Optimization of Anchoring Isonicotinic acid on TiO_2 NP for Applications in Dye Sensitized Photocatalysis

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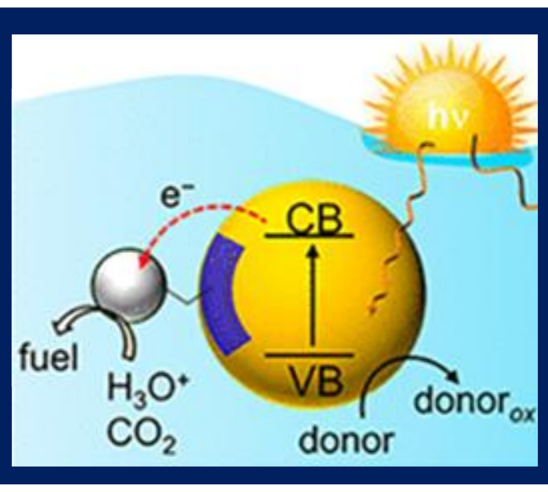


Introduction

Though Dye Sensitized Photocatalysis (DSP) is a rapidly expanding field of research in green chemistry, its applications are limited, which is in part due to the cost-prohibitive nature of the methods currently available. The complex synthetic schemes require skilled chemists and a significant time investment to synthesize, characterize and isolate the catalysts used.

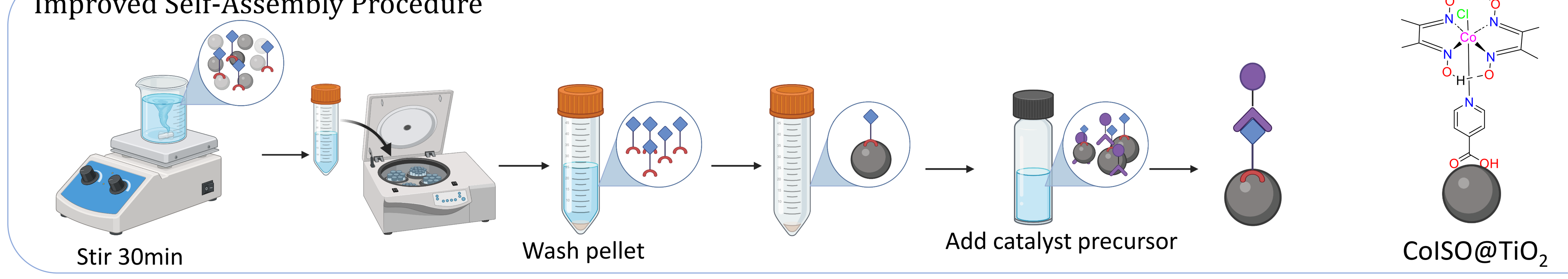
To simplify the process, and decrease costs, we propose to test if pre-anchoring of the axial ligand of a H_2 generating catalyst to TiO_2 will allow catalyst self-assembly on the surface.

Research Questions

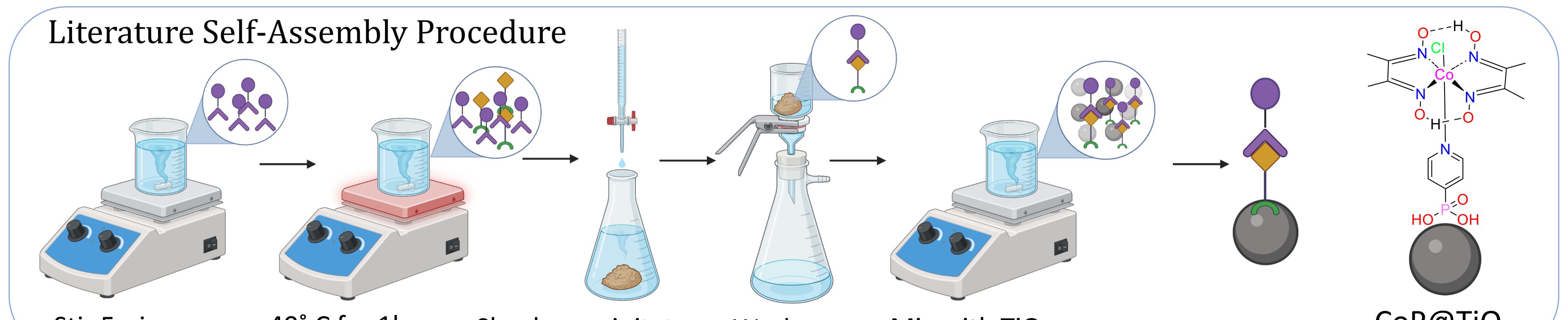
1) Can we optimize iso-nicotinic acid (ISO) loading to maximize catalyst self-assembly on TiO_2?
2) Is this method a significantly cheaper alternative to anchoring a pre-assembled cobaloxime (Co(dmg)$_2$(ISO)Cl)?

