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# I. EXECUTIVE SUMMERY

## Campus as Living Lab Project Report Executive Summary

**Date of Project Report:** June 30, 2014

**Campus:** California State Polytechnic University, Pomona

**Project Title:** Enhancing Mechanical Engineering Senior Capstone Courses by Incorporating Energy and Environment Sustainability Design Activities

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**Campus Physical Plant/Facilities Management Partners:** Mark R. Miller (Director), Monika Kamboures, Chi Kwan Fong, George A. Lwin.

**Other Faculty Participant:** Yan Liu, Department of Chemistry and Biochemistry, California State Polytechnic University Pomona, 3801 W Temple Avenue, Pomona, CA 91768, USA.

**Redesigned Courses:** Two senior capstone design courses EGR 481 (Design Principles and Applications I) and EGR 482 (Design Principles and Applications II), one undergraduate independent study and research course: ME 400, and a duel level course: ME 499/599 (Selected Advanced Topics on Mechanical Engineering: Nanotechnology).

**Student Team Members, Department and Institution:** Kristian Peter Morales, Ahmed Murad Harara, Michael John Nguyen, Jialun Wang, Joseph Jay Barney, Omar De Santos, Jose Roberto Diazvaldez, Kaitlin Elizabeth Hom, Jonathan Caleb Godwin, Sean Robert Ulrich, Howard Hokei Wu, Nurul Zafirah Md Khair, Department of Mechanical Engineering, California State Polytechnic University Pomona, 3801 W Temple Avenue, Pomona, CA 91768, USA.

**Project Period:** 9/1/2013 – 6/30/2014

**Description and Objective:** Generating electricity from waste and wastewater under the irradiation of solar rays, while cleaning the environment is a sustainable way for disposing waste and generating alternative energy. Building novel photo-electrochemical fuel cells has recently been considered be an effective way to achieve the goal. The objective of this project is to design and fabricate a novel biophotofuel cell consisting of a nanostructured electrode as the anode for waste material decomposition, and a low-hydrogen overpotential metal such as Pt, as the cathode for hydrogen generation. The uniqueness of the project is the multiple functions of the fuel cell. It can generate electricity and produce hydrogen from biowastes under sunshine. Meanwhile, noxious gases such as ammonia released from the biowastes can be decomposed at the photosensitive anode and pure water can be generated for reuse at the cathode. To prepare the key component in the system which is able to generate electron under solar illumination, and decompose biomass, doped-$TiO_2$ nanotubes have been prepared and made into a photosensitive anode. The nanotube anode has high surface areas. The biophotofuel cell with such an anode has

been tested in view of electricity and hydrogen generation from biomass, noxious gas decomposition, and clean water regeneration under sunlight.

**Summary of Findings (Outputs/Outcomes):** The project results in a novel nanostructured biophotofuel cell with the capability of energy generation and environmental cleaning. A prototype of the biophotofuel cell was built and the ability of generating energy from waste and wastewater under sunlight, while clean the water for reuse and recycle was demonstrated. Two groups of undergraduate senior students at Cal Poly Pomona were trained in the project. The students practiced on designing the biophotofuel cell and learned using the system for electricity and hydrogen production from waste and renewable sources. Therefore, the project plays an important role in training them on the globally important topic of energy and environment sustainability. Based on the results obtained from the project, one conference paper on energy and environment studies was accepted. One research paper preparation is underway. Two conference presentations were made. A journal paper is in preparation and to be submitted soon. A major proposal was submitted to National Science Foundation in February 2014. Two minor proposals were submitted to the SPICE program and the Department of Homeland Security Science and Technology Directorate, Office of University Programs.

**Conclusions:** Based on the implementation of this Campus as Living Lab project, the following conclusions can be made. The titanium dioxide nanotubes ($TiO_2$ NTs) prepared via electrochemical oxidation of pure Ti in the ammonium fluoride and ethylene glycol-containing solution show light sensitivity. The oxide nanotubes can be doped with transition metal oxide so that visible light sensitivity can be enhanced. Scanning electron microscopic analysis reveals that the nanotubes have an average diameter of 180 nm, wall thickness of 15 nm, and length of 1.5 μm. Such dimensions can be changed by the applied DC voltage level. The higher the voltage is, the thicker the nanotubes. A novel biophotofuel cell with the titanium dioxide nanotube array photosensitive anode has been successfully made. Preliminary data show the feasibility of decomposing environmentally hazardous materials including ammonia, urea and ethanol to produce electricity and clean fuel. These hazardous materials are the major compositions from the degradation of biowastes. Both ultraviolet (UV) light and natural light or visible light sensitivity of the nanostructured anode was demonstrated. Visible light absorption can be enhanced by the doped anode with the transition metal oxide NiO, CoO or the conducting polymer (polyaniline) as the dopant. After doping, the photosensitive anode made from the highly-ordered $TiO_2$ NTs has the capability of decomposing urea, ammonia, and ethanol under solar ray irradiation. The open circuit potential of the fuel cells is affected by the types of the waste materials to be disposed.

**Objectives and Strategies of Future Work:** The objective of the potential future project as delineated in the proposal submitted to National Science Foundation in February 2014 is to scale up the prototyped biophotofuel cell for practical applications. The major technical tasks include two aspects. The first one is to modify the design by making flexible photosensitive electrode which is suitable for field deployment. The second one is to perform field tests in different areas. The project will be completed within three years. In the first scale-up research stage, field tests in the open water channels in Los Angeles County, CA, USA will be conducted. In the second stage of the proposed project, field tests in more counties will be carried out. The strategies are as follows. First, electrospinning will be used to prepare the required flexible electrode containing a conducting polymer matrix, polyaniline, and the photosensitive titanium dioxide

