INTERIM PROGRESS REPORT ON THE PROJECT

Funded by SPS, American Institute of Physics

TITLE OF RESEARCH PROJECT: "Design and Development of Novel Nanocomposite Materials and Reactor Systems for Photocatalysis"

DURATION OF THE ENTIRE PROJECT: **January 1 – December 31, 2013**

SPS CHAPTER, Physics Department, Tuskegee University: ZONE: 06, SPS Chapter #7446

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ORIGINAL ABSTRACT

Photocatalysis is an interdisciplinary field of research which involves the contribution not only from Physicists, chemists, material scientists, chemical and environmental engineers, but also demands often the need of technologists who can build the custom made reactor systems for different applications. Novel solid state materials' development is equally important for the water/air decontamination and/or fuel generation processes. In this research study, we proposed to develop and demonstrate both aspects of reactor and materials' design for the sunlight assisted photocatalysis.

PROJECT OBJECTIVES

Materials' Development: Semiconductor oxide nanoparticles based on titanium oxide (TiO_2) has shown potential photocatalytic activity for destruction of toxic chemical contaminants in water/air by ultraviolet (UV) light irradiation. However, TiO_2 shows rather poor activity on these processes with exposure of only visible (sun) light. It is estimated that only 4% of the sunlight contains UV component and the large proportions (~96%) are with visible light wavelengths (>400 nm). While investigating the plain TiO_2, we have noticed that the poor catalytic activity under incandescent light was due to its wide band gap (~3.2 eV) which needs further optimization procedures. Based on our extensive literature search, we found that Indium Vanadium Oxide ($InVO_4$) has not only exhibit low band gap values (1.8-2.0 eV), but also possess suitable band positions for the photo-oxidation and photo-reduction reactions. In this study, we propose to develop novel TiO_2-Xwt.% $InVO_4$ nanocomposites, which utilizes both UV and visible spectrum for the processes to decontaminate water and generate hydrocarbon fuels.

Reactor Design and Development: There is no commercial manufacture the photocatalytic reactors for different applications. Moreover, the photocatalytic reactors' fabrication often relies on various experimental parameters including the amount of the photocatalysts and degradant, UV light intensity, air flow etc. Another aspect of the reactor design is based on the types such as continuous flow or batch processes. In this research study, we have proposed to develop custom build reactor system design which is suitable for specific photocatalytic applications. We will optimize the experimental parameters for obtaining the maximum efficiency and throughput. The materials' designed in the first part of the proposed study will be incorporated in this second part.

EXPERIMENTAL DETAILS

The TiO_2-Xwt% $InVO_4$ nanocomposites are synthesized by both wet chemical route and solid state mechanochemical process as depicted in flow chart of Figure 1. Various optimization procedures have been adopted in terms of concentration of $InVO_4$, particle sizes of both TiO_2 and $InVO_4$, milling medium and duration of milling etc. to obtain the high yield material with maximum conversion efficiency. The as-synthesized nanocomposites were extensively characterized using metrological tools such XRD, SEM, EDAX, FTIR, UV-Vis and BET to explore the structural, microstructural, elemental, chemical and surface properties. We have fabricated a state-of-the-art photocatalytic reactor for the photo-oxidation of Methyl Orange (MO), an azo-dye contaminant in aqueous water under UV-Visible light (Figure 2. Design and development of photocatalytic reactor for the hydrocarbon fuel production from CO_2 and water vapor is also in progress. Various experimental parameters such as power of light irradiation, amount of photocatalyst, concentration of source gases or initial contaminant, air flow, the time of irradiation etc. have been optimized for maximum yield. Computer simulations (3D) modeling of reactor design also carried out using Autodesk software.

