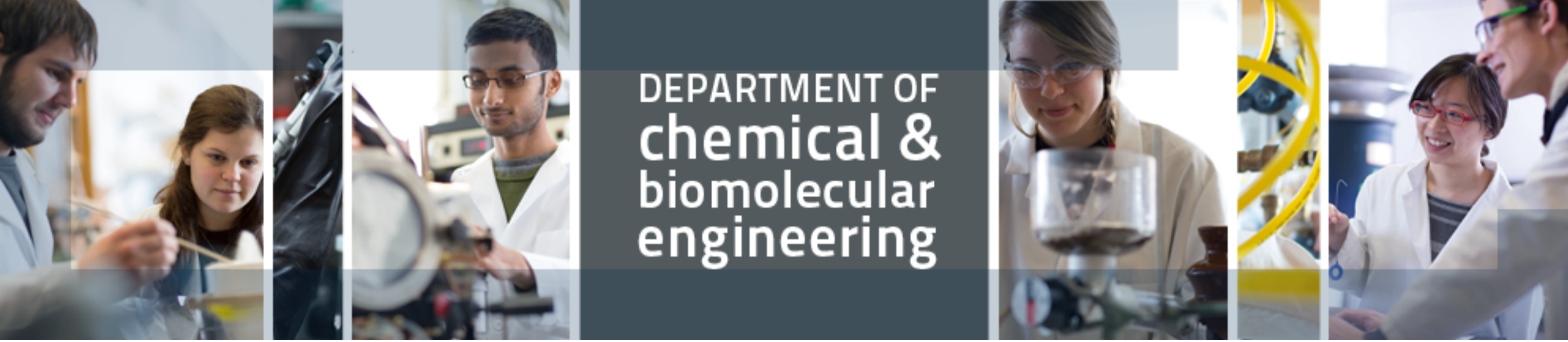


Self-Assembled Polyproline II Peptide Monolayers on Iron(III) Oxide

Chuck Loney,
PI: Dr. Julie Renner

old title: Enhanced Electrochemical Ammonia Production via Peptide-Bound Metal

October 31st, 2018
2018 Annual AIChE Meeting – NH_3 Fuel Association
Pittsburgh, PA