nanotubes. The electrospinning process will force the viscous flowing of the aniline solution from a jet to a target. The driven force for the flow is mainly electrical. Pressure may also be applied to the solution to facilitate the viscous flow. The electrochemical polymerization occurs simultaneously. The jet and the target are attached to a specially designed plate with an applied high voltage. A fairly simple electrospinning system will be designed and set up. It consists of a unit for supplying the charged polymer solution (or melt), a collecting plate and a 30 kV DC power source. The collecting plate will be a metallic screen, or foil. During electrospinning, the solvent gradually evaporates, and a charged polymer fiber is left to accumulate on the target. It must be pointed out that the titanium oxide nanotubes in the solution will be co-spun with the polyaniline to form the required organic-inorganic composite nanofiber electrode. To increase the production rate, a rotating disc or mandrel will be used to collect the nanofibers. The driving force for such an innovative design is not only electrical, but also mechanical, which can increase the efficiency of the process significantly. This design is expected for scalable manufacturing because it is possible for large scale production of composite nanofibers. A non-contact tachometer will be used to monitor the rotation speed of the nanofiber collecting mandrel. A force gauge will be used to measure the stretching force of the nanofiber during the electrospinning process. The relationship of these process parameters and the photosensitive properties of the composite nanofiber will be established through systematic experimental studies. The composite nanofibers in the mat form will be used as the electrode for energy generation and environment cleaning. Field tests in the open water channels in Pomona, Walnut and Diamond Bar of Los Angeles County will be carried out to remove ammonium, organic dyes and other harmful substances in open water ditches connecting to the Ocean. The field tests will also be conducted in some other counties in western coast region where energy challenge and environment sustainability become notable issues.

**Publications/Presentations:**

[1] Adle, M., Bostwick, J., Graves, K., Hipolito, S., & Gan, Y. X. (2014). High impact learning practice through group undergraduate research on energy conversion nanomaterials. *Proceedings of the 2014 American Society for Engineering Education Zone IV Conference*, Long Beach, CA, April 24-26, 2014.

[2] Higgoda, A. M., Abou-Diab, K. M., Moradian, E. S., Ung, W. R., Hom, K. E. (2013). Design a novel biophotofuel cell system, Senior Design Expo and Presentation on *the ASME 2013 International Mechanical Engineering Congress & Exposition*, San Diego, CA, November 15-21, 2013.

[3] Ahmed M. Harara, Jialun Wang, Michael J. Nguyen, Kristian P. Morales, Yong X. Gan and Yan Liu, Cobalt-doped titanium dioxide photoelectrochemical fuel cells for waste water purification, (to be submitted to a peer-reviewed international journal).

**Proposals Submitted:**

[1] IUSE: Cooperative learning of scalable and low cost manufacturing process for making high performance nanomaterials, $451,544, Project period: September 1 2014~August 31 2017, *National Science Foundation, DUE*, February 4, 2014. (Declined, resubmission for next cycle competition is under planning.)

[2] Development of new course modules for ME 499/599 to enhance students' learning, $6,398, Project period: July 1, 2014~June 30, 2015, funded by Special Projects for Improving the Classroom Experience (SPICE) Instructional Innovation program.

[3] Electrochemically synthesized nanocomposites for explosive detection and mitigation, $50,000, Project period: April 1, 2014~March 31, 2015, funded by Department of Homeland Security (DHS), DHS Science and Technology Directorate Office of University Programs.

**Keywords:** Energy conversion, Environment cleaning, Biophotofuel cell, Nanotube, Energy and environment sustainability

# II. BODY OF THE REPORT

## A. Summary of the Results

### A1. Background and Problem Definition

The breakthrough in the intersection of energy and environmental research is considered as one of the solutions to the future sustainability of the world. The forces of global energy needs and climate change are driving new developments in the alternative energy production. The use of biophotofuel cells for electricity and hydrogen production from waste and renewable sources is expected to play an important role in meeting this demand. Research in the area of biophotofuel cells and systems is emerging. 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 photobiological 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 electrodes is not good enough. Studies have shown that both the quantum efficiency and the hydrogen generation rate of biophotofuel 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 found because 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. We have proposed two ways to potentially solve the agglomeration problem 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 the Phase I work, anodic titanium dioxide nanotube membrane has been processed and used as the template to make biophotofuel 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 structures\ with high surface areas was doped with either conducting polymer nanoparticles or transition metal oxide nanoscale phases to form the anode. The un-oxidized Ti substrate was kept to establish the electron collecting path. To prepare a high efficiency cathode, electrochemical etching was conducted to selectively extract metallic elements from alloys to form porous structures. Electrocatalytic property of the porous electrode was characterized. Comparative studies on the electrochemical activity of the nanoporous metallic cathode with the bulk metal cathode were performed. Through both experimental and theoretical studies, how nanoporous structures with high electroactive surface areas are obtained through controlled electrochemical processing are unveiled. It has been found that at what extent 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 biophotofuel cell in view of electricity generation from biomass under solar rays, hydrogen production, noxious gas decomposition, and clean water regeneration.

## A2. Purpose, Objectives, Scope

The objective of this Campus as a Living Lab project is to design a novel biophotofuel cell and develop fundamental understanding of bio- photo- and electrochemical processes related to sustainable energy generation in such a system. The biophotofuel cell consists of a nanoporous electrode as the anode for biomass decomposition, and a low-hydrogen overpotential metal such as Ni or Pt, as the cathode for hydrogen production. The uniqueness of the project is the multiple functions of the fuel cell. It can generate electricity and produce hydrogen from biodegradable fluids under sunshine. Meanwhile, noxious gases such as ammonia released from biowastes are decomposed at the biophotosensitive anode and pure water is generated for reuse at the cathode. To prepare such an anode which is able to generate electron under photon irradiation, and decompose biomass, photosensitive semiconducting nanotubes of $TiO_2$ are prepared. The generated nanotube array structures with high surface areas are made into the anodes. To prepare a high efficiency hydrogen generation cell, Pt cathode has been used. Evaluating the performances of the biophotofuel cell in view of electricity generation from biomass under solar rays, hydrogen production, noxious gas decomposition, and clean water regeneration are performed.

In addition to clean energy generation, this project relates to clean water generation.

The relationship of this project to sustainability is obvious because it helps solve a problem related to both energy challenge and environment sustainability. The significance is that the design model could be scale-up for energy production and clear water generation from waste materials through harvesting solar energy. There is also connection between the project and the regional industry waste management because the idea could be used for industrial dye pollution control. The biophotofuel cell can be modified for decomposing discharged industrial dye or any organic hazardous material under sunlight.

