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

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Introduction

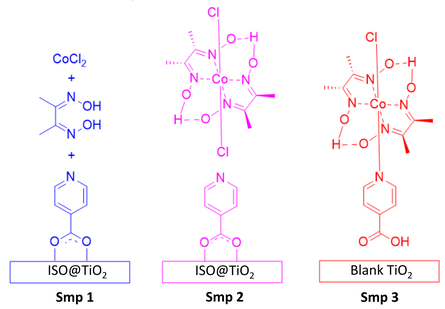
- Photocatalytic evolution of hydrogen gas could be the future of green energy
- Anchoring cobaloxime catalyst on titanium dioxide (TiO_2) has been shown to improve electron transfer[1]
- We investigate the effects of anchoring isonicotinic acid (ISO) on TiO_2 regarding the self assembly of catalyst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

Research Questions

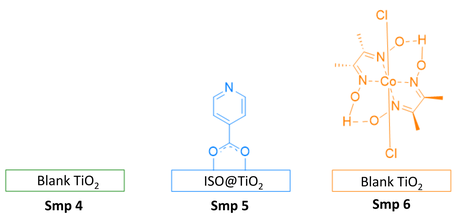
- Does pre-functionalization of TiO_2 allow for self-assembly of cobaloxime on the surface without the need for full synthesis?
- Does adding all the components of the cobaloxime catalyst on to a solution and stirring lead to the formation of an effective catalytic system?
- Does additional mixing time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

Catalyst Structures

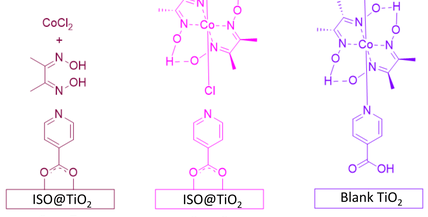
Experiment 1 – 1hr Stir



Experiment 2 - Controls

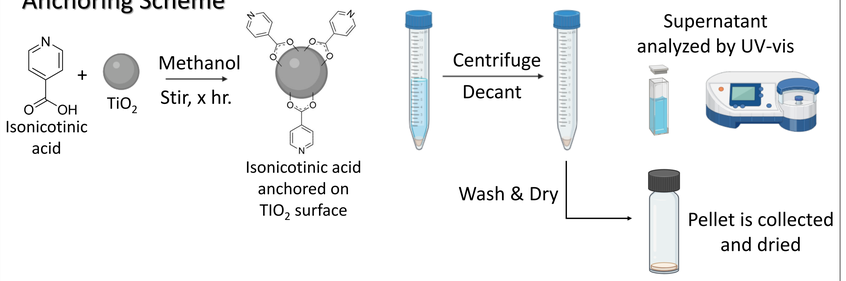


Experiment 3 – 24hr Stir



Assembly of ISO on TiO_2 and Loading Determination

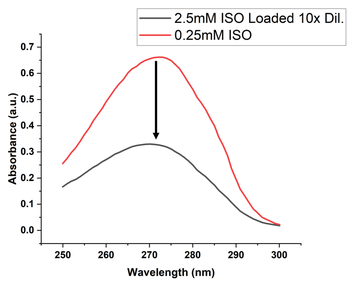
Anchoring Scheme



Loading Data and UV-Vis Analysis

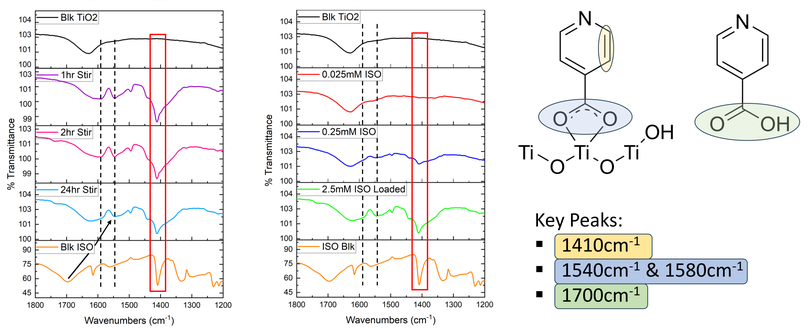
ISO Conc.	Stir Time	Amount of TiO_2	nmol ISO/ mg TiO_2	% Loaded
0.25mM	1hr	100mg	21.5	86.0
2.5mM	1hr	100mg	96.1	38.4
0.25mM	2hr	100mg	21.9	87.6
2.5mM	2hr	100mg	88.7	35.5
0.025mM	24hr	100mg	2.5*	~100
0.25mM	24hr	100mg	25*	~100
2.5mM	24hr	100mg	130	53.9

*UV-vis analysis of supernatant showed no absorbance peak so full loading of ISO was assumed



Characterizations

FT-IR



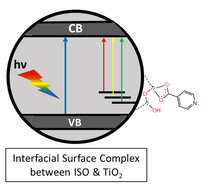
*ISO loading concentration of samples were 2.5mM

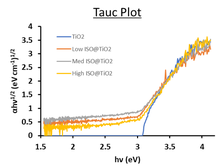
*Each sample was stirred for 24hr

Key Peaks:

