2 to crystalize during the heating. The temperature was set to 500°C. The specimens after heat treatment are shown in Fig. 3.

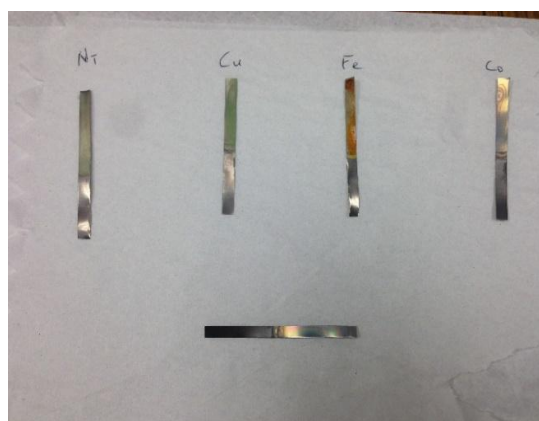


Fig. 1. TiO_2 strips without heat treatment

2.4 Photovoltaic Electrochemical Fuel Cell

Car radiator coolant was chosen to be the fuel solution for the electrochemical fuel cell. The ultraviolet lamp was the UVL-21 (365 nm UV, 4 W, 0.16 A) which supplied the UV irradiation for environmentally hazardous material decomposition. The equipment setup is shown in

Fig. 4. CHI 440C electrochemical workstation was used to monitor the electric potential, which can easily relate to the decomposition processes. Another solution was also prepared to be the fuel of the fuel cell, which is higher concentration of ethylene glycol at 90% concentration.



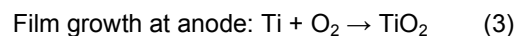
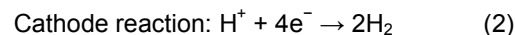
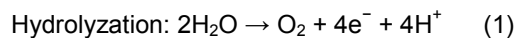
Fig. 2. Heat treatment equipment

3. RESULTS AND DISCUSSION

3.1 Electrochemical Reaction for TiO₂ Nano-porous Structure Generation and Doping

The titanium strip was first put into the electrolyte to start the oxidation processes. TiO₂ film was first formed on the surface of the strip when the electrochemical reaction started. Titanium oxide is essentially the insulator when it formed on the pure titanium strip. When the TiO₂ film was dissolved into the electrolyte, the proper electrochemical conditions were established. During the process, the fluorine ion (F⁻) attacked and drilled holes through the titanium oxide film to form self-organized titanium nanotubes. Titanium oxide dissolves more slowly in neutral or base solutions than in acids, which helped titanium oxide to self-organize into nanotubes in a controllable way [28]. The current fluctuates during the process, because when the fluorine ion broke through the oxide film, the electric currents are easier to conduct through the nano-sized tunnels. Because the charged fluorine ions repel each other, it is possible to control the size of the holes during the process by controlling the voltage and time.

The electrochemical reaction related to the growth of the TiO₂ nanoporous structures are described as follows [27,29]:



Film dissolution, nanostructure growth:



In order to confirm this phenomenon, we measured the cyclic voltammetry curves of the anode in the potential scanning range from 0 V to 10 V. The scanning rate is 0.01 V/s and the data acquisition rate is 1000 data per second, the cyclic voltammetry I-V curves are shown in Fig. 5. In the forward scan or the lower curve in the figure, we can easily observe that the current increased rapidly in the beginning. This is because the TiO₂ film was broken through to form nano-sized tunnels, so the electric current became easier to conduct. During the entire processes, the current fluctuating indicated that the oxidations and the breakage of the oxide film were constantly affecting the electric current. Fig 6 shows the surface structure of the TiO₂ nanoporous structure. It was expected to have nanotube structure, however the processing time might not be enough for the TiO₂ to self-organize into nanotube structure. All the samples were later determined to have nano-porous structures and to be photo-responsive.