The approaches used to implement the senior capstone team design project as an education tool can be summarized as follows.

***(1) Fundamental Studies Integrated with Hands-on Design Work:*** As known, the photochemical or electrochemical reaction of materials under visible or ultraviolet irradiation is a complex topic for undergraduate students. In order for the student team members to understand the phenomena, extensive fundamental studies are performed. The PI has worked with graduate students and undergraduate students to performed in-depth preliminary studies before the undergraduate student teams started the design work. Theory learning through assigning reading materials was scheduled before the hands-on design task. All the team members are required to read the research articles assigned by the PI. The students are also required to read through the research reports from the preliminary studies carried out by the PI and his previous students. At the end of the design, students who joined this project feel that they learned new knowledge, and designed a new product. The project provides them a challenging experience.

***(2) Multiple Group Cooperative Learning Approach***

The PI has recruited students from different background. For example, women students, minority students (Hispanics and African Americans) with Mechanical Engineering training are involved in the project. This project allows students to have the cooperative learning opportunity.

***(3) The Designed Module as a Teaching Tool***

The design biophotofuel cell module is used as the teaching tool. The PI used it to show photosensitivity of various oxide anode materials to students. How open circuit voltage changes in a photochemical fuel cell is routinely demonstrated to undergraduate students.

**A3. Data Findings, Outputs/Outcomes**

The results related to the proposed goals and objectives can be summarized as follows. In the proposed work, a novel photoelectrochemical fuel cell consisting of a titanium dioxide nanotube array photosensitive anode and a platinum cathode was made for decomposing environmentally hazardous materials to produce electricity and clean fuel. Titanium dioxide nanotubes ($TiO_2$ NTs) were prepared via electrochemical oxidation of pure Ti in an ammonium fluoride and glycerol-containing solution. Scanning electron microscopy was used to analyze the morphology of the nanotubes. The average diameter, wall thickness and length of the as-prepared $TiO_2$ NTs were determined.

Figure 1 shows the schematic of the fuel cell and the surface morphology of the anode with $TiO_2$ nanotube arrays. Figure 1(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. Figure 1(b) is an SEM image showing the open end of the nanotubes. The outer diameter of the $TiO_2$ nanotubes is about 180 nm. The wall thickness is around 15 nm.

The photosensitive anode made from the highly-ordered $TiO_2$ NTs has good photo-catalytic property, as proven by the decomposition tests on urea, ammonia, sodium sulfide and automobile engine coolant under ultraviolet (UV) radiation. To improve the efficiency of the fuel cell, doping the $TiO_2$ NTs with a transition metal oxide, NiO, was performed and the photosensitivity of the doped anode was tested under visible light irradiation. It is found that the NiO-doped anode is sensitive to visible light. Also found is that polyaniline-doped photosensitive anode can harvest photon energy in the visible light spectrum range much more efficiently than the NiO-doped one. It is concluded that the nanostructured photoelectrochemical fuel cell can generate electricity and clean fuel by decomposing hazardous materials under sunlight.

The titanium dioxide nanotubes ($TiO_2$ NTs) prepared via electrochemical oxidation of pure Ti in an ammonium fluoride and glycerol-containing solution show UV light sensitivity. The oxide nanotubes can be doped with transition metal oxide and conducting polymer materials so that visible light sensitivity can be obtained. Scanning electron microscopic analysis reveals that the nanotubes have an average diameter of 150 nm, wall thickness of 30 nm, and length of 1.5 μm. Such dimensions can be changed by the applied DC voltage level. The higher the voltage is, the thicker the nanotubes.

The novel photoelectrochemical fuel cell with a titanium dioxide nanotube array photosensitive anode has been successfully made. Preliminary data show the feasibility of decomposing environmentally hazardous materials to produce electricity and clean fuel. Although major tests were made by using the UV light source, the visible light sensitivity was also demonstrated. Visible light can be used as the photon energy source upon doping the anode with either the transition metal oxide NiO, or the conducting polymer, polyaniline. The polyaniline-doped photosensitive anode can harvest photon energy in the visible light spectrum range much more efficiently than the NiO-doped nanotubes.

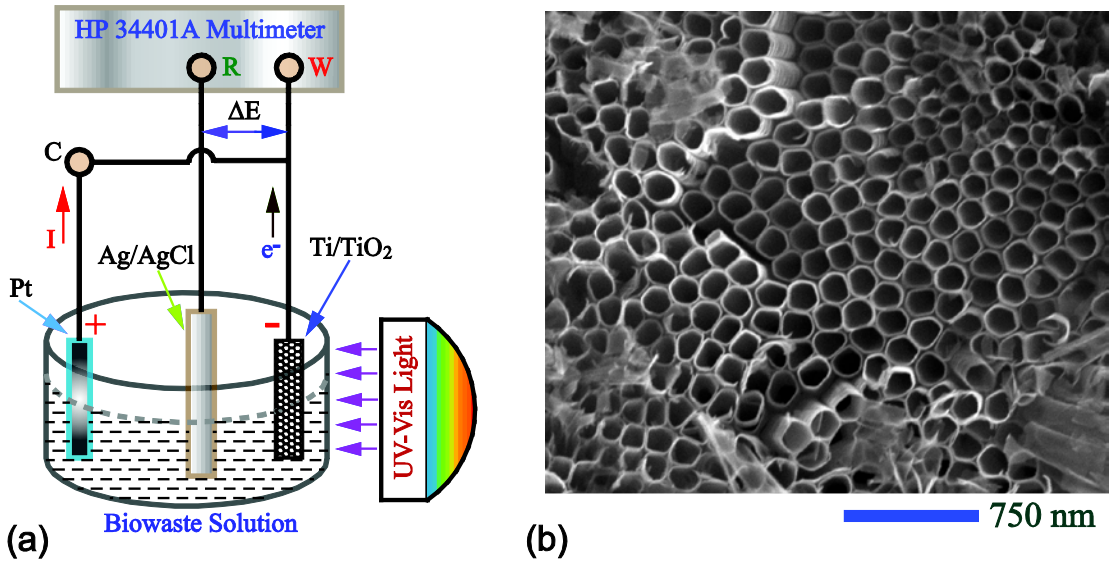


Figure 1: Schematic of the biophotofuel cell (a) and the morphology of $TiO_2$ nanotube anode (b).