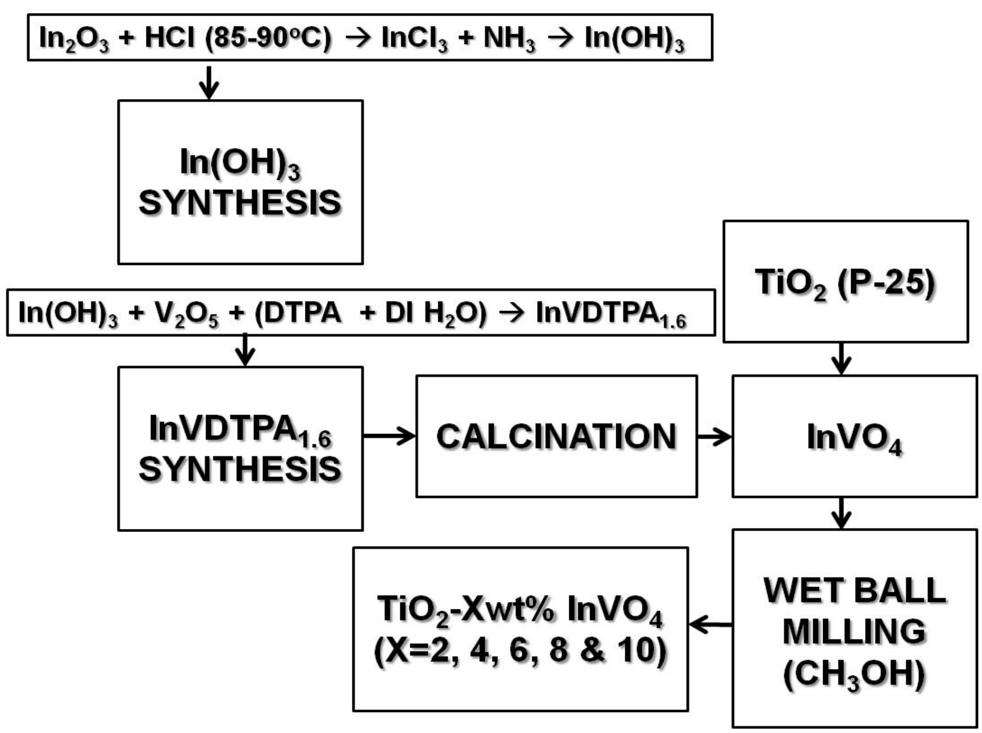


Figure 1: Flow chart synthesis of $InVO_4$ and TiO_2-Xwt% $InVO_4$

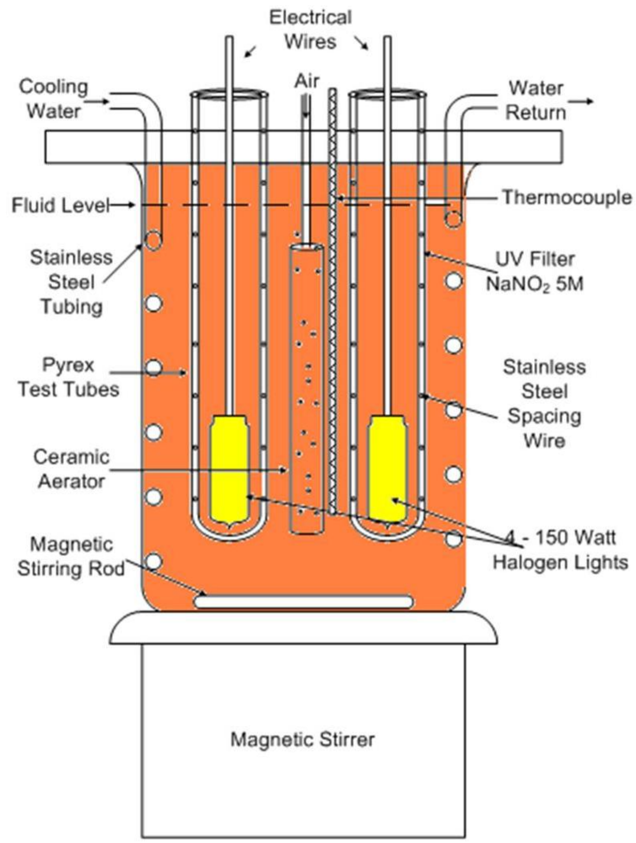


Figure 2: Schematic diagram for the design of photocatalytic batch reactor for the degradation of MO in 1000ml of aqueous water under UV-Visible light.