After the specimens went through electrochemical reaction processes and air dried, the titanium strips were then dipped into different solutions to allow the nano-porous structure to soak for a short period of time, about 10 to 20 seconds. The outcome of the doping process depended on the surface morphology of the titanium nano-porous structure and also the chemical properties of each solutions. The specimens that were dipped in the solutions are as shown in Fig. 1. Then all the specimens were put into a furnace to start the heat treatment. This process allowed TiO₂ to crystalize and combine with the doping elements. The end products after heat treatment are shown in Fig. 3. The heat treatment was processed with 3 different stages of temperatures. It was first heated up in small increment and stayed at each increment for a period of time to prevent the temperature from over shooting. The temperature was increased to 500°C and stayed for two hours before decreasing the temperature.

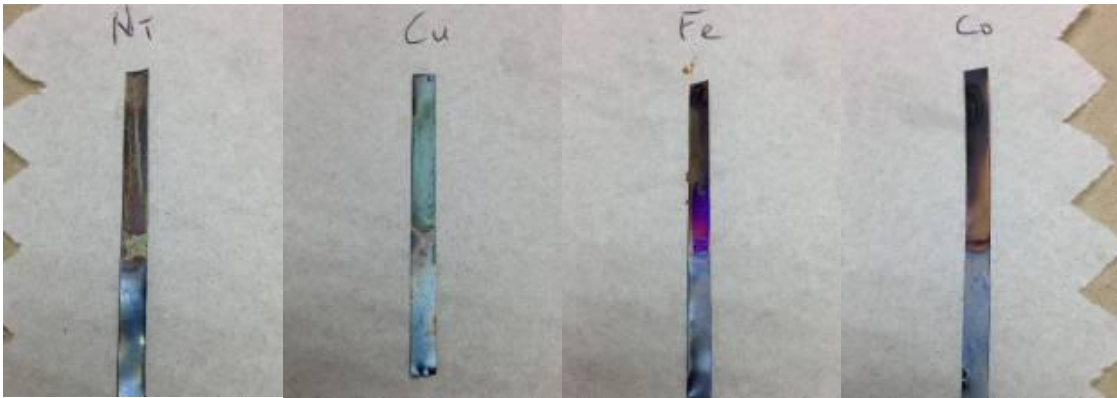


Fig. 3. TiO₂ strips after heat treatment

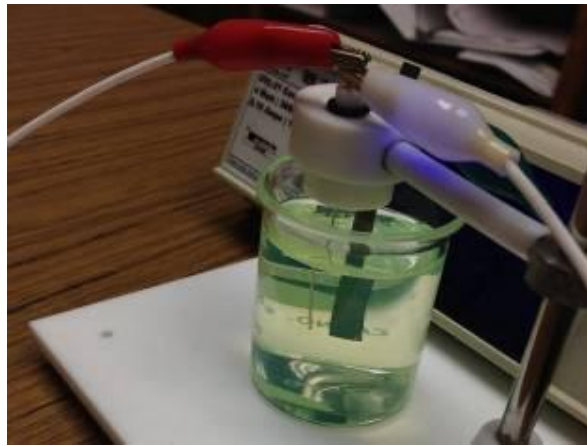


Fig. 4. Car coolant fuel cell set up

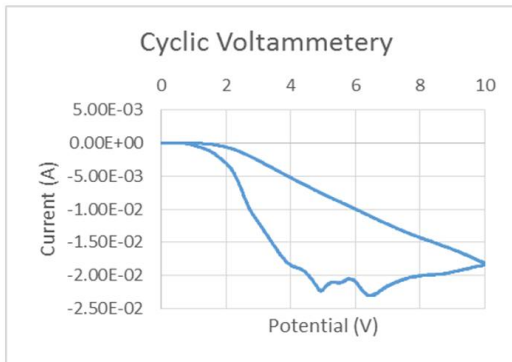


Fig. 5. Cyclic voltammetry I-V curves

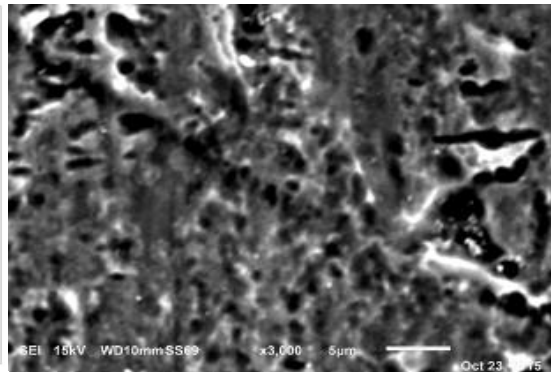


Fig. 6. TiO₂ SEM Image

3.2 Surface Morphology of the TiO₂ Nanostructures and Doped Surface Structure

The surface structures of each specimens were first inspected by eyes then revealed by using