Doping has been proven to be an effective way to increase the absorption of titanium oxide material. In order to enhance the photocatalytic activity of the $TiO_2$ nanotube anode, preliminary studies of doping the $TiO_2$ NTs with a transition metal oxide, NiO, was performed via electroplating Ni to the nanotubes and followed by high temperature annealing at 500°C for 2 h to convert Ni into NiO. The morphology of the NiO nanoparticles was observed by SEM and it is found that the majority of the NiO nanoparticles were deposited inside the nanotubes as shown in Figure 2(a) and (b). In some places, there are nanoparticles sticking to the top end of the $TiO_2$ nanotubes. Before Ni was converted to NiO, high resolution transmission electron microscopic (TEM) analysis was performed. Ni nanoparticles with the dimension of about 8 nm were shown in the TEM image of Figure 2(c). The diffraction pattern reveals the cubic crystal structure of Ni. Composition analysis was performed by energy dispersive X-ray diffraction (EDX), revealing strong Ni, O, and Ti signal, which is revealed by Figure 2(d).

The photosensitive anode made from the highly-ordered $TiO_2$ NTs has the capability of decomposing urea, ammonia, sodium sulfide and automobile engine coolant under ultraviolet (UV) radiation. Also, the anode can decompose these hazardous materials under visible light illumination, but at a lower efficiency. The open circuit potential of the fuel cell is affected by the type and concentration of the waste material solutions.

The solutions containing bio-hazardous materials were inducted into the one-compartment photochemical fuel cell. UV radiation was generated by the light source. Indeed, only the anode is necessary to be kept under the irradiation. It is observed that there is a voltage across the two electrodes of the fuel cell. At the Pt cathode, hydrogen bubbles formed in ammonia and the ethanol solutions as long as the fuel cell is air-tight and the UV lamp is on. The open circuit voltage was measured as a function of time using the HP 34401A multimeter. Also recoded are the dynamic response data when the UV light ON and OFF were switched.

Figure 3(a) and (b) show the open circuit potential (ΔE) v.s. time (t) curves obtained from the tests on the solutions containing 1.0 M urea and 1% ammonia, respectively. Figure 3(a) shows that when the UV light is ON, the voltage at the photosensitive anode drops. When the UV light is OFF, the voltage goes up as revealed by Figure 3 (b).

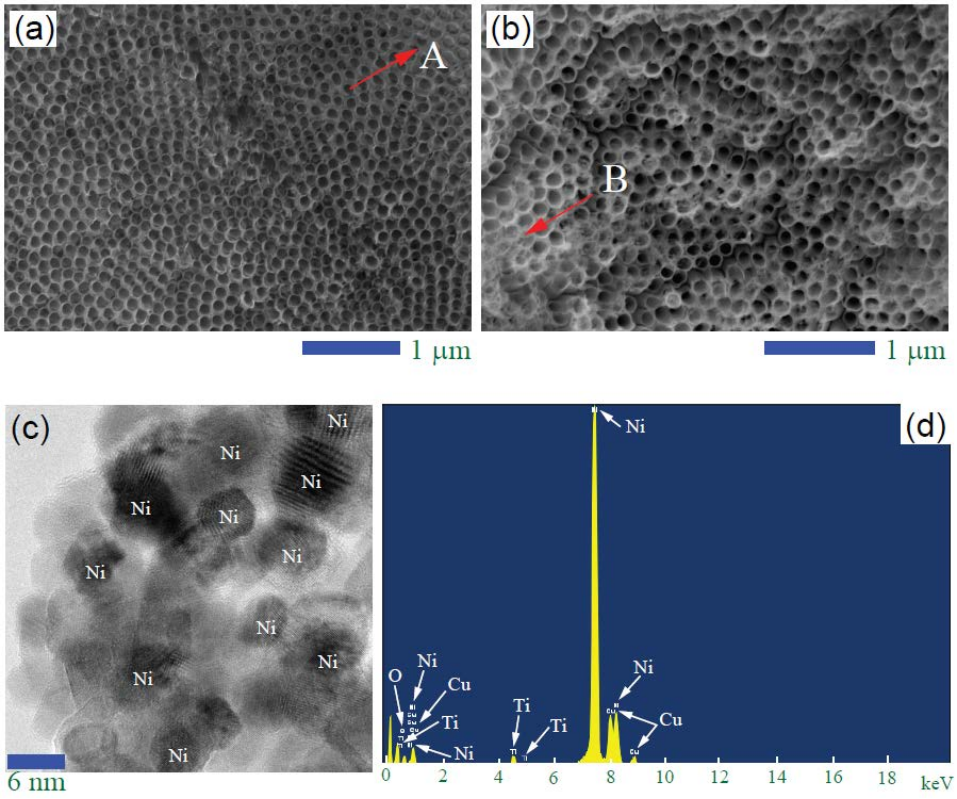


Figure 2 Electron microscopic analysis showing: (a) NiO particles within and at the top end of $TiO_2$ nanotubes, (b) NiO particles on the top end of $TiO_2$ nanotubes, (c) Ni particles with the size of about 8 nm, (d) EDX spectrum.

The dynamic response of the fuel cells to the light may be analyzed as follows. When the UV light is ON (i.e. in the charging cycle), the change in the anode potential shown in Figure 3(a) as a function of irradiation time, t, can be expressed as:

$$\Delta E = Ae^{-Bt} - E_o \quad (1)$$

where $A$ and $B$ are constants associated with the charging cycle, and $E_o$ is the equilibrium potential. When the UV light is OFF (i.e. in the discharging cycle), the change in the potential as shown in Figure 3(b) is also a function of recovery or relaxation time, t, which is in the form as follows:

$$\Delta E = E_o - Ce^{-Dt} \quad (2)$$

where $C$ and $D$ are constants related to the discharging cycle.