RESULTS AND DISCUSSION

Fourier Transform Infrared spectra for the plain TiO_2, plain $InVO_4$ and TiO_2-Xwt% $InVO_4$ (X=2, 4, 6, 8, 10) have been recorded using Shimadzu FTIR spectrometer. Table 1 shows the indexing of the bonding stretches and bending modes of C-H, C-N, V-O, V-O-V, V-O-In, $InVO_4$ vibrations at respective wavenumber. From the FTIR profiles (not shown a graph here), it is noticed that the composite nanoparticles of TiO_2 with increasing concentrations of $InVO_4$ thus enhances the bonding bands at the order of at least 10 cm^{-1}. BET surface area analysis (physisorption) of the TiO_2-Xwt% $InVO_4$ have been carried out under liquid nitrogen temperature using Autosorb iQ equipment and are also compared with the plain TiO_2 and pristine $InVO_4$. Figure 3 shows the variation of surface area with respect to different samples mentioned above. It is noteworthy to mention 4%$InVO_4$ ad-mixed with TiO_2 shows at least 1.5 times more surface area (~92 m^2/g) than plain TiO_2 (~63 m^2/g).

Table 1: Fourier Transform Infrared Spectra bonding information of TiO_2-Xwt% $InVO_4$

Wavenumber, cm^{-1}	Chemical Bonding Information
448.6	V-O-V
767.4; 903.5	V-O-In
943.7	V-O
3415.4	InVO4
2925; 2851	C-H Stretches
1420	C-N Stretch

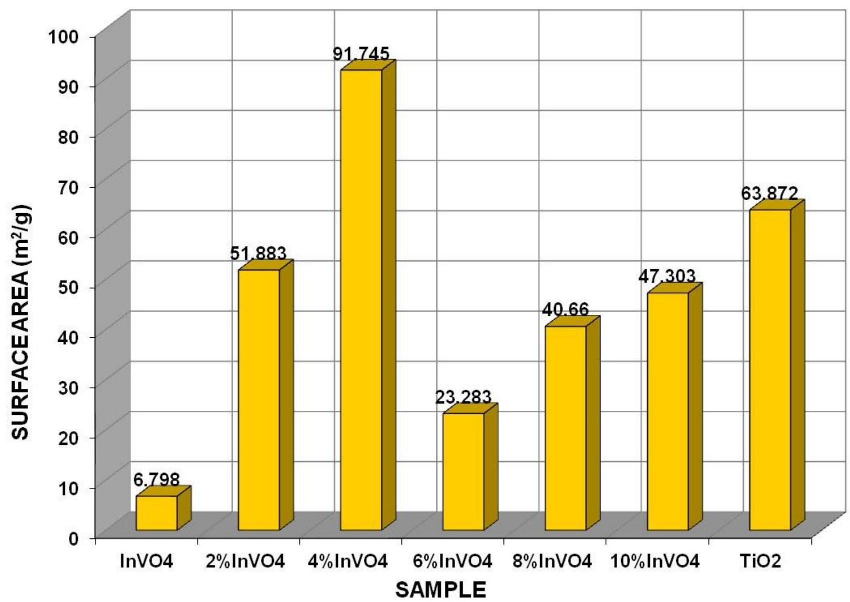


Figure 3: BET Surface area analysis of plain TiO_2, plain $InVO_4$ and TiO_2-Xwt% $InVO_4$.

The increase in the surface area of this $TiO_2/InVO_4$ nanocomposite will enhance the photocatalytic behavior since the photo-oxidation of MO is apparently a surface phenomenon. The photocatalytic oxidation experiments have been conducted using the plain TiO_2, plain $InVO_4$ and TiO_2-Xwt% $InVO_4$ under UV-Visible irradiation of MO/DI H_2O for different time durations. Plain TiO_2 under UV light demonstrated higher activity of degrading MO in at least 5 hours due to its intrinsic photocatalytic behavior (Figure 4(a)). On the other hand, plain $InVO_4$ was inert towards the photo-oxidation reaction and decoloration was noticed over 7hours of light exposure (Figure 4(b)). For the TiO_2-4wt% $InVO_4$ samples, the degradation of 80% of MO was systematically occurred in 7 hours (Figure (c)), however, the kinetics of this degradation reaction needs to be improved which will be our future direction given in the respective section of this report. In addition to the UV-Visible light experiment, we will also examine thoroughly the effect of the new nanocomposites on the visible light response at the same experimental conditions. This will enable us to use the entire solar spectrum for higher photonic yield for efficient water detoxification processes.

