Density Functional Theory and Non-Equilibrium Green Function based First-Principles Study on the Effect of Substitutions in Z-Scheme Photocatalytic Materials: The case of TiO_2

Nolan Hines, BS[1]; Anveeksh Koneru, PhD[1]

[1]The University of Texas Permian Basin

Abstract

It is well known that alternative methods of renewable energy production are needed for the sustainability of Earth. Hydrogen gas has been identified as an integral part of the future of clean renewable energy which may be used in hydrogen fuel cells such as what is in the new Toyota Mirai. However, methods of obtaining H_2 need further development. Photocatalysis is a promising field in which hydrogen gas may be evolved without generating a carbon footprint while using otherwise wasted solar energy. In an effort to increase photocurrent activity in the visible light region, a Titanium Dioxide (TiO_2) based impurity band Z-Scheme junction with an ohmic contact was developed utilizing band structure engineering via doping method. The following cation and anion dopants were studied: W, Cu, Mo, Al, Fe, V, Cr, Co, Ta, C, N, S [1].

Introduction

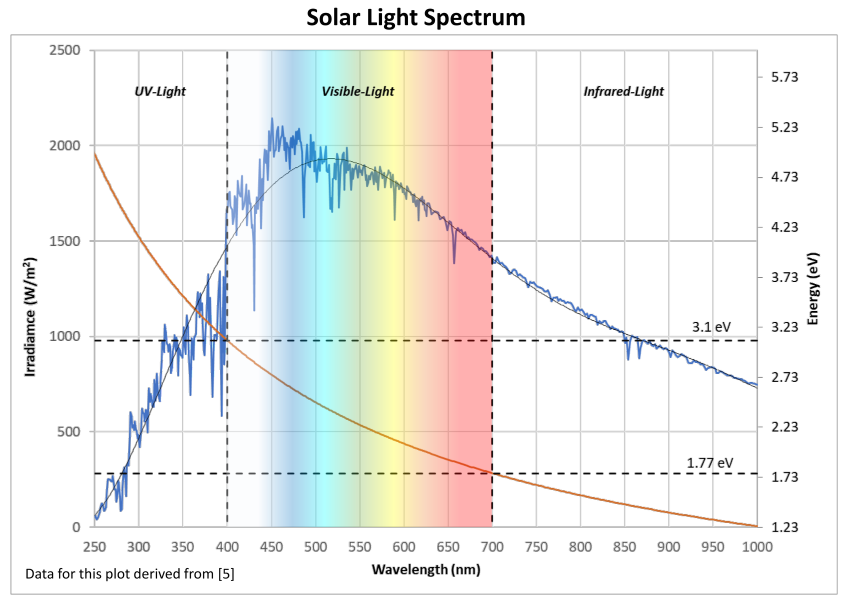
Current Hydrogen Generation Techniques:

Nonrenewable methods make up 90-95% of current H_2 production with the majority produced through steam methane reforming. Electrolysis makes up 4-6% of H_2 production and can be carried out with renewable or nonrenewable energy. Other renewable techniques include: biomass gasification, pyrolysis, photocatalysis, etc. [2][3].

Problem Statement:

Hydrogen is the most abundant element in the universe and is proven to be clean and efficient when used in a hydrogen fuel cell [4]. However, generally Hydrogen does not exist naturally in pure H_2 gas form on earth, and current methods of production are net negative and release green house gases.