In the urea solution, the main photosensitive reaction at the anode is as follows:

$$TiO_2 + h\nu \text{ (UV light)} \rightarrow TiO_2(h^+) + TiO_2(e^-) \quad (3)$$

where $h^+$ and $e^-$ stand for hole and electron, respectively. In the solution, urea decomposes by combination with the holes.

$$O{=}C(NH_2)_2 + 6h^+ + H_2O \rightarrow CO_2 \uparrow + N_2 \uparrow + 6H^+ \quad (4)$$

To verify the carbon dioxide formation in the anodic region, data generated by a $CO_2$ gas sensor were obtained. The results show that when the UV light was OFF, the concentration of $CO_2$ gas in the anode region of the fuel cell was less than 700 ppm. After the UV light was ON for about 5 min and the fuel cells were approaching to steady state, detectable $CO_2$ gas was generated. The monitored $CO_2$ gas concentration increased to 800 ppm.

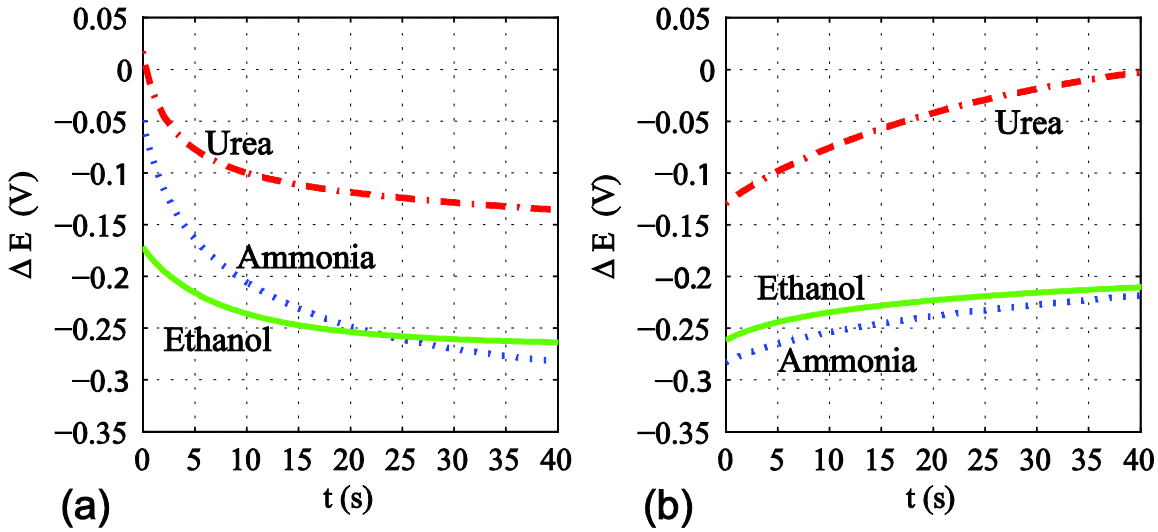


Figure 3: Open circuit potential (ΔE) v.s. time (t): (a) UV light ON (b) UV light OFF.

At the cathode, clean water generation is the main reaction.

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad (5)$$

If the cathode region is sealed or oxygen-free, hydrogen generation becomes the main reaction. The measurement results clearly reveal that the photodecomposition of urea and ammonia solutions can generate electricity. In addition, the clean fuel, hydrogen, can be produced when the cell was air-tight or oxygen-free. In the ammonia solution, the main reaction at the anode is still the electron-hole charge pair generation under the excitation of photons. Nitrogen gas forms in the solution due to the combination of hole with ammonia, i.e.

$$2NH_3 + 6h^+ + H_2O \rightarrow N_2 \uparrow + 6H^+ \quad (6)$$

At the cathode, either hydrogen or clean water generation is the main reaction depending on the availability of oxygen. In ethanol solution, the following reaction occurs [6]

$$C_2H_5OH + 3H_2O + 12h^+ \rightarrow 2CO_2 + 12H^+ \quad (7)$$

Solutions containing different concentrations of environmentally hazardous materials were made to perform photoelectrochemical decomposition tests using the nanostructured fuel cell anode. The justifications for choosing those hazardous materials for the studies are given as follows. Ammonia and urea are major compositions from fertilizers. They are pollutants in surface water. Diluted ammonia ($NH_3 \cdot H_2O$) solutions were made with the concentration of 1 wt% (pH=10.63), 0.25 wt%, and 0.025 wt%. The concentrations for urea were 1.0 M, 0.5 M, and 0.25 M. Sulfide is the major composition from the burning of coal. It is harmful for environment. Although the directly released sulfides from coal burning have multiple constituents, we use sodium sulfide in the test for the preliminary study. The typical concentration of sodium sulfide solution used in this work is 0.5 M. The antifreeze/coolant with the brand name of PEAK® was purchased from WalMart. The reason for choosing an antifreeze/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. According to the purchased product specification for this work, the concentration of ethylene glycol in the antifreeze/coolant is about 20 wt%.

Comparative studies of the photocatalytic behavior of the $TiO_2$ nanotube anode in the urea solutions with different concentrations were performed. The urea solutions used have the concentrations of 0.5 M and 0.25 M. An obvious concentration effect was identified as shown by

the results in Figure 4. When the urea solution with the concentration of 0.5 M was used, the potential changed from 0.05 V to -0.2 V when the UV light was ON. Figure 4(a) shows the dynamic response of potential, $\Delta E$, v.s. time, $t$, for $TiO_2$ nanotube anode to UV light in the 0.5 M urea solution. For the 0.25 M urea solution, smaller changes in the voltage were seen in Figure 4(b) when UV light was switched between ON and OFF states.

In ammonia solutions with different concentrations, the same effect on the open circuit potential was found. When the ammonia concentration was decreased from 0.5% to 0.25%, a slightly draft of the potential to a less negative range ($\Delta E_{min}$ from -0.31 V to -0.29 V) caused by UV irradiation was found and shown in Figure 5(a) and (b). For the solutions containing 0.025% ammonia, appreciable change in the voltage was found. The results as shown in Figure 5(c) indicated that the minimum value of potential ($\Delta E_{min}$) was -0.25 V. This reveals that with the fuel running out gradually, the absolute value of the open circuit voltage of the fuel cell is decreased.