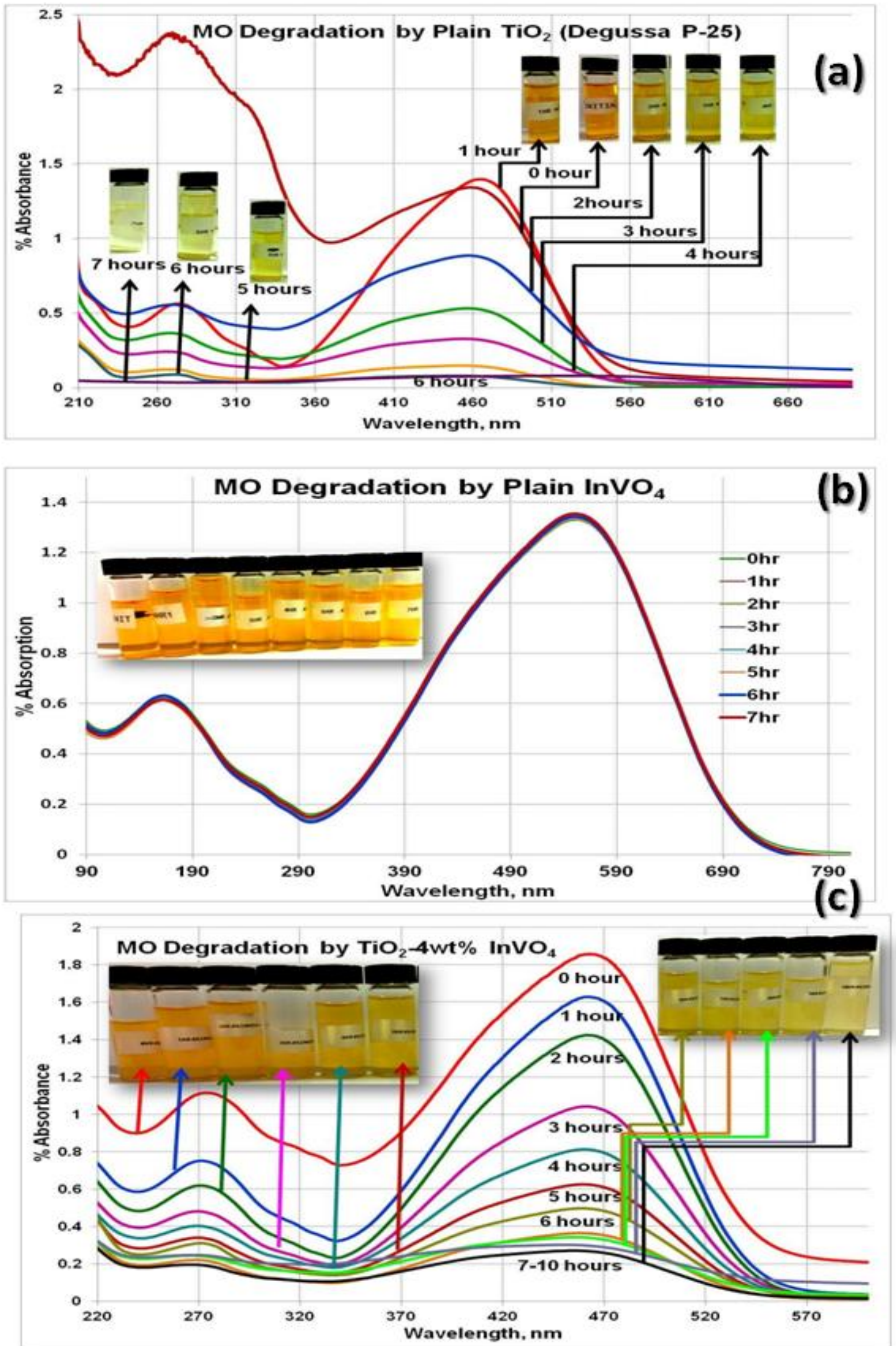


Figure 4: Photo-oxidation of 20 ppm of MO in aqueous water using photocatalysts.