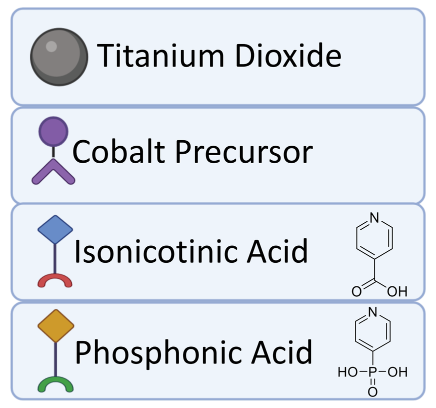
Experimental

Improved Self-Assembly Procedure

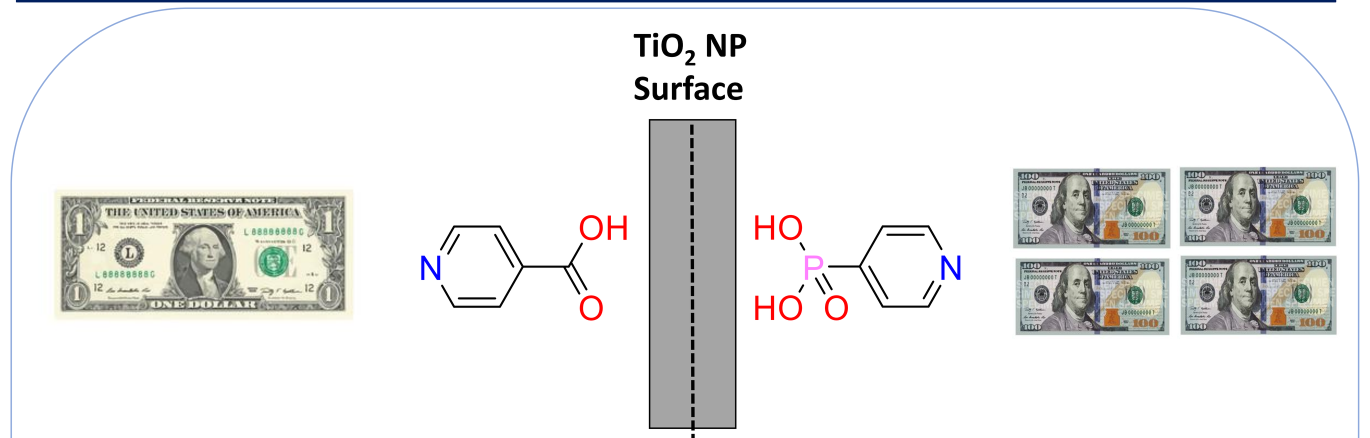


Literature Self-Assembly Procedure





Cost Analysis



Isonicotinic Acid

Substance	Amount used (g)	Cost ($)
TiO_2	0.1	0.00028
ISO	0.000025	4.13E-08
Co(dmg)$_2$Cl$_2$	0.00436	0.12
Phosphonic acid	0	0
Cost per 100mg	-	0.0012
Cost per umol H_2	-	2.70E-05