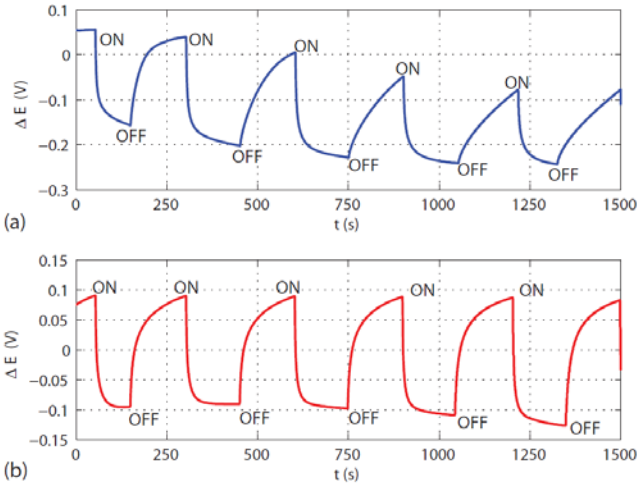


Figure 4 Effect of concentration on the open circuit voltage of the fuel cell using urea as the fuel: (a) 0.5 M urea solution, (b) 0.25 M urea solution.

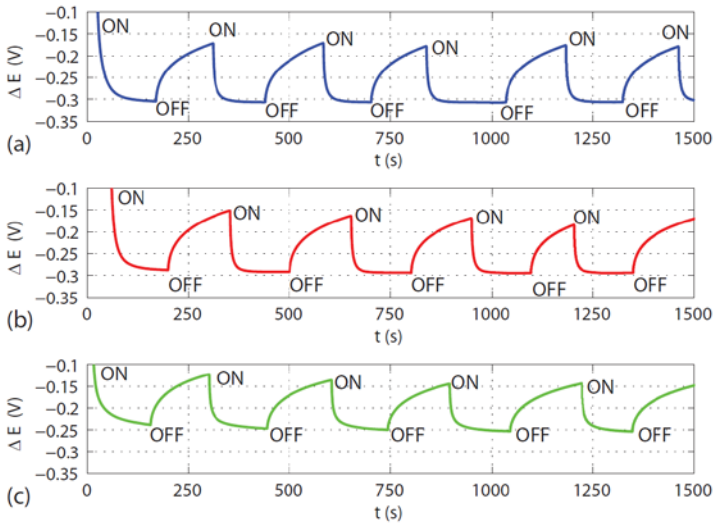


Figure 5 Effect of concentration on the open circuit voltage of the fuel cell use ammonia as the fuel: (a) 0.5% ammonia, (b) 0.25% ammonia, (c) 0.025% ammonia.

Other types of hazardous materials including $Na_2S$ and ethylene glycol-containing coolant were also used as fuels. Figure 6(a) and (b) show the open circuit potential ($\Delta E$) v.s. time ($t$) curves obtained from the tests on the solutions containing 0.5 M $Na_2S$ and the coolant with 20% ethylene glycol, respectively. Both Figure 6(a) and (b) show that when the UV light is ON, the voltage at the photosensitive anode drops to more negative ranges. The 0.5 M $Na_2S$ fuel causes the anode voltage dropping from -0.47 V to -0.58 V when the UV light was switched from OFF to ON. In the coolant, the anode potential was changed from -0.22 V to -0.4 V when the UV light was switched from OFF to ON. Similar to the tests on ammonia and urea solutions, the tests on the photocatalytic decomposition of $Na_2S$ and the coolant can generate electricity. Again, the clean fuel, hydrogen can be produced when the cell was air-tighten or oxygen-free. Due to the limitation to access to hydrogen measurement facility, the hydrogen measurement experiments have not been done.

When $Na_2S$ was put into the fuel cell, the step-by-step oxidation reactions in the solution can be expressed as:

$$S^{2-} + 3OH^- + 6h^+ \rightarrow SO_3^{2-} + 3H^+ \quad (8)$$

$$SO_3^{2-} + OH^- + 2h^+ \rightarrow SO_4^{2-} + H^+ \quad (9)$$

At the cathode, clean water generation is the main reaction because the pH value of the 0.5 M $Na_2S$ solution is as high as 13.9. Even under the oxygen-free condition, hydrogen formation is inhibited.