CONCLUSIONS

In summary, our preliminary results show that the new catalysts TiO_2-Xwt% $InVO_4$ are promising in water purification applications because they do possess higher surface area in comparison to either plain TiO_2 or plain $InVO_4$. The next step is to use these as-synthesized catalysts for the photo-reduction process of generating hydrocarbon fuels from CO_2 and H_2O vapor. The reactor design both by experimental and theoretical simulations are in progress the results will be communicated in the final report. Another important aspect of this research study is that this experimental research work has successfully incorporated in our Modern Physics Laboratory course. Students enrolled in this course will routinely trained to work on the state-of-the-art research tools such as FTIR, UV-Vis spectrometers, High Energy Ball Mill, Photocatalytic batch reactors, Autosorb iQ surface area tool etc.

FUTURE WORK

The future work will follow up with our preliminary results given above in both fronts of materials design and reactor design aspects. The following future work is planned in align with the project goals and objectives.

- Demonstrate the effects of TiO_2-Xwt% $InVO_4$ for the visible light assisted (Edmund Optics cut-off filter will be used to filter the UV wavelength <400nm) photocatalysis of MO in aqueous DI water.
- Develop a reaction chamber for the treatment of CO_2 and H_2O for the photo-reduction to produce CH_4 or higher hydrocarbons.
- Investigate the structural, microstructural characteristics of the new type of nanocomposite materials using XRD and SEM, study their relation with the materials' photocatalytic behavior

BUDGET UTILIZATION AND JUSTIFICATION

Since Tuskegee University's Office of Sponsored Research and Office of Grants and Contracts are setting up an account for this AIP financial award of $2,000, we have not yet utilized the budget for this interim project reporting period. However, we will use the grant money this summer to procure materials and supplies/accessories, for both materials' design and reactor design as well.

ACKNOWLEDGEMENTS

The project participants, faculty mentors and SPS TU chapter advisors are grateful to the American Institute of Physics (AIP), Society for Physics Students (SPS) and Sigma Pi Sigma (ΣΠΣ), National Science Foundation (Energy Sustainability) for financial support. The project participants also thank Dr. Luther Williams (Executive Vice President and Provost) and Dr. Fitzgerald Bramwell, (Dean, College of Arts and Sciences) of Tuskegee University for their support and encouragement.

PUBLICATIONS/CONFERENCE PRESENTATIONS

1. STUDENT POSTER/ORAL COMPETITIONS AT THE 90TH ALABAMA ACADEMY OF SCIENCES (SAMFORD UNIVERSITY)
    a. Poster Title: Combinatorial Synthesis and Characterization of Zinc Iron Oxide Nanoparticles for Biomedical Applications, Bria Moore, (2nd Prize winner) of the 90th Annual Meeting of AAS, Samford University, March 21, 2013.
    b. Poster Title: Design and Optimization of Photocatalytic Disinfection System for Biological and Environmental Health Applications, Jeremiah Wilson, 90th Annual Meeting of AAS, Samford University, March 21, 2013.
    c. Poster Title: Reversible Solid State Hydrides for Fuel Cell Vehicles, Lamont Henderson, 90th Annual Meeting of AAS, Samford University, March 21, 2013.

2. STUDENT POSTER/ORAL COMPETITIONS AT THE 4TH JOINT ANNUAL RESEARCH SYMPOSIUM (TUSKEGEE UNIVERSITY)
    d. Poster Title: Combinatorial Synthesis and Characterization of Zinc Iron Oxide Nanoparticles for Biomedical Applications, Bria Moore (2nd Prize winner) of the 4th Joint Annual Research Symposium (JARS), March 15, 2013.
    e. Poster Title: Design and Optimization of Photocatalytic Disinfection System for Biological and Environmental Health Applications, Jeremiah Wilson, P.C. Sharma, 4th Joint Annual Research Symposium (JARS), March 15, 2013.
    f. Oral Presentation Title: Reversible Solid State Hydrides for Fuel Cell Vehicles, Lamont Henderson, Sesha, P.C. Sharma, 4th Joint Annual Research Symposium (JARS), March 15, 2013.