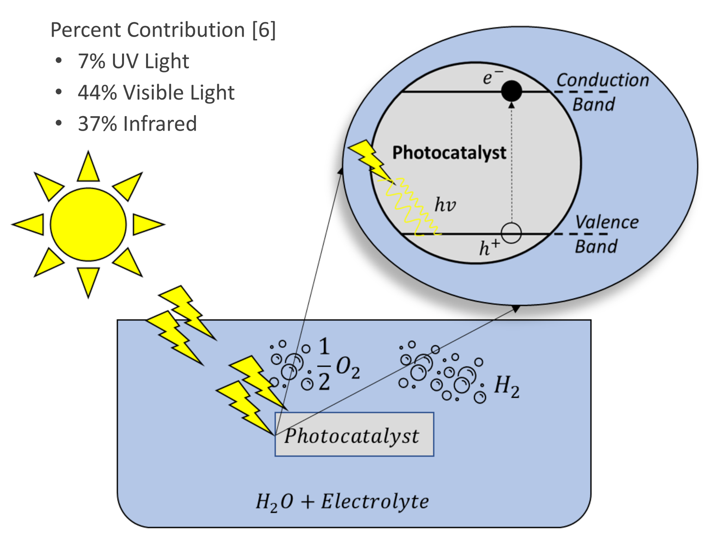
Solar Light Spectrum



Data for this plot derived from [5]

Percent Contribution [6]

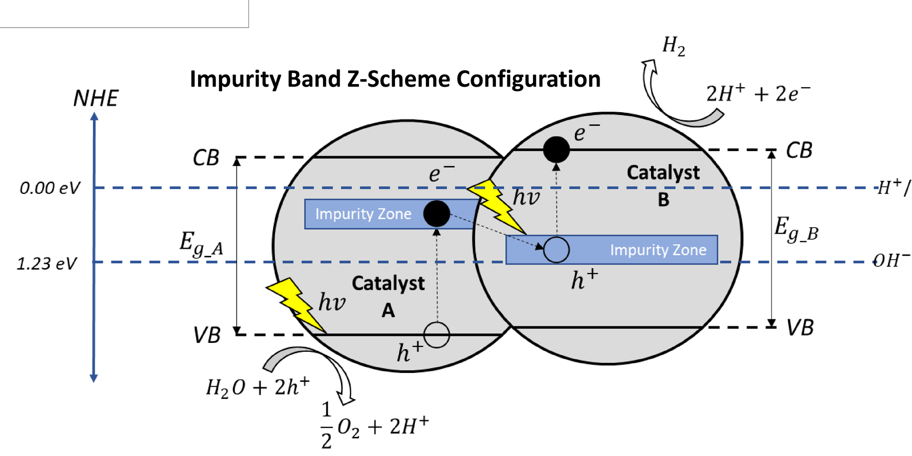
- 7% UV Light
- 44% Visible Light
- 37% Infrared



$$E = \frac{hc}{\lambda}$$

E = Energy
h = Plank's Constant
c = Speed of Light
λ = Wavelength

Impurity Band Z-Scheme Configuration



Objective:

- Identify ideal substitution materials for both titanium and oxygen sites in TiO2
- Complete a DFT study using SGGA Hybrid exchange correlation and HSE06 functionals on each configuration to determine apt band edge positions and recognize potential n-type and p-type catalysts to be used in a Z-Scheme.
- Using first-order perturbation theory within the 1st Born approximation, calculate total photocurrent activation for each Z-Scheme configuration.

Methods and Materials

Base Catalyst Material

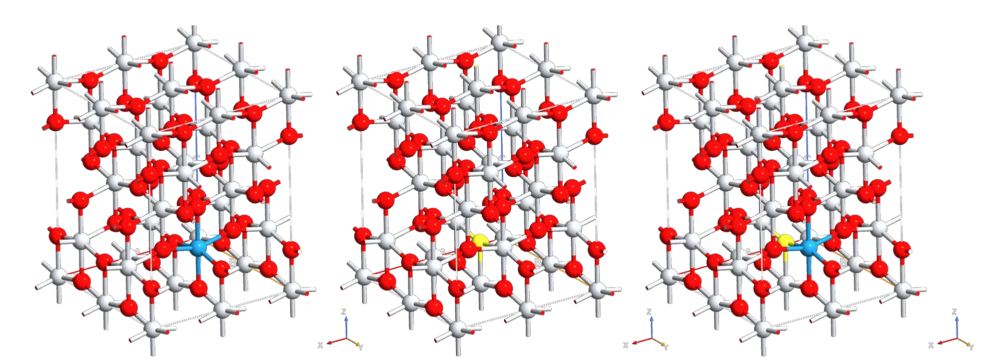
- Anatase TiO_2 [7][8]
  - 3.2 eV band gap
  - UV light activated

