Surface Functionalization of Titanium Dioxide Nanoparticles For Enhanced Interaction with a Guest-Functionalized Catalyst

Tim Murphy, Charles Wilson, Dylan Stolba, Christine A. Caputo*
Department of Chemistry, University of New Hampshire, Durham, NH 03824

Introduction

In the fight against climate change, many energy alternatives have been explored to reduce carbon emissions and continue to produce the energy we need to thrive. Solar photocatalysis is one such avenue, primarily in the production of clean fuels like hydrogen, which can be burned whilst avoiding carbon dioxide generation. One method to generate H_2 exploits electron transfer from a light-absorbing photosensitizer to a proton reducing transition-metal complex.

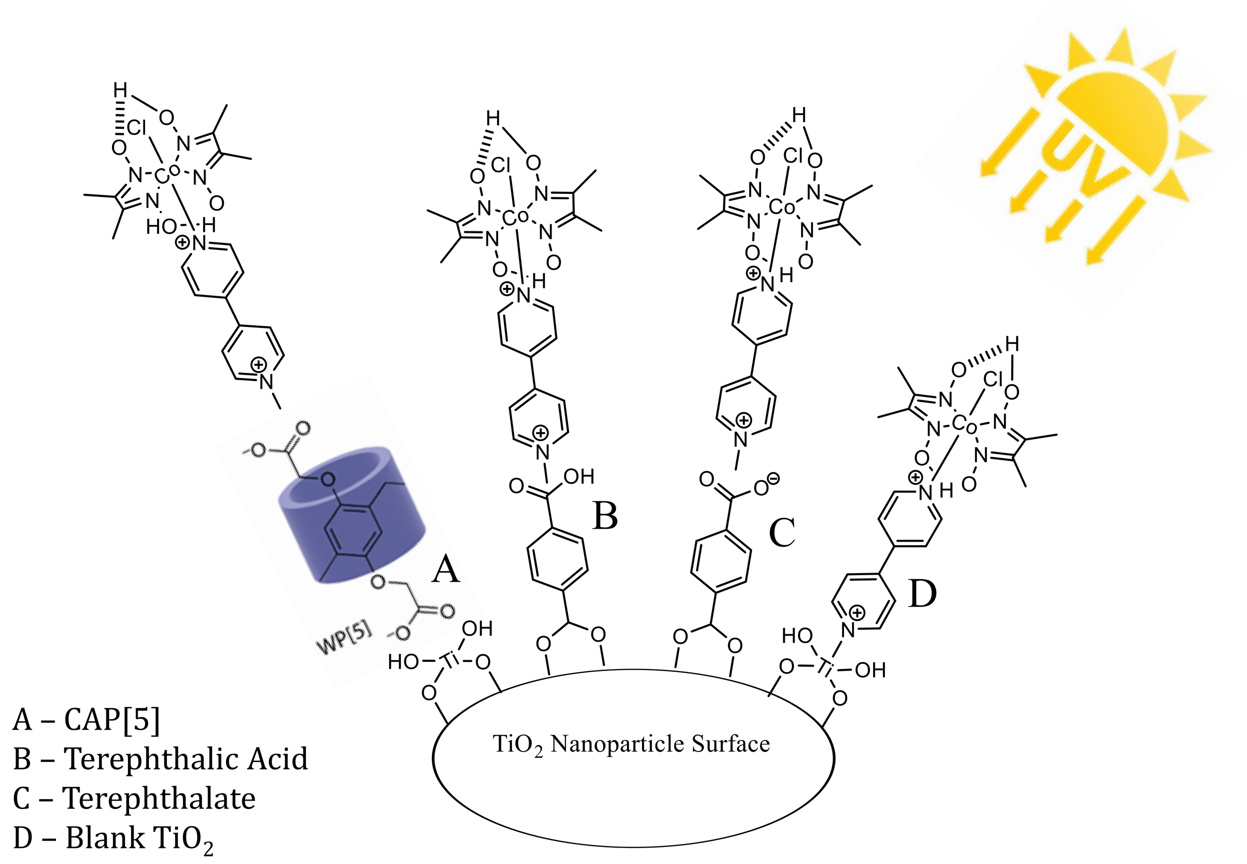
In the Caputo Group, Titanium Dioxide (TiO_2), a semi-conducting nanoparticle, is the chosen photosensitizer for surface functionalization. Previously, a macrocyclic carboxylic acid-functionalized pillar[5]arene (CAP[5]) has been loaded onto TiO_2 to test host-guest self assembly with a guest-functionalized cobaloxime hydrogen generation catalyst. CAP[5] is formed through a multi-step synthetic route, which raised the question of whether the anchoring of commercially available, non-macrocyclic compounds might lead to similar non-covalent interactions, and ultimately result in a similar catalytic activity.