Optimized

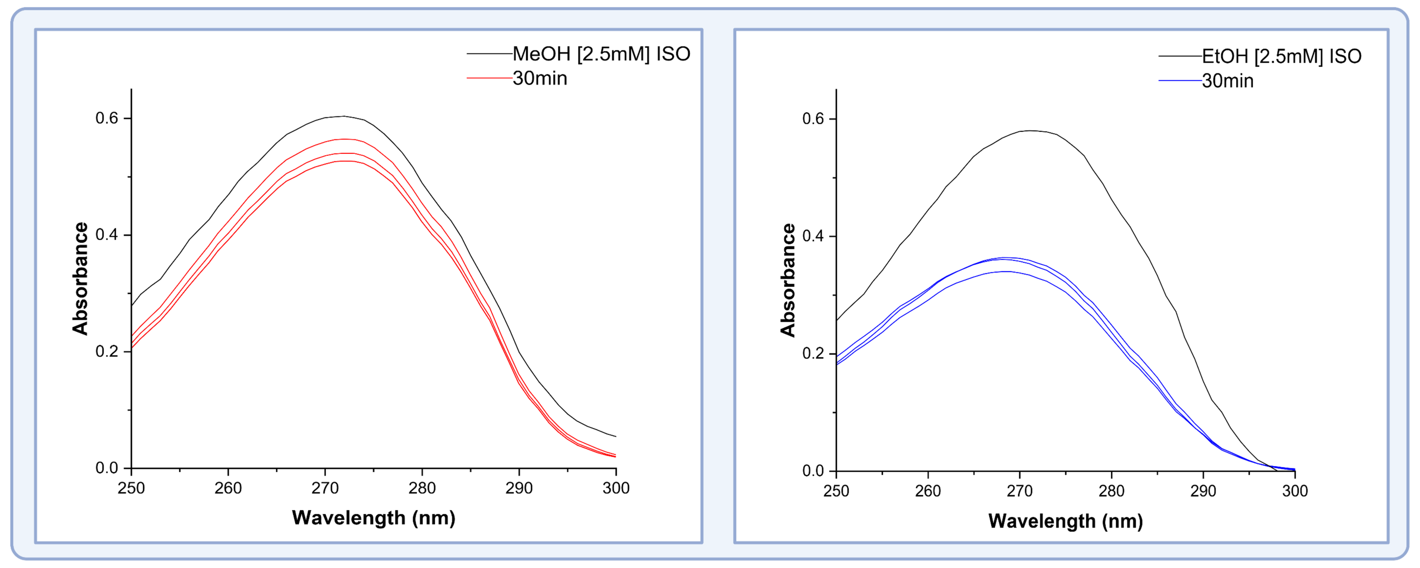
Phosphonic Acid

Substance	Amount used (g)	Cost ($)
TiO_2	0.1	0.00028
ISO	0	0
Co(dmg)$_2$Cl$_2$	0.054	1.51
Phosphonic acid	0.024	6.76
Cost per 100mg	-	1.3
Cost per umol H_2	-	0.011