DFT Parameters

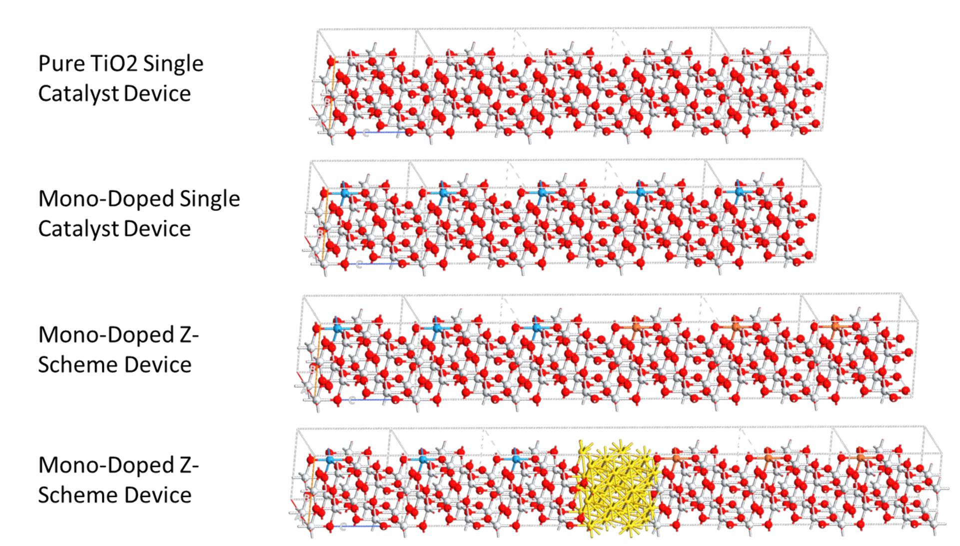
- QuantumATK from Synopsis software used for all calculations.
- Hybrid SGGA exchange correlation with HSE06 functionals were used
- 2x2x1 48 atom unit cell
  - 16 Titanium Sites
  - 32 Oxygen Sites
- 4x4x4 K-Point path
- 125 Hartree density mech cutoff

NEGF Parameters

- Left and right electrodes made up of a single unit cell on either side.
- Scattering region between the left and right electrodes.
- Gold contact placed with equal lattice constants between catalysts.