Research Question:

Will surface functionalization with terephthalic acid promote non-covalent interactions with bipyridinium-functionalized cobaloxime catalysts?

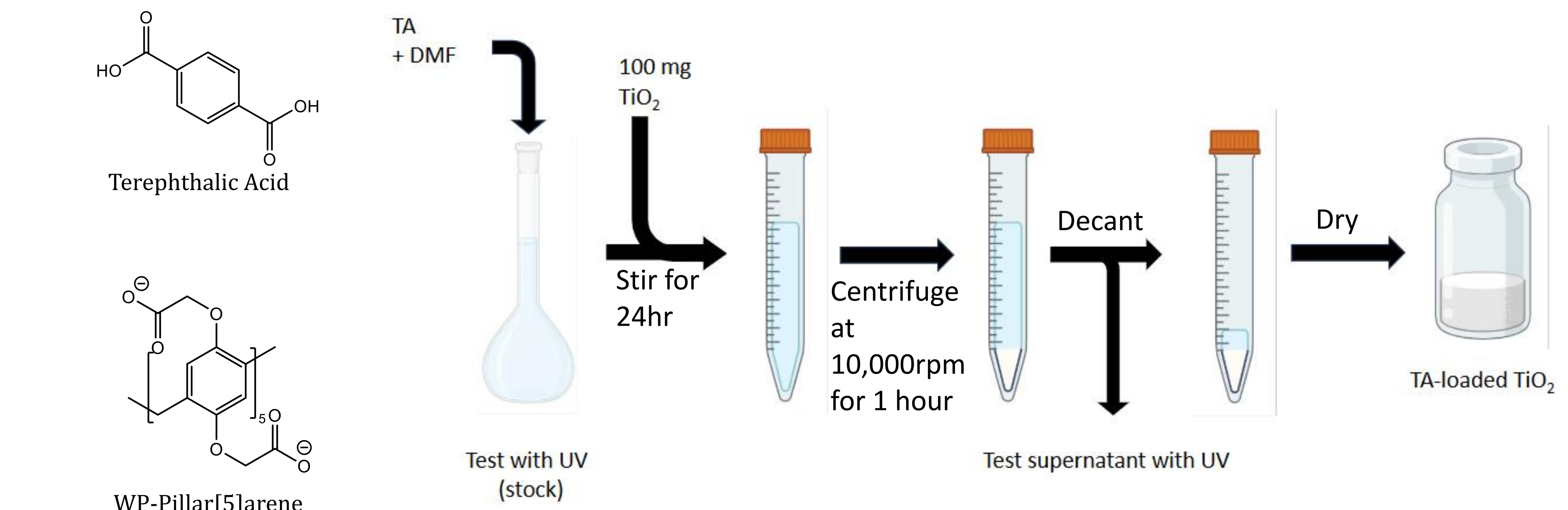
Hypothesis

Commercially available terephthalic acid can promote non-covalent π-π stacking and electrostatic interactions with bipyridinium cobaloxime. A similar TiO_2 surface loading and hydrogen generation is possible when compared to threading with CAP[5].



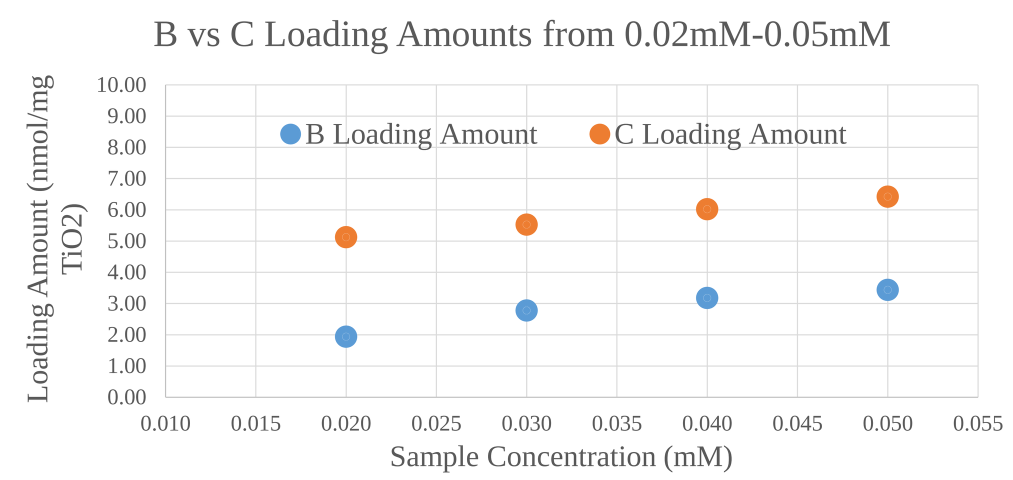
A – CAP[5]
B – Terephthalic Acid
C – Terephthalate
D – Blank TiO_2