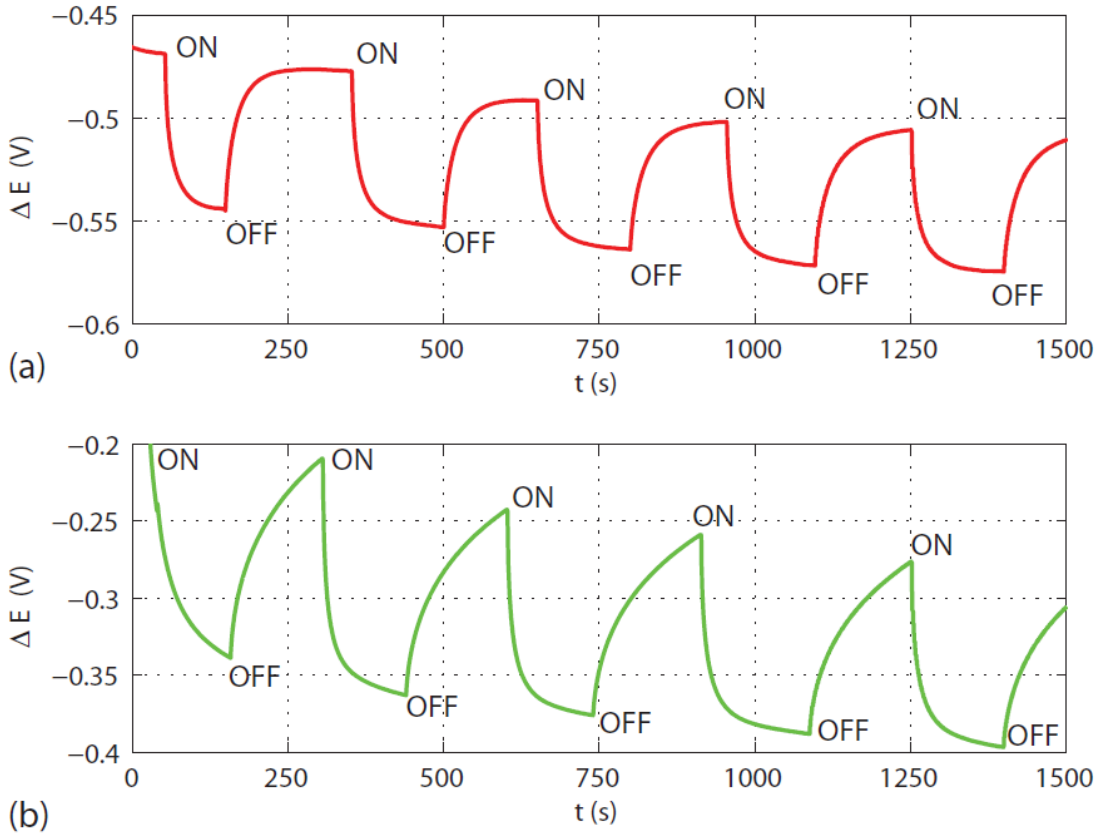


Figure 6 Open circuit voltage and dynamic response of the photoelectrochemical fuel cell: (a) potential ($\Delta E$) v.s. time ($t$) from the test on the solution containing 0.5 M $Na_2S$, (b) potential ($\Delta E$) v.s. time ($t$) from the test on the commercial antifreeze/coolant containing 20% ethylene glycol.

## A4. Analysis, Discussion and Conclusions

***i. Did the project contribute to sustainability?***

The project contributes to sustainability in a very obvious way. The designed biophotofuel cell module generates clean energy, produces clean water and decomposites biowaste materials. The photochemical reaction associate with the energy conversion is a sustainable process. The project has the potential to bring the positive impacts in progress towards sustainability in view of two aspects. The first aspect is on energy sustainability because the designed system harvests solar energy and partially converts it into electricity. The designed fuel cell also extracts useful chemical energy from waste materials. The second aspect is on environment sustainability. The biophotofuel cell has the capability of decomposing biowaste and purifying waste water.

***ii. Was the project successful (based on the definition of success provided in the proposal)?***

The project is successful in view of concept demonstration, fundamental studies of the feasibility, data collections and prototype biophotofuel cell design. The crucial to achieving the success lies in the team members' motivation and the extensive studies.

***iii. Did the tasks performed by the team members contribute in a substantive and constructive manner?***

The activities performed by the team members contribute in a substantive and constructive manner. For example, all the students are from Mechanical Engineering discipline, they contribute to system component design. Students also did the nanotube material processing and biophotofuel cell reaction mechanism analysis. Some students contribute to the circuit design and electrical measurement.

***iv. Are the potential impacts broadly applicable and transferable to various industry sectors or did the project have a significant impact within a given process or context?***

The potential impacts are broadly applicable and transferable to the industry sectors including solar cell companies, energy generation companies, and clean water generation or water purification companies. In addition, the potential impacts are broadly applicable and transferable to various situations. For example, in western coast region, solar energy is abundant. Therefore, the system designed from this project should be useful and has a significant impact on the photochemical energy conversion process.

***v. Can the project's impacts be quantified in terms of reduced environmental impact (water, waste, toxic emissions, etc.) and/or in terms of improved environmental health (reduced probability of illness)?***

The project's impacts can be quantified in terms of reduced environmental impact (specifically, water). If the designed system is scale-up, it can reduce biowaste compositions such as ammonia and urea discharge to ocean.

***vi. Can the benefits of the project be qualitatively determined?***

The benefits of the project may be qualitatively determined in three parts. The first part is the energy generation and environment cleaning in the remote areas could significantly improve the quality of life of the people living there. Secondly, the implementation of the project in developed area such as Los Angeles area could significantly reduce the discharge of ammonium-

based biowaste to the Ocean. This could reduce the risk of poisoning fish and suppress the rampant growth of algae in sea water. Thirdly, the designed biophotofuel cell system improved environmental health by reducing the impacts of fertilizers, pesticides, industrial dyes etc. These hazardous materials are cleaned by sunlight, which could reduce the cost for waste treatment significantly. This benefits the local economy and protects the land.

***vii. Was the project focused on original discoveries or an adaptation of existing knowledge to result in innovative approaches?***

The project is based on the original discoveries of new nanomaterials and nanostructures for energy conversion and environment cleaning. The fundamental research in the project helps further our understanding the photon-materials reactions. The research is innovative in fields of energy nanotechnology and environment nanotechnology.

# B. Future Work

## B1. Description of Future Project

The objective of the possible future project is to scale up the prototyped biophotofuel cell for practical applications. The major technical tasks include two aspects. The first one is to modify the design by making flexible photosensitive electrode which is suitable for field deployment. The second one is to perform field tests in different areas. The project will be completed within three years. In the first stage, field tests in the open water channels in Los Angeles County, CA, USA will be conducted. In the second stage of the future project, field tests in other western coast counties will be carried out.

The strategies are as follows. First, electrospinning will be used to prepare the required flexible electrode containing a conducting polymer matrix, polyaniline, and the photosensitive titanium dioxide nanotubes. The electrospinning process will force the viscous flowing of the aniline solution from a jet to a target. The driven force for the flow is mainly electrical. Pressure may also be applied to the solution to facilitate the viscous flow. The electrochemical polymerization occurs simultaneously. The jet and the target are attached to a specially designed plate with an applied high voltage. A fairly simple electrospinning system will be designed and set up. It consists of a unit for supplying the charged polymer solution (or melt), a collecting plate and a 30 kV DC power source. The collecting plate will be a metallic screen, or foil as schematically shown in Figure 7(a).