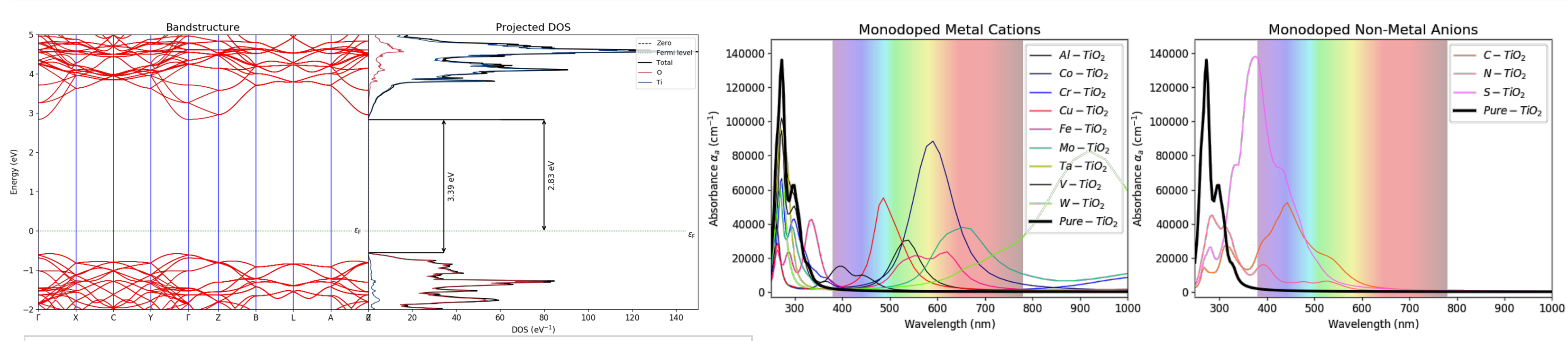


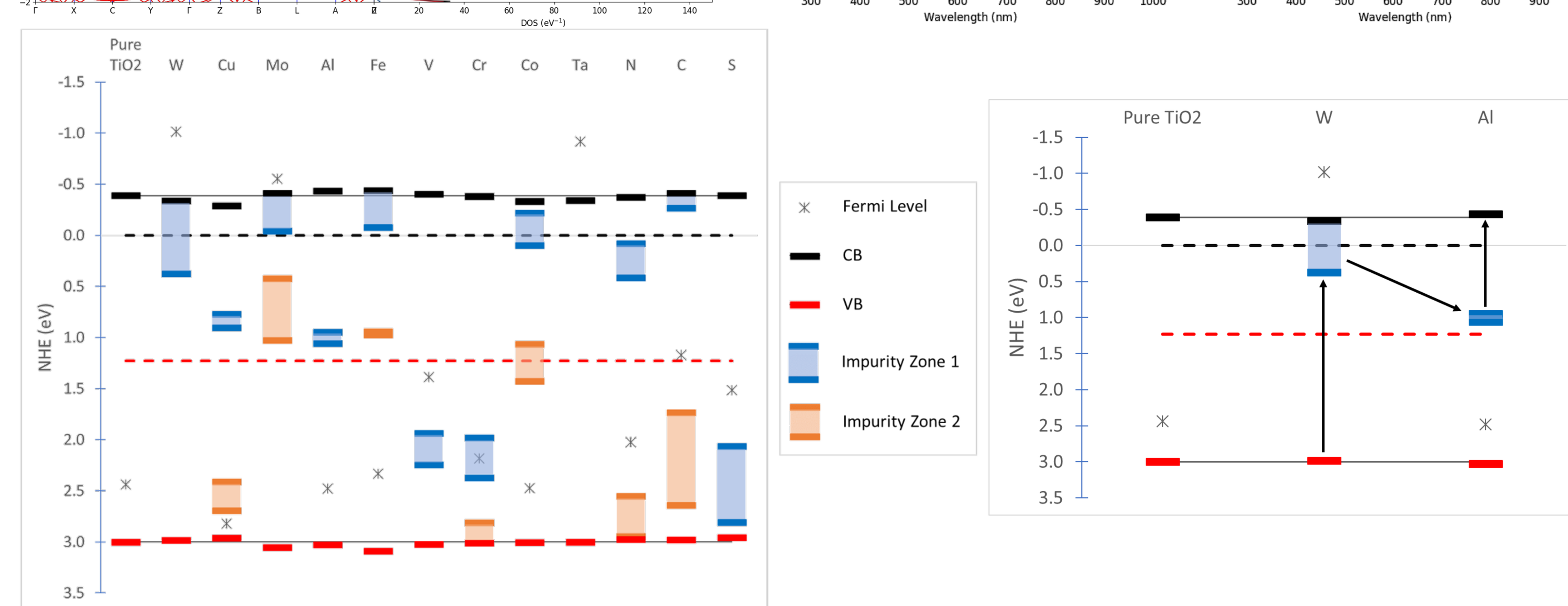
Mono-Doped Cation | Mono-Doped Anion | Co-doped Cation and Anion