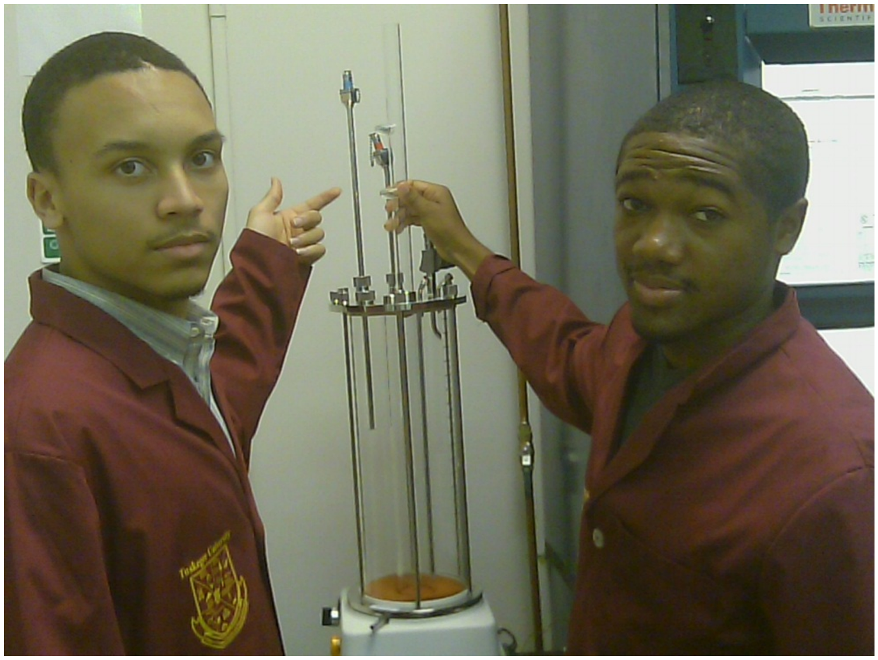
3. NSBP STUDENT TRAVEL AWARD TO ATTEND PHYSICS QUADRENNIAL CONFERENCE
    g. Mr. Sammie Ely III, Quadrennial Physics Congress, NASA Kennedy Space Center, November 8-10, 2012, Title of Poster Presentation: Ball Milling of $TiO_2/InVO_4$ Nanocomposites for the Visible Light Photocatalysis, Sammie Ely III, Jeremiah F. Wilson, P.C. Sharma.
    h. Mr. Lamont Henderson, Quadrennial Physics Congress, NASA Kennedy Space Center, November 8-10, 2012, Title of Poster Presentation: Custom Design and Demonstration of UV-Vis Photocatalytic Reactors, Lamont Henderson, Jeremiah F. Wilson, Sammie Ely III, P.C. Sharma.

GROUP PHOTO AND SNAPSHOTS OF RESEARCH IN ACTION

Provost & Executive Vice President Dr. Luther S. Williams meeting with award winning physics major students

Left to Right Standing – Dr. P.C. Sharma (Head, Physics), Dr. Luther S. Williams (Provost & Executive Vice President), Dr. A. Kumar (Associate Professor) & Dr. Sesha (Assistant Professor, Physics) and Mr. Steven Gaillard.

Left to Right Sitting – Mr. Jeremiah F. Wilson, Ms. Alejandra Sandoval, Ms. Bria M. Moore & Mr. Lamont Henderson.



Jeremiah Wilson and Lamont Henderson constructing a Photo-reduction reactor for liquid fuel production from CO_2 and H_2O

Sammie Ely III, Jeremiah F. Wilson and Lamont Henderson – Research in action at Tuskegee University Hydrogen, Renewable Energy and Bio-Nanomaterirals Laboratory

Tuskegee University Physics students' research presentation at the 90th Annual Meeting of Alabama Academy of Science Meeting, Samford University, Birmingham, AL