Literature

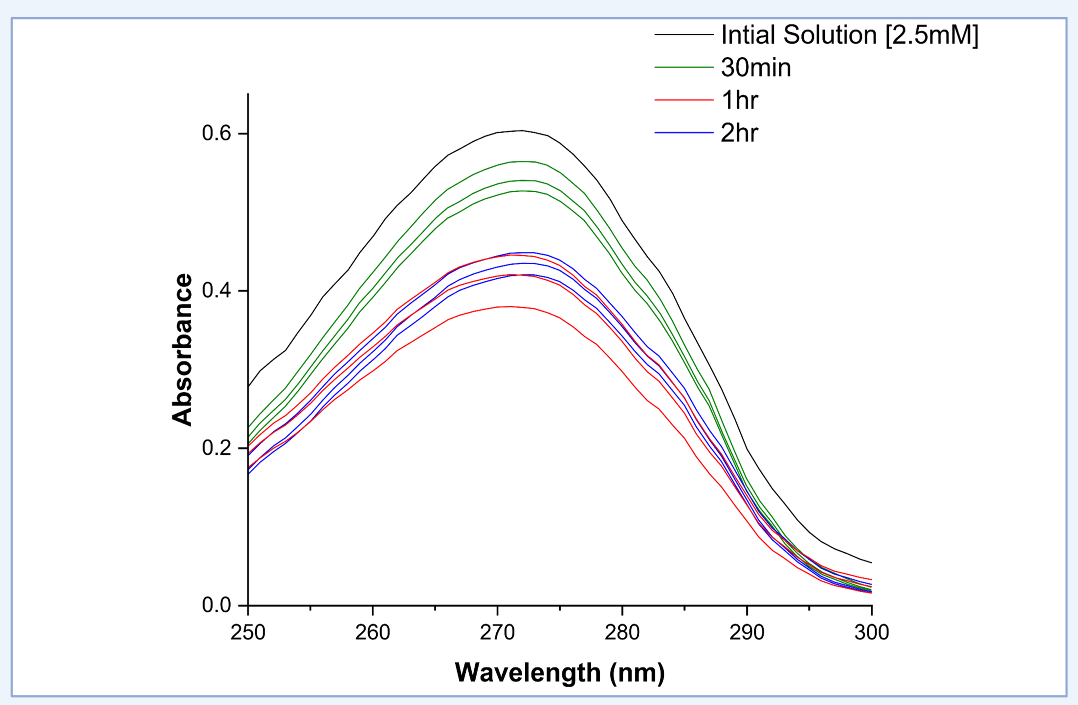
Results

Effect of Solvent on Loading % of ISO



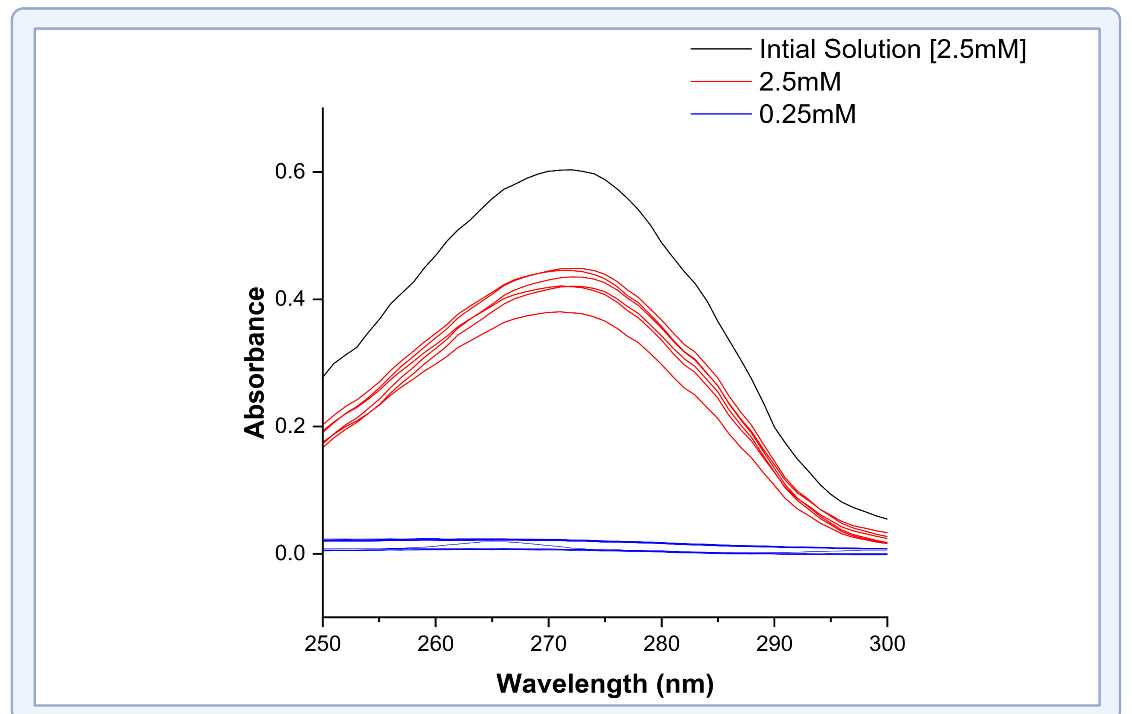
Solvent	Amount Loaded (nmol/mg TiO_2)	Std Dev	% Loaded
EtOH	109.51	6.45	43.84%
MeOH	49.17	7.09	19.76%

Effect of Loading Time on Loading % of ISO



Stir Time (hr)	Average (nmol/mg TiO_2)	Std Dev	% Loaded
2	88.70	5.76	35.94%
1	96.07	12.06	38.75%
0.5	49.17	7.09	19.76%