the JEOL JSM-601PLUS/LA Analytical Scanning Electron Microscope. Also the doped elements were shown by the mapping function of the SEM. It scanned the surface to determine what elements were actually presented on the surface of each specimens. The surfaces of each

specimen are shown as Fig. 3. For the Nickel doped Ti strip, it shows light green color on the strip. It can be interpreted that the Nickel (II) Oxide (NiO) is presented on the surface of the titanium strip. NiO is commercially use for the battery anode in many type of battery cells such as NiMH battery. The copper (Cu) doped strip showed the light green color after heat treatment, which indicated the presence of Copper (II) Oxide (CuO). Copper in this state can be found on a copper sculpture. Iron doped strip had bright purple color and also the orange color, which indicate the presence of iron oxide. The last doped strip, with cobalt, looked very similar to the pure TiO₂ strip. The reason is that cobalt has relative low melting temperature. In the furnace, it was heat up to 500 degree, which was way above of the melting point of cobalt. It was then to be determined by SEM mapping in which the presentation of Cobalt was relative low compare to other elements.

After the visual inspections, the samples were send to SEM lab to be inspected by JEOL JSM-601PLUS/LA Analytical Scanning Electron Microscope. The experiment was done without carbon coating. This affect the image quality in a way that when the material has lower conductivity, it would not have a good resolution while taking the image. Scanning electron microscope is the technique that put the electron charge to the sample and use it to create the image, so the conductivity of the material can greatly affect the image quality.

Fig. 6 TiO₂ strip without doping, it is clear that the holes like structures were presented on the surface. The surface did not form the nanotube structure, because of the processing time was not long enough to have the TiO₂ self-organized into nanotube structure. But with nano-porous structure, the doping process could still be proceeded. In Fig. 7(a), Ni doped TiO₂ strip, the