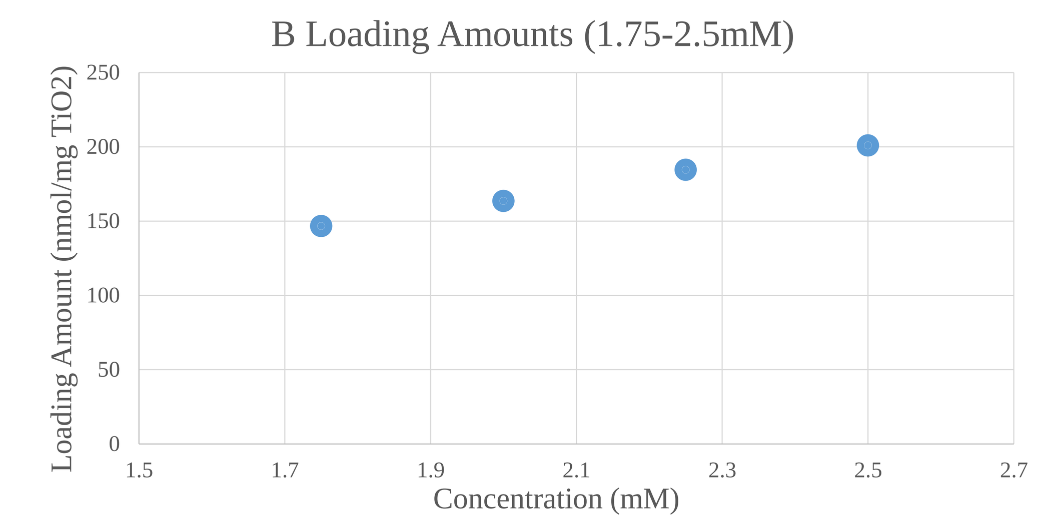
General TiO_2 Loading Procedure

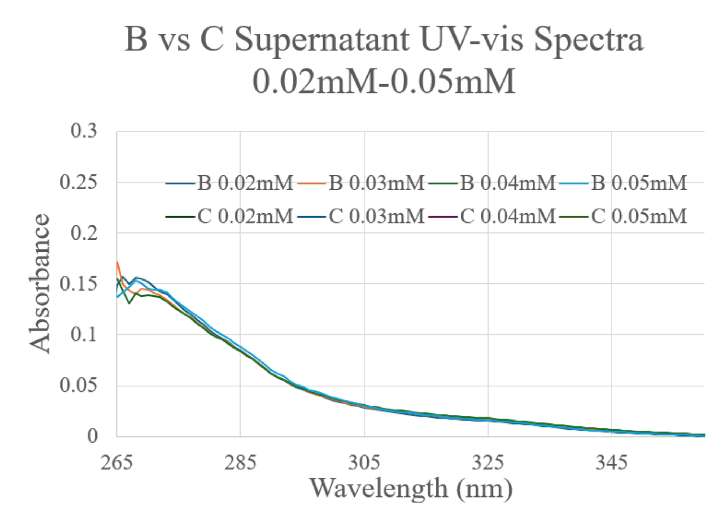


General procedure for TiO_2 loading

Terephthalic Acid (B) Loading vs Terephthalate (C) Loading





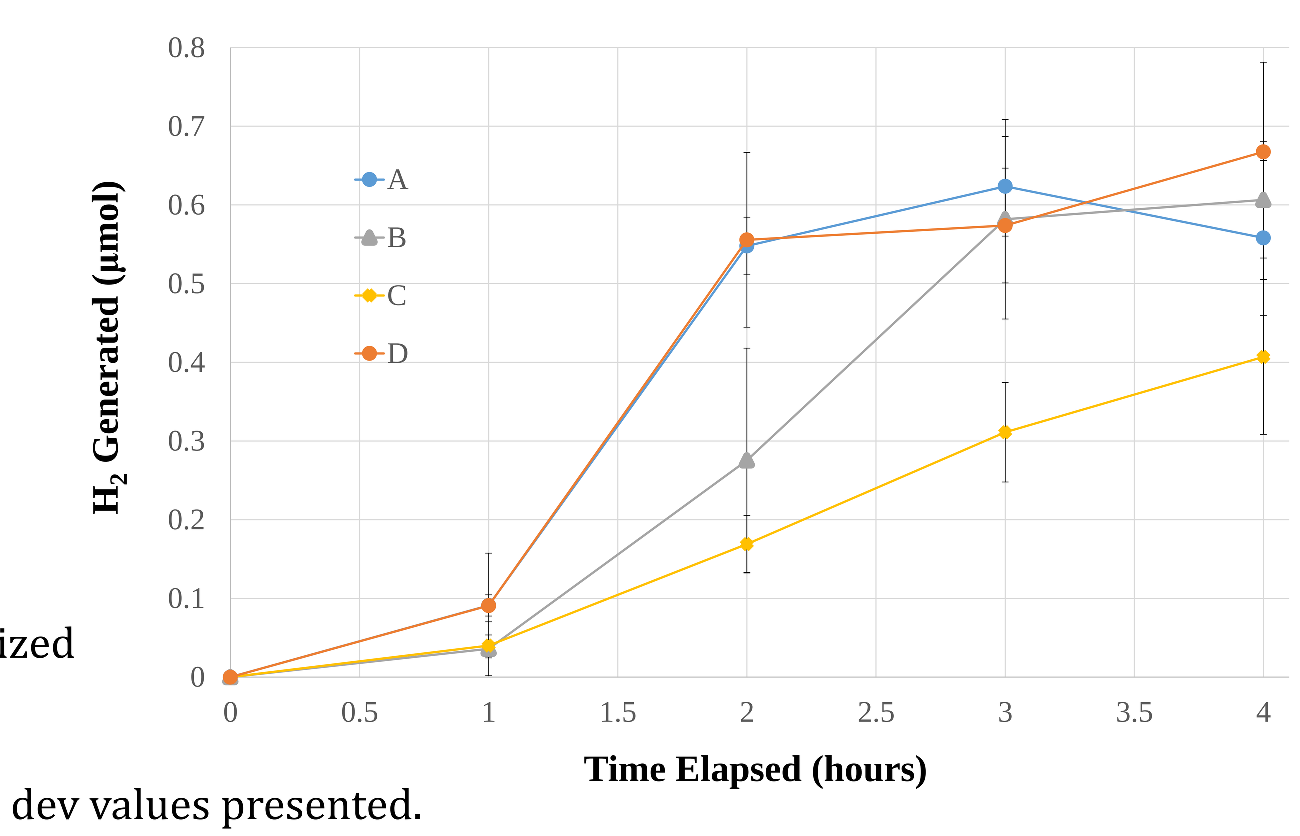


Sample	Loading using 0.25mM solution (nmol/mg TiO_2)
A	24.5
B	20.7±5.56
C	19.6±0.857

Photocatalytic H_2 Generation from A, B, C, and D at 0.25mM

Sample	TON_{4h} (mol H_2/mol Co)	TOF
A	3±0.074	0.75
B	3±0.166	0.75
C	2±0.098	0.5
D	4±0.114	1

Photocatalysis Conditions:
SRI 8610C Gas Chromatograph, Mol. Sieve Column
Argon Carrier Gas with TCD Detector
Stirred under UV radiation ≥300nm AM 1.5G
All solutions prepared with 1 mg surface functionalized TiO_2 in 4 mL of 10% v/v H_2O:TEOA.
Catalyst concentration was 0.2 µM in 4 mL solution
Experiments were run in triplicate. Average and std dev values presented.



Discussion

1. Samples B and C are both capable of photocatalytic H_2 generation via guest-functionalized catalyst.
2. Sample C gave a higher loading Sample B, on average, however it produced lower H_2 generation, implying that terephthalate may have a lower maximum loading amount that is viable for photocatalysis
3. Photocatalytic results showed similar H_2 generation for all 4 samples at the loading levels obtained. More concentrated loading solutions are needed to increase the loading since this is most likely due to the catalyst simply being reduced by bare TiO_2 (likely that the loaded compounds were present at levels below monolayer coverage).

Future Work

1. Determine the optimal loading concentrations for B and C on TiO_2 needed to achieve monolayer coverage on the surface.
2. Test the dependence of the photocatalytic hydrogen generation on the loading of A, B, and C.
3. Test the dependence of the hydrogen generation on the concentration of catalyst used.
4. Test photocatalytic stability by pushing the system longer than 4 hours.
5. Attempt generation of other products using different guest-functionalized catalysts

Acknowledgements

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References

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