- 1410cm^{-1}
- 1540cm^{-1} & 1580cm^{-1}
- 1700cm^{-1}

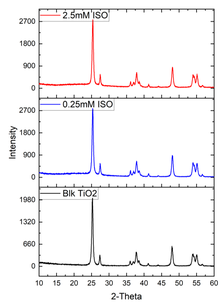
Diffuse Reflectance Spectroscopy





- Surface functionalization create midgap states that absorb lower energy photons
- Absorption of lower energy light is shown in rising of Urbach tail

X-Ray Diffraction Spectroscopy



- No TiO_2 crystal structure change
- No Isonicotinic acid crystallization

References and Acknowledgments

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.
[2] 1. Lakadamyali, F. & Reisner, E. Photocatalytic H2 evolution from neutral water with a molecular cobalt catalyst on a dye-sensitised TiO2 nanoparticle. Chem. Commun. 47, 1695–1697 (2011).

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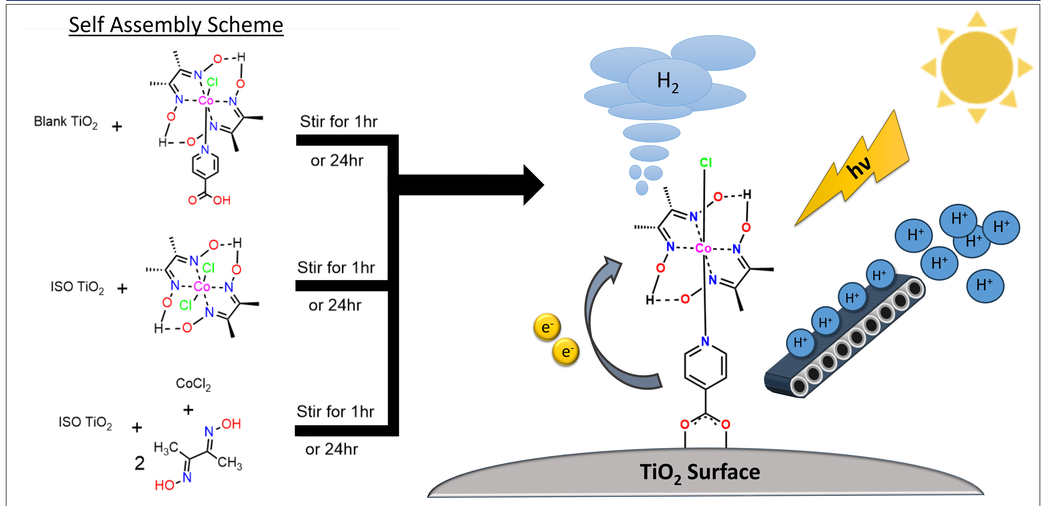
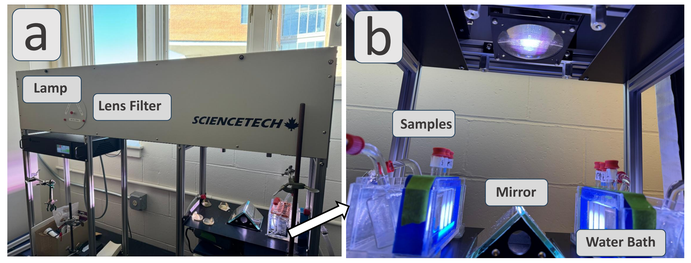
Catalyst Self Assembly and Photocatalysis

Self Assembly Scheme





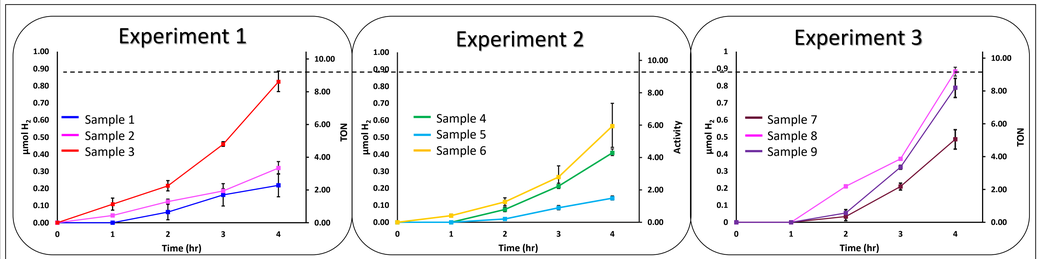
a) Xe lamp that irradiates our sample for photocatalysis (100mW/cm^2 = 1 Sun)

b) Water bath to keep samples a set temperature during experiment (25 ˚C)

Reaction Conditions:
Performed in 10:90 TEOA in DI H_2O Solution
pH ~7 with N_2 headspace
Stirred vigorously under ultraviolet radiation ≥300nm AM 1.5G

SRI 8610C Gas Chromatograph
Packed molesieve column
Argon carrier gas with TCD detector

Catalysis data



- Fully synthesized catalyst was most efficient
- Activity of TiO_2 decreases with loading of ISO
- Cobalt catalyst precursor caught up to full catalyst

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 precursor to stir.
- Many steps could be made to optimize conditions regarding ideal amount of catalyst, optimization of loading process, ideal solvent, etc.