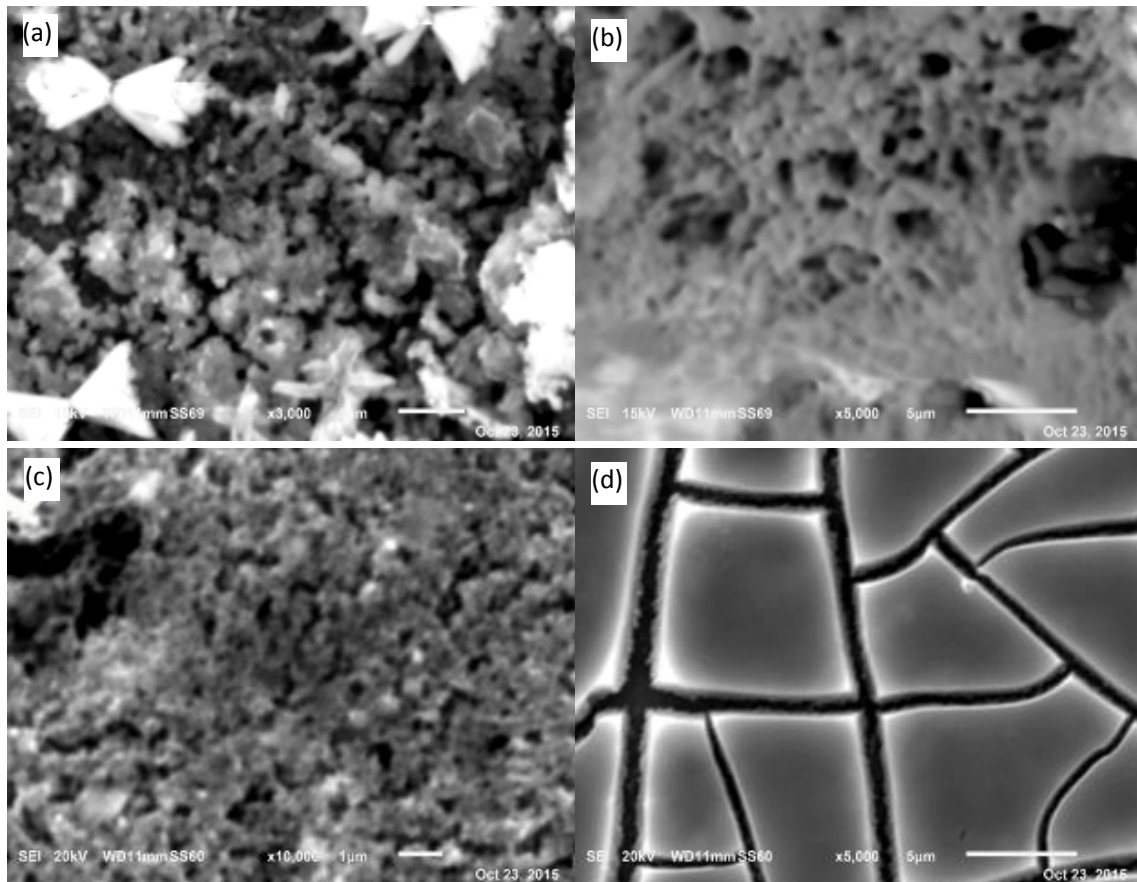


Fig. 7. (a) Nickel doped surface. (b) Copper doped surface. (c) Cobalt doped surface. (d) Iron doped surface

SEM image clearly showed the crystal structure of Ni and also the nano-porous structure on the surface of the sample. Nickel (II) Oxide is well-characterized form of nickel. It has the same simple crystalline structure as NaCl and is also nonconductive material. This resulted in poor image quality while using SEM. Fig. 7(b), the TiO₂ doped with Cu has clear nano-porous structure. Also, from the SEM Mapping, Fig. 7(b), it indicated the presence of Cu. Fig. 7(d) TiO₂ doped with Iron, the SEM image was very clear because of the conductivity of the material was high. In this image, there was no visible sign of nano-porous structures. The possible reason for this was that the iron film on the surface was too thick and completely covered the surface of the nano-porous structure. Fig. 7(c) Cobalt doped TiO₂, the nano-porous structure was presented. The SEM image quality was low because of the

low conductivity of TiO₂ on the surface. It has a similar surface structure compare to pure TiO₂ strip.

From SEM Mapping, Fig. 8(e), of the TiO₂-Co, we can easily see that the presence of Co was very low compare to other elements, which explained why the doped surface did not have visible characteristic of the metal as other doped material. In the SEM mapping, there were many other elements such as C, Ca, Mg, Na, and also S presented, because the experiment used regular tap water instead of distill water. Those elements could be from the regular tap water. The result of containing other elements may not affect the test outcome during the photocatalysis process. In fact, the experiment is to simulate the real-world situations while certain elements are doped into the nano-porous structure.