Effect of ISO Concentration on Loading % of ISO



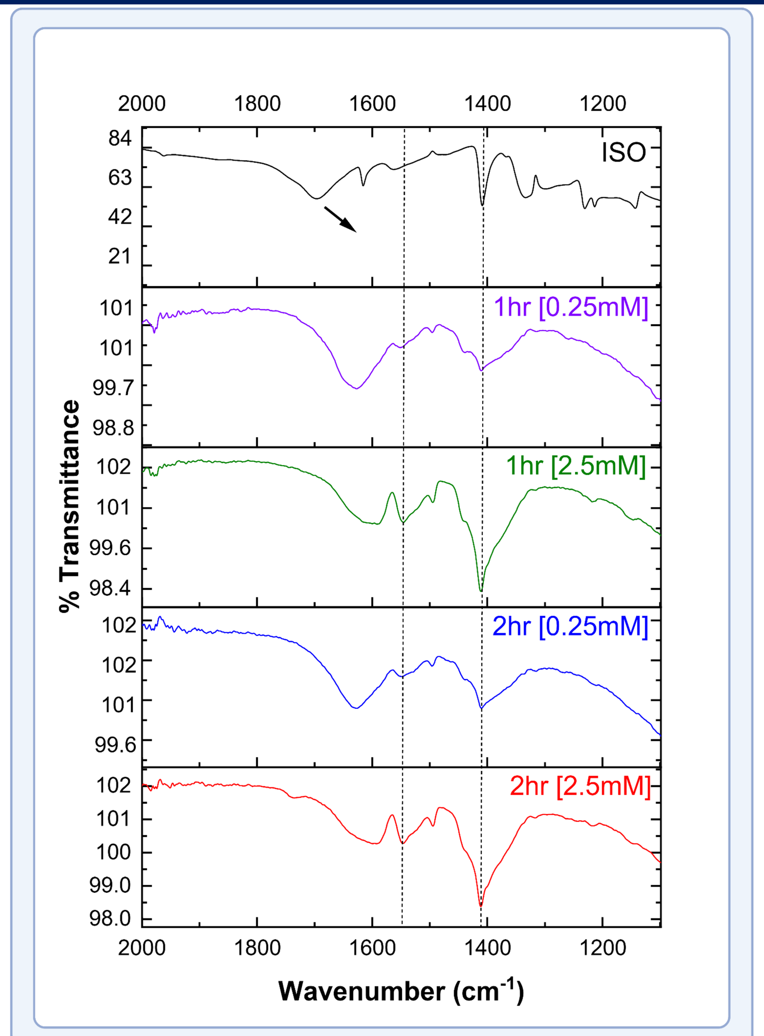
Concentration (mM)	Average nmol/mg TiO_2 Loaded	Standard Deviation
0.25	21.94	0.05
2.5	88.70	5.76

Characterization Methods

Infrared Spectroscopy

ATR-FTIR is used to ensure that ISO is loaded onto the surface.

Peak at 1408cm^{-1} is the symmetric stretching peak of a CO double bond. Peak at 1550cm^{-1} is asymmetric stretching of the CO double bond and confirms ISO loading