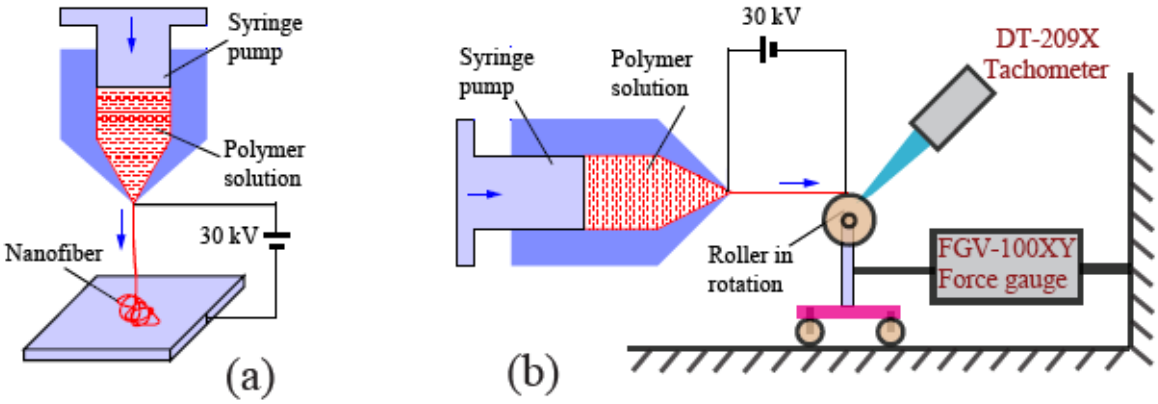


Figure 7: Electrospinning polyaniline/$TiO_2$ nanofibers with (a) electrical force, (b) electrical and mechanical force.

During electrospinning, the solvent gradually evaporates, and a charged polymer fiber is left to accumulate on the target. It must be pointed out that the titanium oxide nanotubes in the solution will be co-spun with the polyaniline to form the required organic-inorganic composite nanofiber electrode. To increase the production rate, a rotating disc or mandrel will be used to collect the nanofibers as shown in Figure 7(b). The driven force for such an innovative design is not only electrical, but also mechanical, which can increase the efficiency of the process significantly. This design is expected for scalable manufacturing because it is possible for large scale production of composite nanofibers. A non-contact tachometer will be used to monitor the rotation speed of the nanofiber collecting mandrel. A force gauge will be used to measure the

stretching force of the nanofiber during the electrospinning process. The relationship of these process parameters and the photosensitive properties of the composite nanofiber will be established through systematic experimental studies. The composite nanofibers in the mat form will be used as the electrode for energy generation and environment cleaning. Field tests in the open water channels in Pomona, Walnut and Diamond Bar of Los Angeles County will be carried out to evaluate the effectiveness of removing ammonium, organic dyes and other harmful substances in open water release to the Ocean. The field tests will also be conducted in some other counties where energy challenge and environment sustainability become notable issues.

The field tests will be implemented in City of Pomona, Los Angeles County, CA. As shown in Figure 8, typically, surface water goes to Pacific Ocean through open ditches in Los Angeles area. We will make the photosensitive electrospun nanofibers into mats or fabrics. These mats or fabrics will be deployed in the ditch to convert waste materials in water into clean energy. The fabrics may be put at the bottom or attached to the side walls of the ditch, depending on the geographical conditions. The effectiveness of biowaste decomposition will be assessed by monitoring the water quality before and after the photoelectrochemical treatment by the designed biophotofuel cell.

Figure 8: Picture showing the surface running water from city of Pomona, CA to Pacific Ocean.

**B2. Schedule**

The technical task of this project is to design and fabricate a novel photoelectrochemical fuel cell consisting of a nanoporous electrode as the anode for biomass decomposition, and a low-hydrogen overpotential metal such as Pt, as the cathode for hydrogen production. The uniqueness of the project is the multiple functions of the fuel cell. It can generate electricity and produce hydrogen from biodegradable fluids and waste materials under sunshine. Meanwhile, noxious gases such as ammonia released from wastes can be decomposed at the photosensitive anode. Pure water can be generated for reuse at the cathode. In order to prepare such a key component

in the system which is able to generate electron under irradiation, and decompose biomass, photosensitive semiconducting substances such as pure $TiO_2$ and doped-$TiO_2$ nanotubes will be made into membranes with regularly aligned nanopores. The generated nanoporous array structures with high surface areas will be transferred onto a conductive substrate to form the anode. Coating metal thin film may be applied on the top of the electrode to establish the electron moving path. The photoelectrochemical fuel cell will be tested in view of electricity and hydrogen generation from biomass under solar rays, noxious gas decomposition, and clean water regeneration. It is proposed that the project start on January 1, 2015 and end on December 31, 2017. The timeline and the milestone of proposed activities are shown in Table 1.

Table 1: Milestones of the proposed follow-on project

| Proposed activities | 1/15 | 06/15 | 12/15 | 06/16 | 12/16 | 06/17 | 12/17 |
|---|---|---|---|---|---|---|---|
| Literature Review | | | | | | | |
| Materials and Suppliers | | | | | | | |
| Nanotube processing | | | | | | | |
| Nanotube doping | | | | | | | |
| Nanotube structure and composition analysis | | | | | | | |
| Nanofiber electrospining | | | | | | | |
| Biophotofuel cell design | | | | | | | |
| Biophotofuel cell field testing in Los Angeles | | | | | | | |
| Student advising | | | | | | | |
| Biophotofuel cell field testing in L.A. | | | | | | | |
| Biophotofuel cell field testing in other counties | | | | | | | |

## B3. Partnerships

The PI will contact the Los Angeles County, and Walnut Valley Water Resource Board to build potential partnerships on water purification and hazardous materials control to protect the environment. In addition, a company on electrospinning and a solar cell company will be contacted to explore the commercialization opportunity of the scale-up system.

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# III. EXPENDITURE REPORT

***a. Equipment:*** $5,851 was spent on purchasing the CHI 440C electrochemical microbalance for biophotofuel cell anode surface adsorption property characterization.

***b. Supplies:*** $3,777 was used for purchasing high voltage power supply for doping the titanium dioxide nanotubes.

***c. Travel:*** $41 was used for supporting the PI traveling to CSU Long Beach. The purpose for this trip was to attend the workshop on materials analysis via X-ray diffraction.

***d. Students' support:*** $331 was used to pay students' stipend or scholarships.

Total cost: $5,851+$3,777+$41+$331=$10,000, which is the same amount awarded.