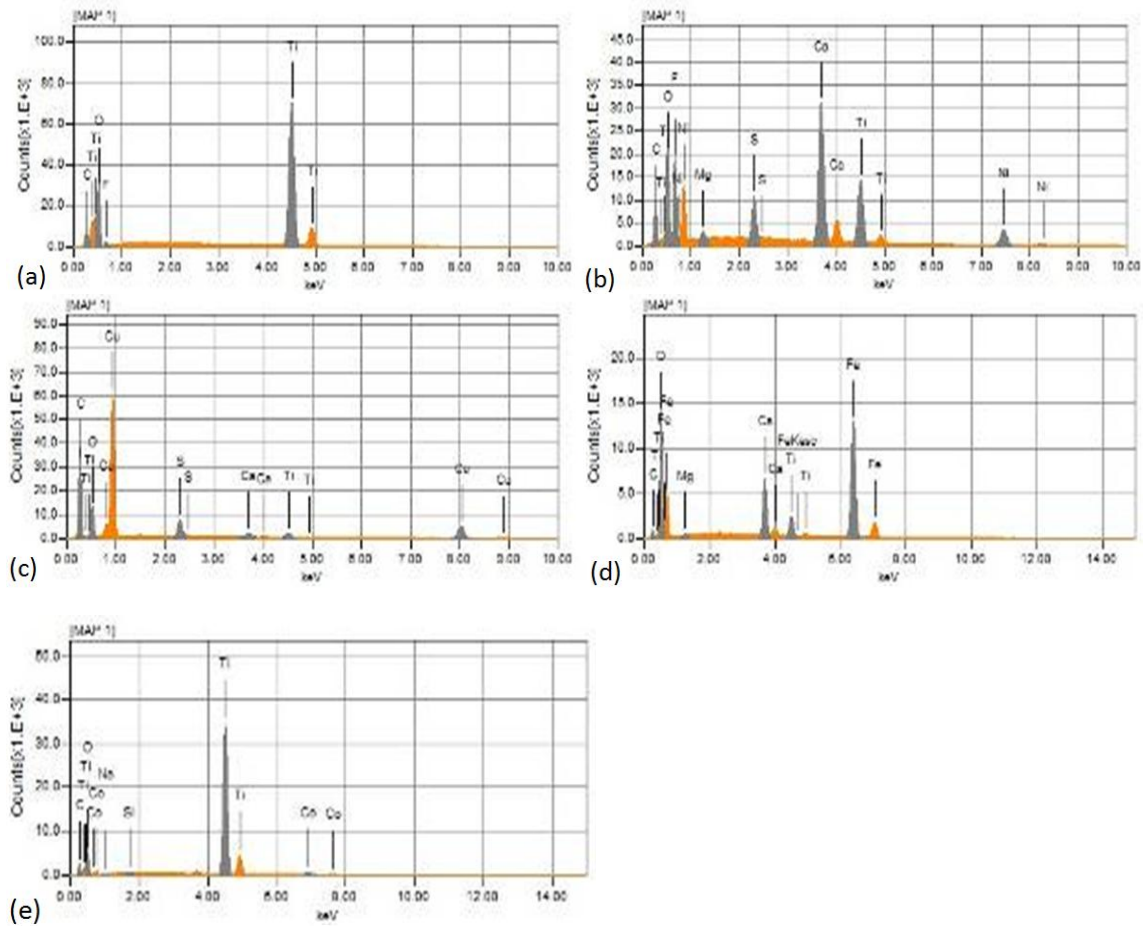


Fig. 8. (a) TiO₂ without doping. (b) Nickel doped TiO₂. (c) Copper doped TiO₂. (d) Iron doped TiO₂. (e) Cobalt doped TiO₂