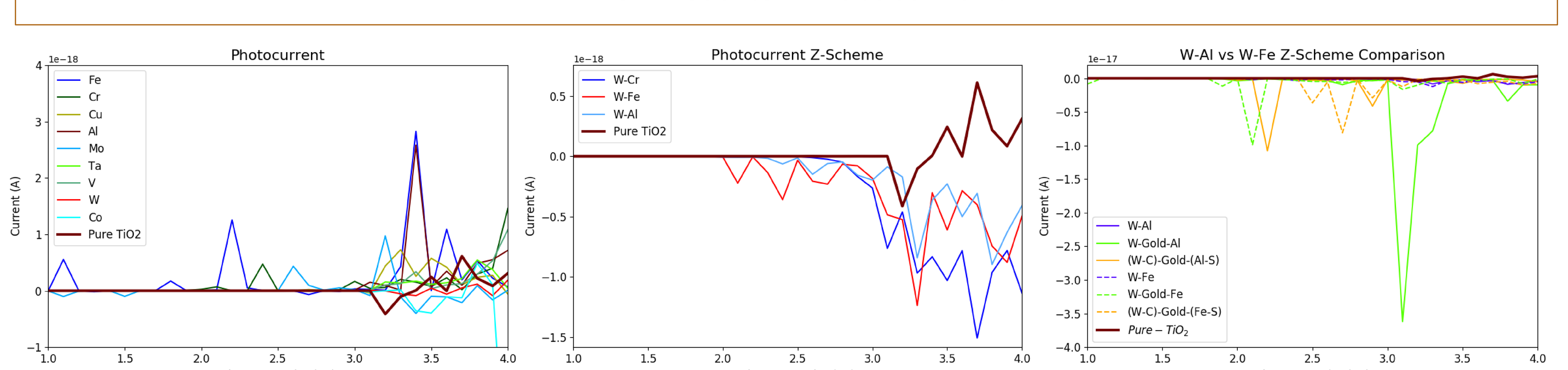
Results

DFT Results: Bandstructure – Projected Density of States – Optical Absorption



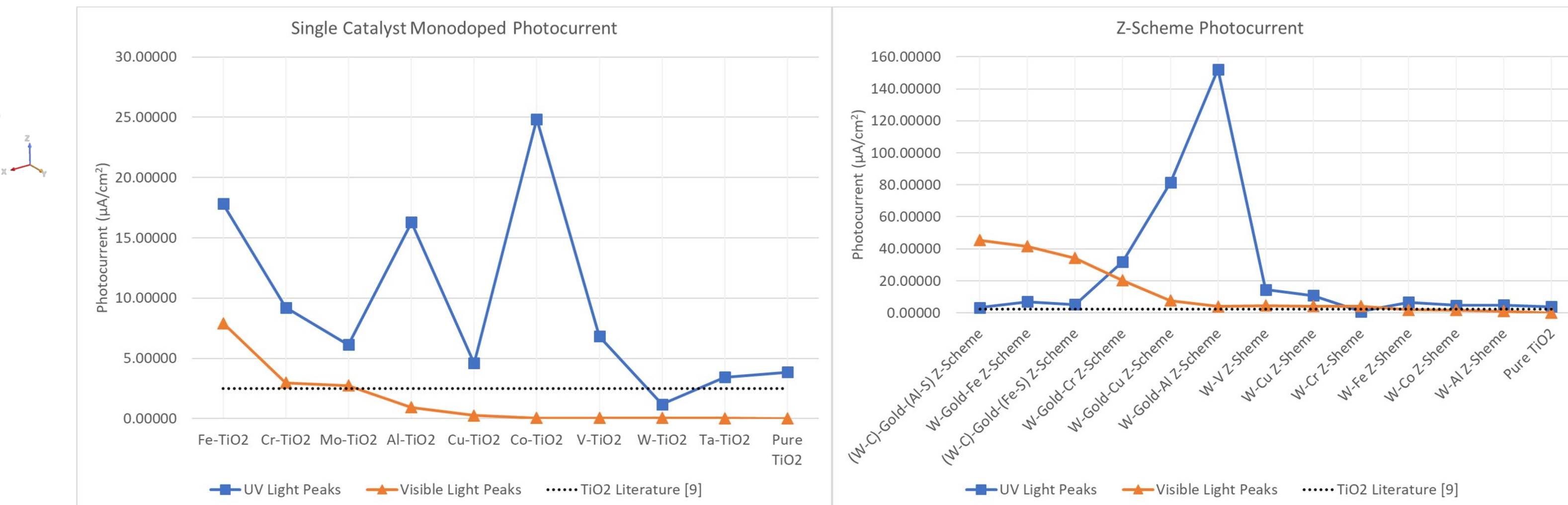


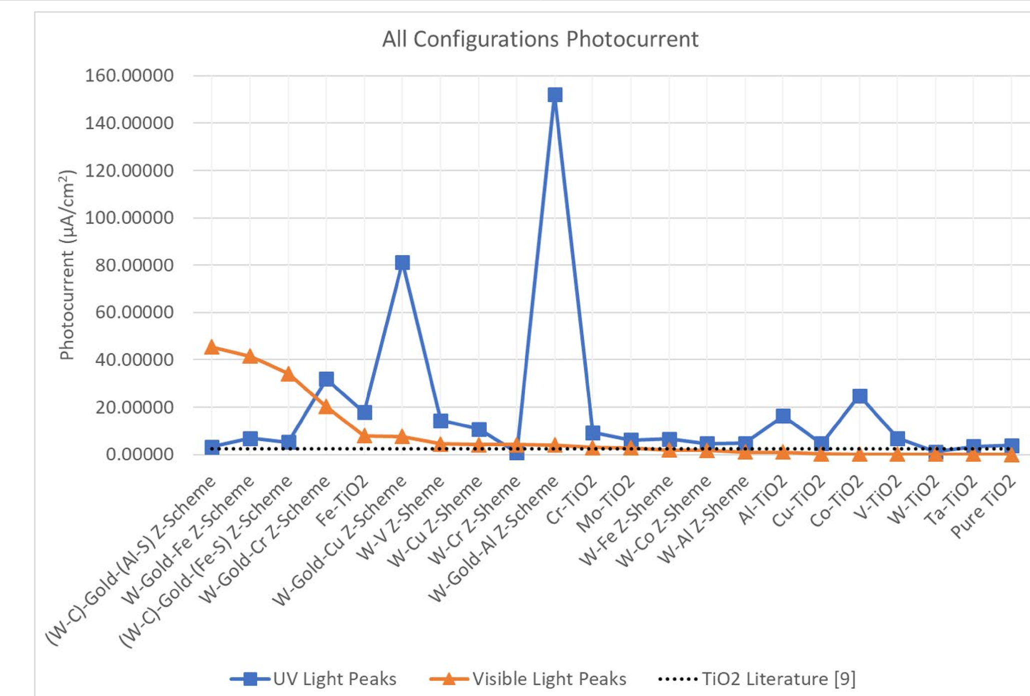
NEGF Results: Photocurrent



Discussion and Conclusions

Photocurrent activation was normalized for comparison by dividing the total photocurrent by the device surface area. Subsequently, each of the materials photocurrent activation was plotted from greatest to least visible light peak output and compared to experimental photocurrent activation of pure TiO_2 reported in literature [9].

