Self-Assembly of Cobaloxime on TiO_2 Nanoparticles for Solar Driven H_2 Production

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Introduction

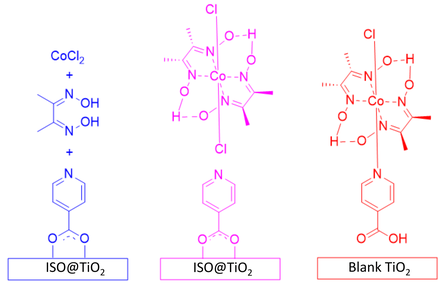
- Photocatalytic evolution of hydrogen gas could be the future of green energy
- Anchoring cobaloxime catalyst on titanium dioxide (TiO_2) has been shown to improve electron transfer[1]
- We investigate the effects of anchoring isonicotinic acid (ISO) on TiO_2 with regard to the self assembly of catalyst on the semiconductor surface

Research Questions

- Does pre-functionalization of TiO_2 allow for self-assembly of cobaloxime on the surface without the need for full synthesis?
- Does adding all the components of the cobaloxime catalyst on to a solution and stirring lead to the formation of an effective catalytic system?
- Does additional mixing time improve catalytic activity?

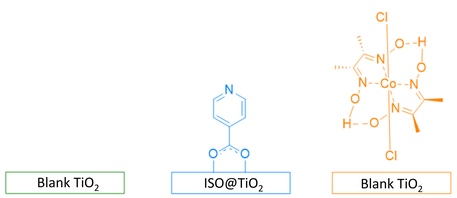
Catalyst Structures

Experiment 1 – Stirred 1hr



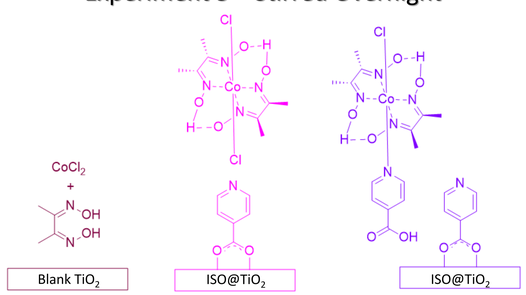
Smp 1 | Smp 2 | Smp 3

Experiment 2 - Controls



Smp 4 | Smp 5 | Smp 6

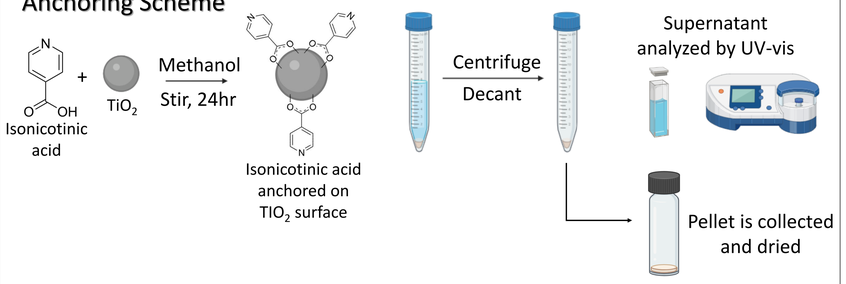
Experiment 3 – Stirred Overnight



Smp 7 | Smp 8 | Smp 9

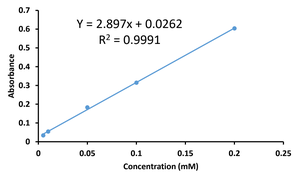
Assembly of ISO on TiO_2 and Loading Determination

Anchoring Scheme



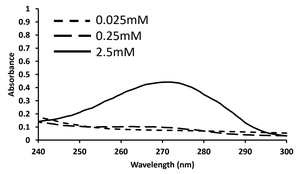
Isonicotinic Acid Calibration

Sample #	ISO Conc.	TiO_2 mass	nmol ISO/ mg TiO_2
Sample 1	0.025mM	100mg	2.234
Sample 2	0.25mM	100mg	24.07
Sample 3	2.5mM	100mg	120.1



UV-vis of Supernatant

- Beer's Law: A = εbc
  Used to calculate [ISO] remaining in supernatant
- *2.5mM ISO sample was diluted 10x to be able to use Beer's law

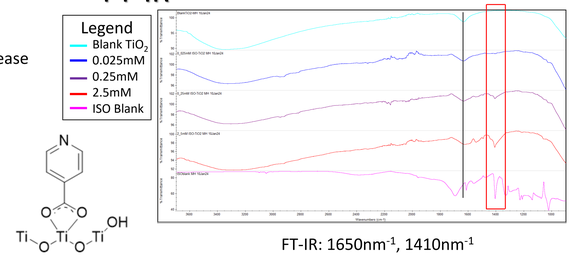


Characterizations

FT-IR

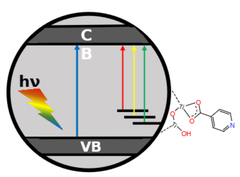
The peak at 1410nm^{-1} shows the increase in loading with each increase in concentration