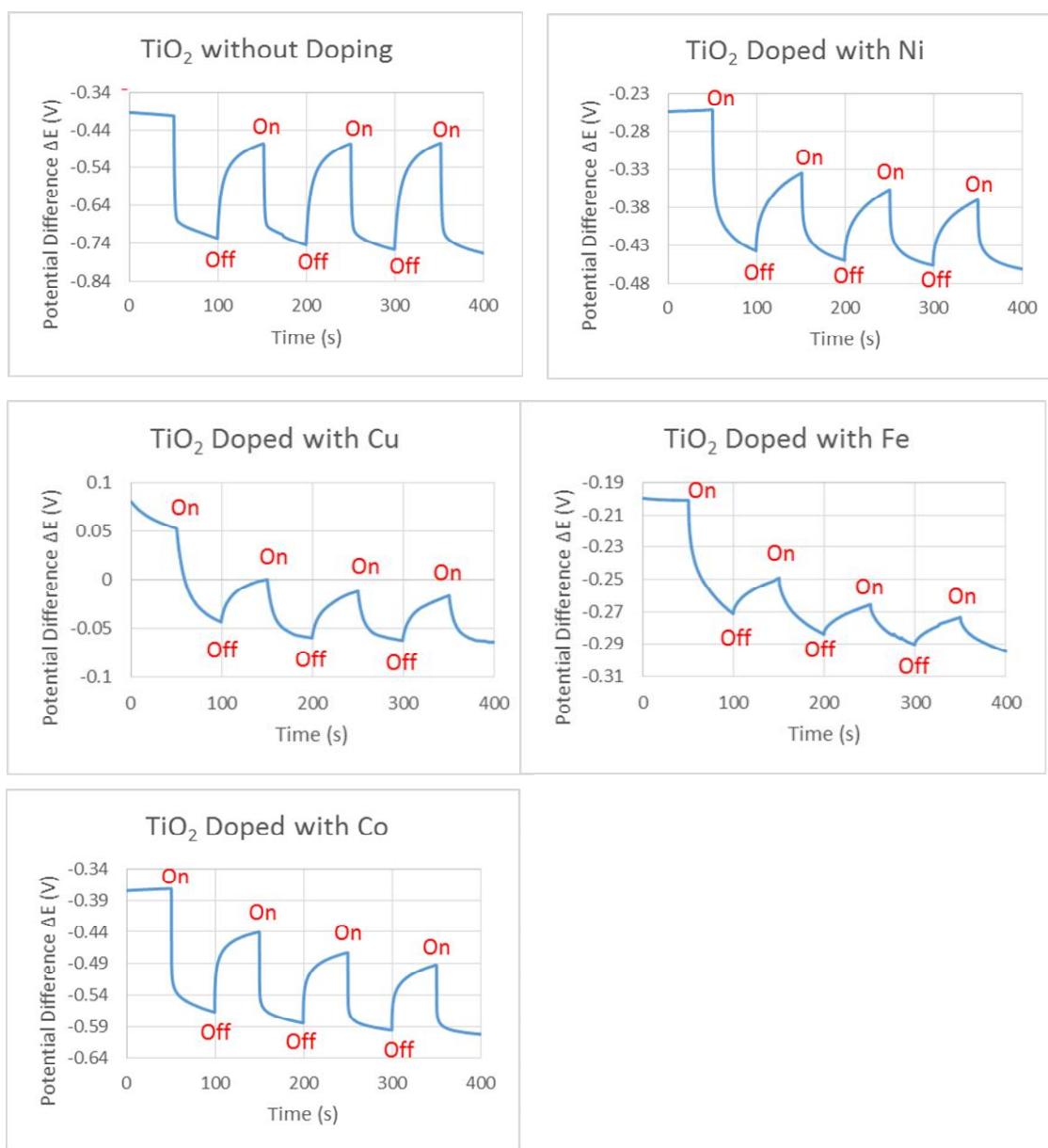


Fig. 9. Photovoltaic reaction response to UV light source

3.3 Photocatalytic Property of the TiO₂ Anode

In the photovoltaic processes, the car coolant was used as the fuel of the TiO₂ fuel cell. UV radiation was generated by the light source, UVL-21 (365 nm UV, 4 W, 0.16 A). During the processes, TiO₂ anode was kept under the UV radiations and allowed to capture the energy from the UV radiations. The voltage difference between Pt cathode and TiO₂ anode was been monitored. At the Pt cathode, hydrogen formation

was presented when the UV light source continued to shine on the TiO₂ strip. The open circuit voltage was measured as a function of time by using the CHI400 electrochemical workstation to obtain the ΔE vs. time (t) curve. The voltage fluctuations and also the voltage difference across the electros were shown in the graphs and can be understood as the electros responded to the UV light switch ON and OFF. The curves were constructed with 400s time limit. Some of the material showed a better photocatalytic response than others.

When the UV light is ON (i.e. in the charging cycle), the change in the anode potential as a function of irradiation time, t , may be expressed as:

$$\Delta E = Ae^{-Bt} - E_0$$

Where A and B are constants associated with the charging cycle and E_0 is at the equilibrium

potential. When the UV light is OFF, the change in the potential is a function of recovery or relaxation time, t , which is in the form as follows:

$$\Delta E = E_0 - Ce^{-Dt}$$

Where C and D are constants related to the discharging cycle.