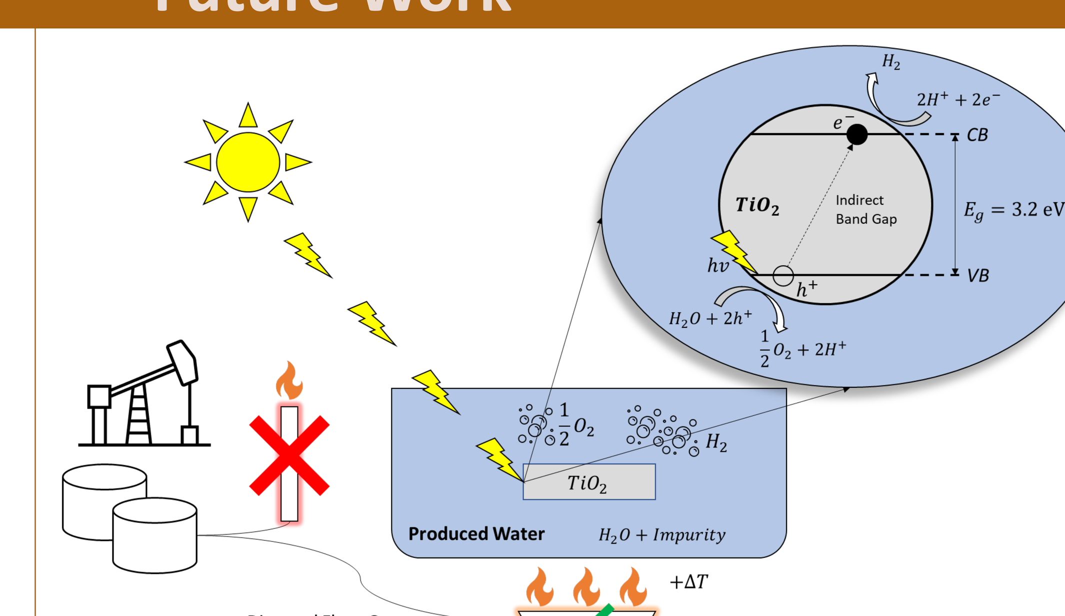




- Z-Scheme configurations with the same base catalyst and gold contact show promise to generate hydrogen without carbon footprint using visible solar light irradiance.
- The study shows that most doped configurations at least facilitate some visible light activation, and generally will increase the UV light activation simultaneously.
- Monodoping with cations or anions result in helpful impurity band zones which contribute to visible light photoactivation
- Both mono/co doping to with transition metal cations and non-metal anions show a strong tendency to increase visible light absorption compared with pure TiO_2.
- Z-Schemes with a gold junction between them yield the highest visible light photo activation inducing a peak shift from UV to visible.

Future Work

- Begin experimental fabrication of proposed Z-Scheme photocatalytic materials.
- Long term goal: Experimentally test the feasibility of lab fabricated photocatalytic materials on local produced water.



References

1. Please consult Table 2.1 from my thesis paper for a list of literature supporting dopant selection.
2. DOE: Hydrogen and Fuel Cell Technologies Office, “Fuel Cells” (2021)
3. C. M. Kalamaras and A. M. Efstathiou, "Hydrogen Production Technologies: Current State and Future Developments," in Conference Papers in Science, 2013.
4. R. Y. Kannah, S. Kavitha, . Preethi, O. P. Karthikeyan, G. Kumar, N. V. Dai-Viet and J. R. Banu, "Techno-economic assessment of various hydrogen production methods - A review.," Bioresource Technology, vol. 319, p. 124175, 2021.
5. US Department of Energy (DOE), The National Renewable Energy Laboratory (NREL), Alliance for Sustainable Energy, LLC (ALLIANCE), “Solar Spectra”, https://www.nrel.gov/grid/solar-resource/spectra.html, 2021.
6. Iowa State University, “Thermal Energy Radiation Spectrum”, http://agron-www.agron.iastate.edu/courses/Agron541/classes/541/lesson09a/9a.3.html , 2021.
7. J. Zhang, P. Zhou, J. Liu and J. Yu, "New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO2," Physical Chemistry Chemical Physics, vol. 16, no. 38, pp. 20382-20386, 2014.
8. Pei, Fei & Wu, Song & Wang, Gang & Xu, Ming & Wang, Songyou & Chen, Liang-Yao & Jia, Yu. (2008). Theoretical Study on the Point Defects in N-Doped Anatase TiO(2). Journal of the Korean Physical Society. 53. 2292-2298. 10.3938/jkps.53.2292.
9. Tan, Furui, et al. “Rough Gold Films as Broadband Absorbers for Plasmonic Enhancement of TiO2 Photocurrent over 400-800 Nm.” Scientific Reports, vol. 6, no. 1, 2016, pp. 33049–33049.