Key peaks:
- TiO_2 C-O bond stretching
- Aromatic C=C stretching

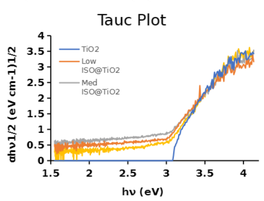


FT-IR: 1650nm^{-1}, 1410nm^{-1}

Diffuse Reflectance Spectroscopy



Interfacial Surface Complex between ISO & TiO_2



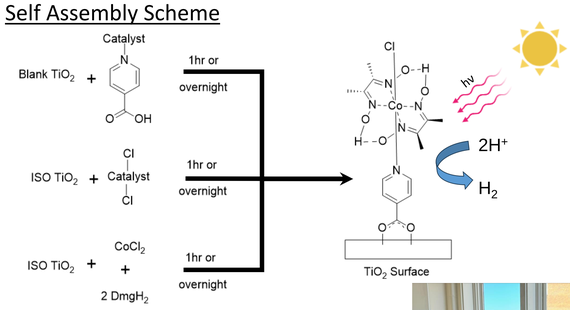
The conjugation of the aromatic rings create the different band gaps shown above

Conclusions

- Stirring overnight increases self-assembly of catalyst on the TiO_2 surface.
- Time and effort needed to synthesize cobaloxime catalysts can be reduced by loading TiO_2 beforehand and then adding in catalyst to stir.
- Many steps could be made to optimize conditions regarding ideal amount of catalyst, type of sacrificial electron donor, solvent, etc.

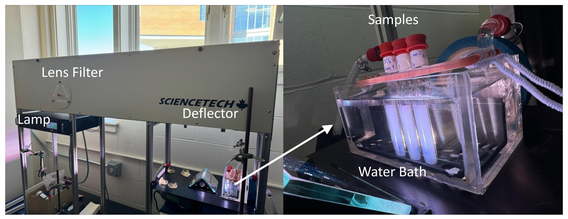
Catalyst Self Assembly and Photocatalysis

Self Assembly Scheme



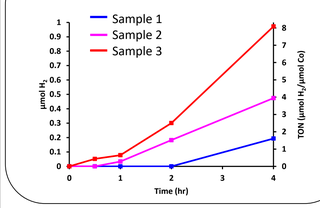
- Ultraviolet light excites two electrons that are used to reduce hydrogen
- Evolution Equation: $2H^+ + 2e^- \leftrightarrow H_2$
- Hydrogen gas can be burned for clean energy

- Ultraviolet lamp that irradiates our sample for photocatalysis (Left)
- Water bath to keep samples a set temperature during the experiment (Right)



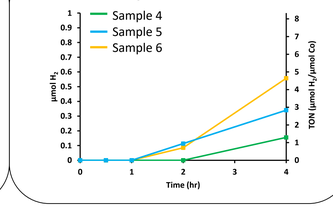
Catalysis data

Experiment 1



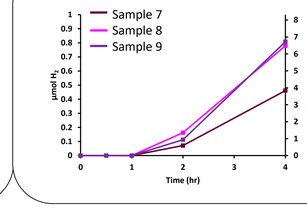
- Fully synthesized catalyst was most efficient

Experiment 2

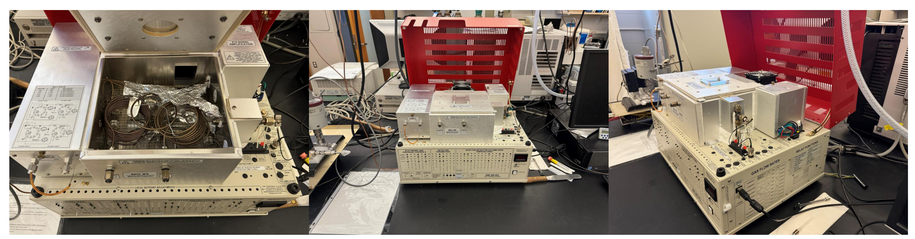


- Activity of TiO_2 decreases with loading of ISO

Experiment 3



- Sample 8 increases with stirring overnight
- Sample 8 reaches 83% activity of fully synthesized catalyst



Reaction Conditions:
Performed in 10:90 TEOA in H_2O Solution
pH ~8
Ultraviolet radiation was ≥300nm
AM 1.5G

SRI 8610C Gas Chromatograph
Packed GC column with argon flow

References and Acknowledgements

References:
[1] Gong, L.; Yin, H.; Nie, C.; Sun, X.; Wang, X.; Wang, M. Influence of Anchoring Groups on the Charge Transfer and Performance of P-Si/TiO2/Cobaloxime Hybrid Photocathodes for Photoelectrochemical H2 Production. ACS Applied Materials & Interfaces 2019, 11 (37), 34010–34019. https://doi.org/10.1021/acsami.9b12182.

Acknowledgements:
Dr. Christine Caputo (UNH)
Charles Wilson (UNH)