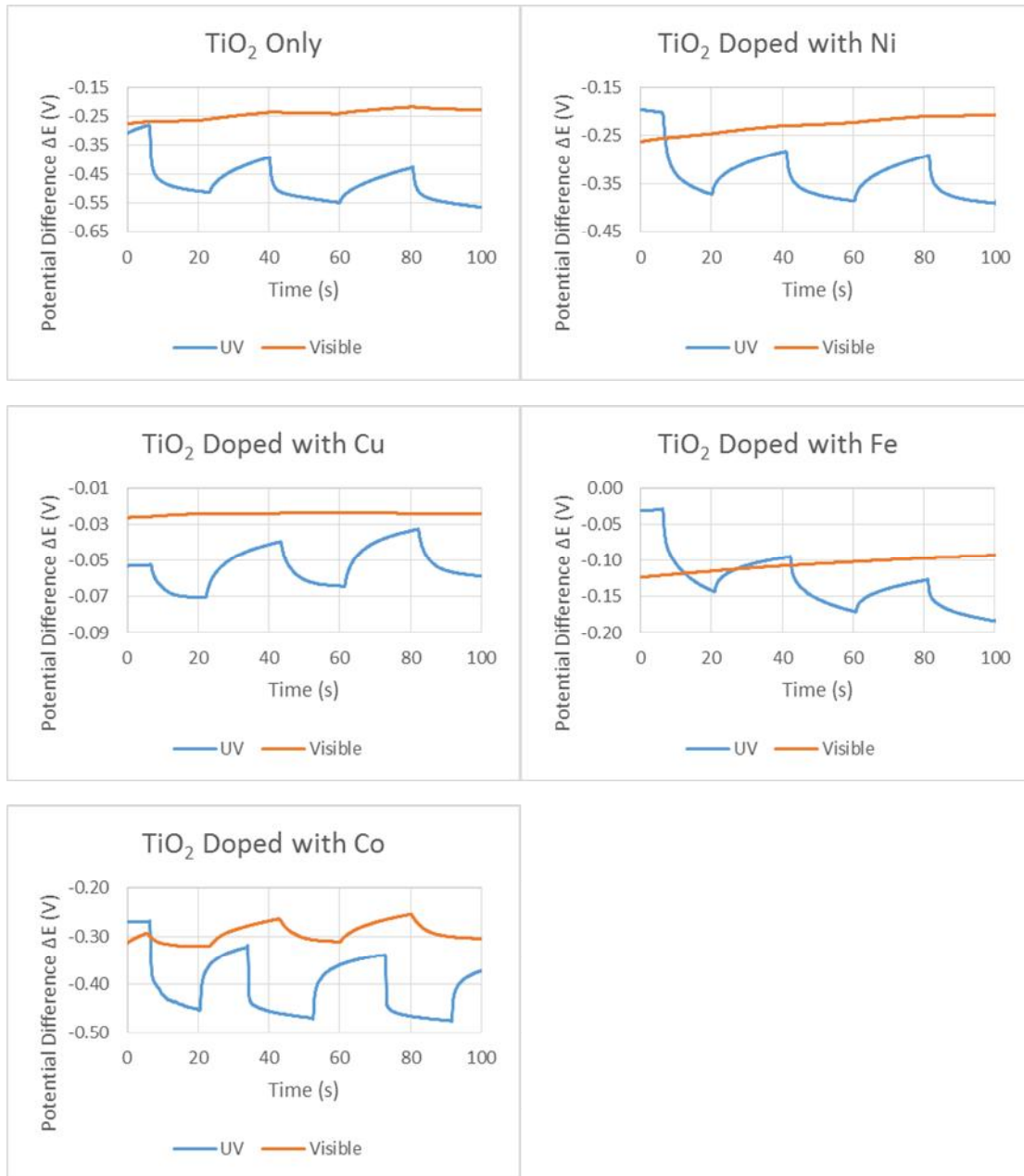
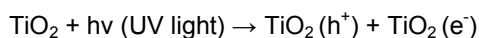


Fig. 10. Photovoltaic response with respect to Visible light and UV light with different doping material

In the car coolant solution, the main photoresponse reaction at the anode is as follow:



Where h^+ and e^- stand for hole and electron, respectively.