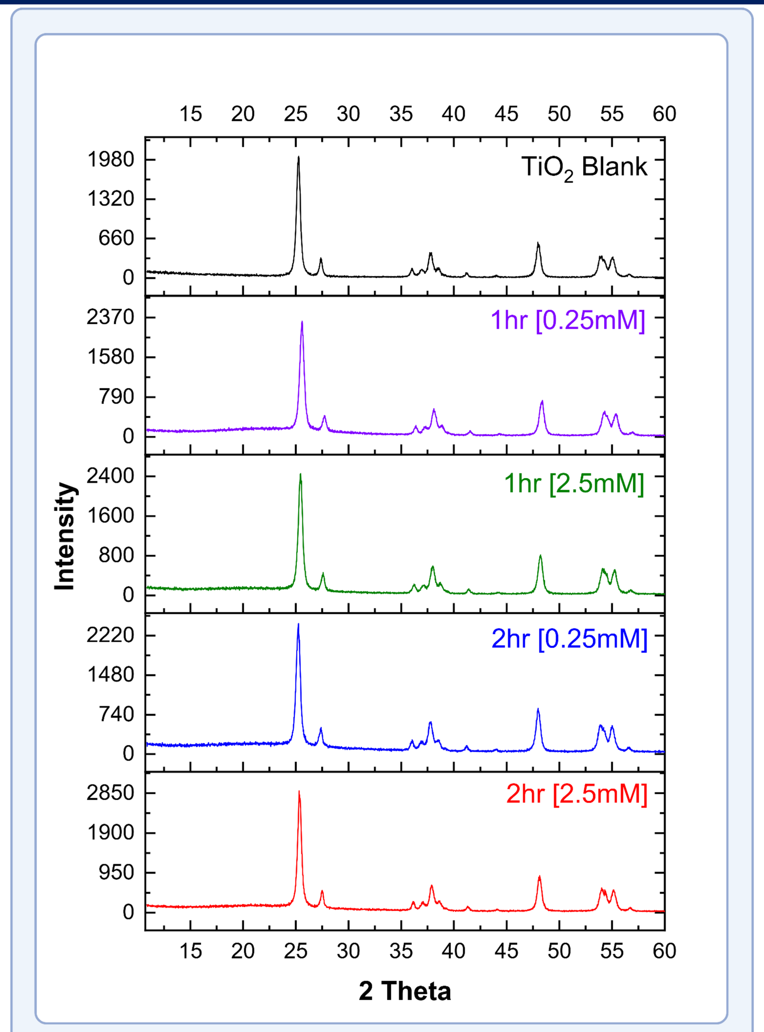
X-ray Diffraction

This data is used to assess the crystal structure of the loaded TiO_2 to blank TiO_2.

The mixture of TiO_2 used is a unique ratio of rutile and anatase phase titanium called P25.

This confirms that loading the ISO does not alter the crystallinity of the TiO_2 nanoparticles.

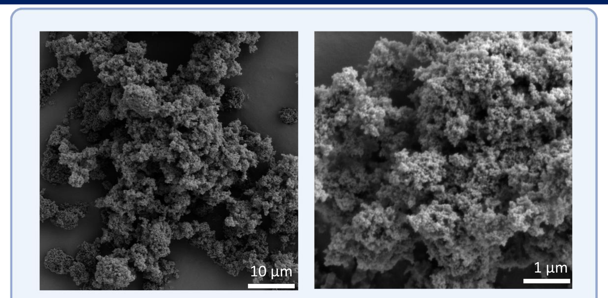
Scanned from 10-60 2Θ (°) at 1.5 °/min



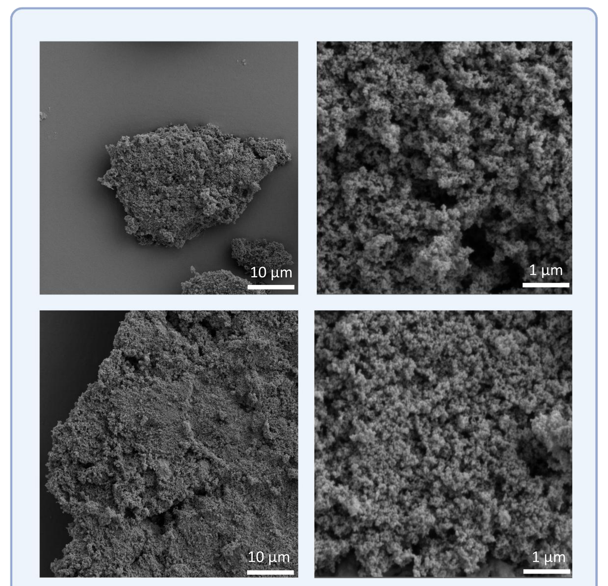
SEM

This technique is used to examine the morphology of TiO_2. The original structure is mesoporous and should not be altered by loading ISO to the surface.

These images confirm preservation of TiO_2 morphology when TiO_2 is loaded with [2.5mM] ISO conditions.



Blank TiO_2



ISO@TiO_2

Conclusions

The pre-anchoring of Isonicotinic acid to TiO_2 and allowing Co(dmg)$_2$Cl$_2$ to self-anchor is effective and is a significantly cheaper alternative to anchoring a pre-assembled of Co(dmg)$_2$(ISO)Cl. This method decreases the total material cost to produce a micromole of hydrogen gas 400-fold.

Green energy will continue to be an unsolved problem if it cannot become affordable. This work demonstrates a creative strategy to minimize costs while maintaining the similar efficiency.

Acknowledgements

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References

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