The environmentally hazardous material used was the car coolant that included 20% of ethylene glycol. When the UV light shined on the electro, the electric potential drop to a more negative region. The test of the photocatalytic showed the ability of TiO_2 strips to response to the UV light. In Fig. 9, the label ON indicates that when the UV light was turned on, and OFF indicates otherwise. When the UV light was ON the potential difference of the TiO_2 strip and the cathode decreased to the more negative region. It was shown that all the material were responsive to the UV light energy.

In the experiment, the car coolant was used. However, the commercial car coolant usually adds green color dye to distinguish it from other edible liquid. The ingredient, Ethylene Glycol, is a highly toxic substance with some sweet taste. If accidentally ingest, there is a high chance to cause kidney failure. Because of the green color dye, it is possible to affect the outcome during the visible light test, so the experiment was run again with a different solution with 90% Ethylene Glycol. Each specimen was tested under UV light for about 100 seconds and then under regular light bulb for another 100 seconds. In Fig 10, the orange line represents the response of the specimen to the visible light, and the blue line represents the UV light response. The result for TiO_2 strip without doping showed that TiO_2 was only sensitive to UV light. The outcome for visible light in Fig 10 (TiO_2 only) shows a little fluctuation because the regular light bulb can generate a small amount of UV light. However, it is not hard to see that TiO_2 nanostructure does not respond to visible light very well. The result for Ni, Cu and Fe doped specimen are very similar to the TiO_2 strip without doping. They do not respond to the visible light. In Fig. 10 (Co doped), the Co doped TiO_2 , the curve for visible light actually respond to the visible light as we switch the light ON and OFF. This indicates that Co doped TiO_2 can response to visible light and potentially harvest solar energy at a higher efficiency since the solar spectrum includes a large part of visible light.

As compared with other work, there is some similarity. For example, the work reported in [28] focuses on TiO_2 nanotubes. The nanotubes also

shown similar behavior, but due to the nanotubes aligned vertically on the surface, mechanical damage of the tubes are there. The integrity of the photosensitive electrodes is hard to keep.

4. CONCLUSION

The photocatalytic properties of TiO_2 and metal doped TiO_2 under UV irradiation and visible light irradiations were investigated using TiO_2 and metal doped TiO_2 as photoelectric fuel cell electrodes for solar energy conversion and environmentally hazardous material decompositions.

The titanium dioxide nano-porous structures can be developed through electrochemical oxidation of pure Ti sheet in the solution with ethylene glycol, and ammonium fluoride. The doping of the Ti/ TiO_2 sheets can be achieved by dipping the specimens into metal salt solutions. The TiO_2 has porous structure. Also, the surface morphology is greatly dependent on the doping material. It shows great surface differences between each specimens especially for Fe doped strip. Fe doped strip is not in porous structure.

All the specimens are sensitive to UV light, but Co doped TiO_2 is the only sample that shows visible light sensitivity. The ability of absorbing visible light can help to improve the efficiency of the solar energy conversion since a large portion of the solar spectrum lies in the visible light range. The photosensitive anode has the capability of decomposing ethylene glycol, the main ingredient of car coolant, and produce the potential difference between the electrodes.

ACKNOWLEDGEMENTS

This work is supported by the US National Science Foundation (NSF) under Grant Numbers CMMI-1333044 and DMR-1429674. Research reported in this publication was also supported by the MENTORES (*Mentoring, Educating, Networking, and Thematic Opportunities for Research in Engineering and Science*) project, funded by a Title V grant, Promoting Post-baccalaureate Opportunities for Hispanic Americans (PPOHA) | U.S. Department of Education, Washington, D.C. PR/Award Number: P031M140025. The content is solely the responsibility of the authors and does not necessarily represent the official views of the Department of Education. We appreciate Mr. Anan S Hamdan's assistance on morphology

analysis using the SEM (scanning electron microscope).

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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