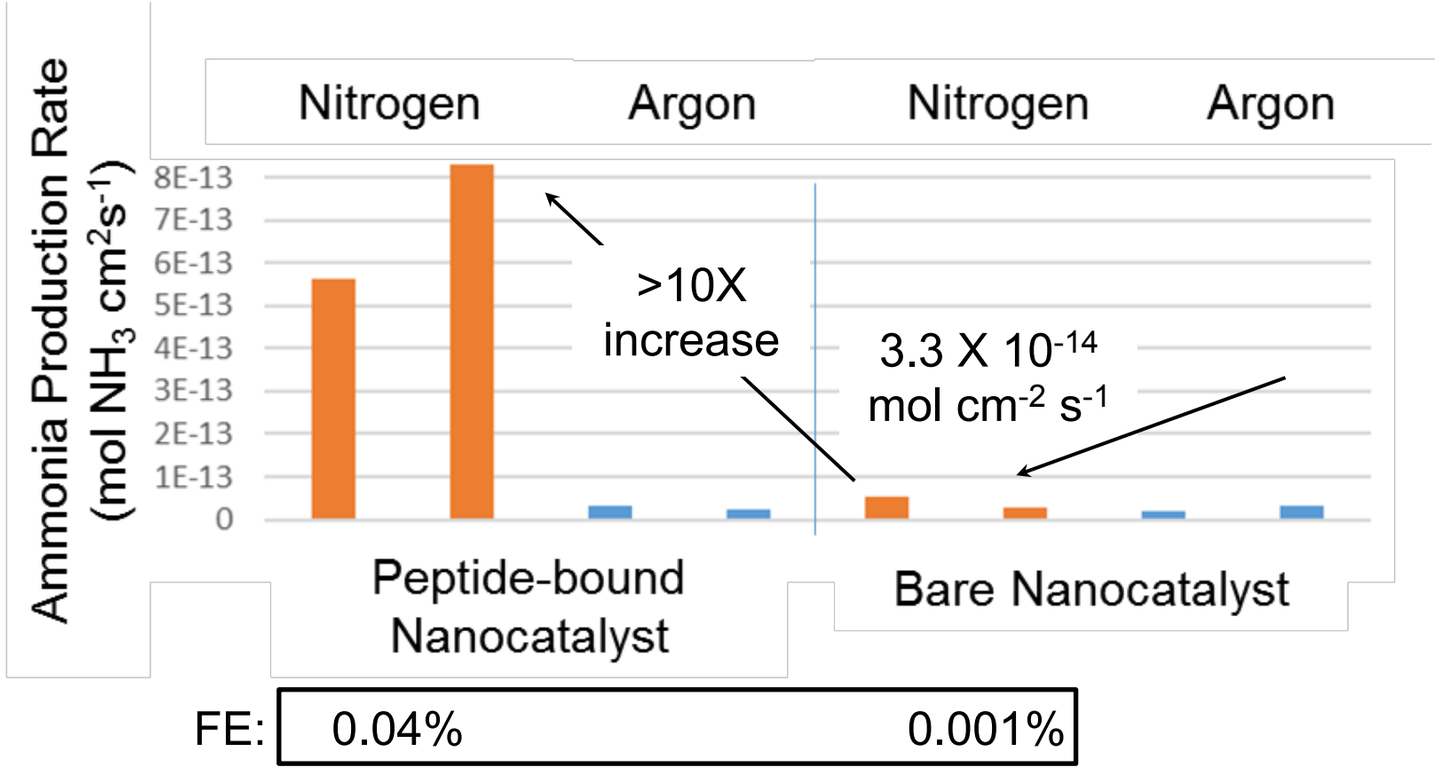
18AIChE
Annual Meeting, Pittsburgh, PA

CASE WESTERN RESERVE UNIVERSITY EST. 1826

NH3 FUEL ASSOCIATION

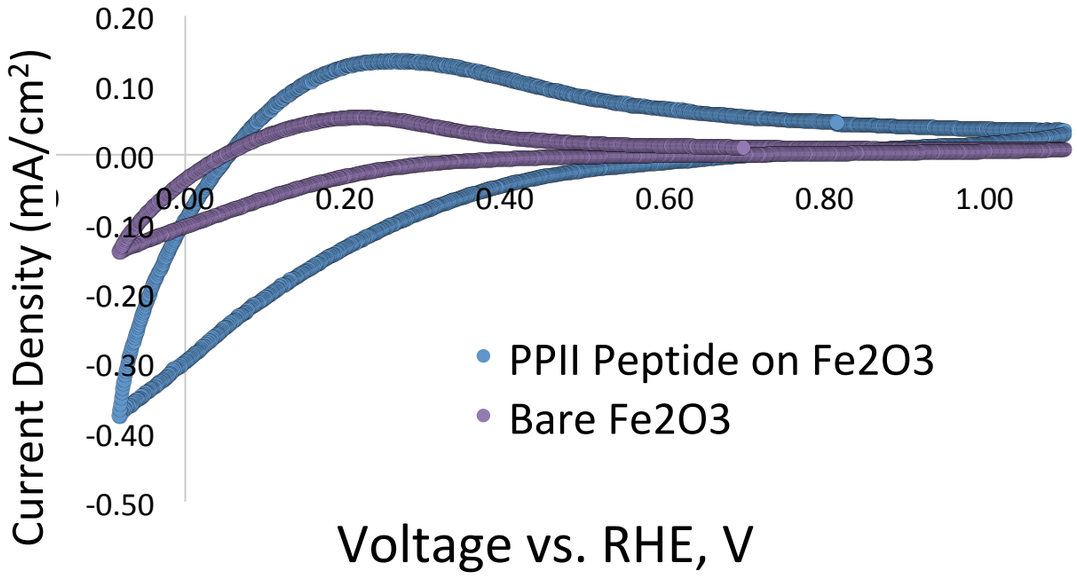
Last Time: PPII Peptide on Fe_2O_3 to Synthesize NH_3 via Electrolysis

- Solid-state electrolyzer: PPII peptide on iron(III) oxide had quantifiable, 10X increase in ammonia compared to controls.



FE:	0.04%	0.001%

- Liquid electrolyzer: The PPII incubated Fe_2O_3 had consistently higher current densities than the control Fe_2O_3 nanoparticles.



3 hour of operation at -2.5 V; IrOx CE; 50°C

20 mV/s; WE is C cloth, spraycoated; CE is graphite; RE is Ag/AgCl; 1 M NaOH; 50°C

Why Study PPII Peptide for NH_3 Production?

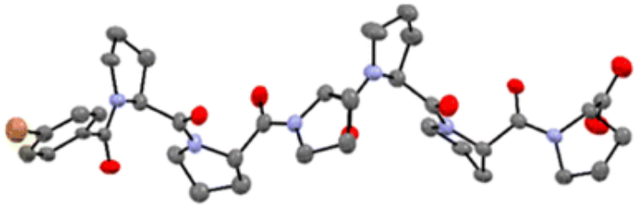
- Iron oxide is also useful for biomedical applications: cancer therapy, macromolecular delivery, & resonance imaging.

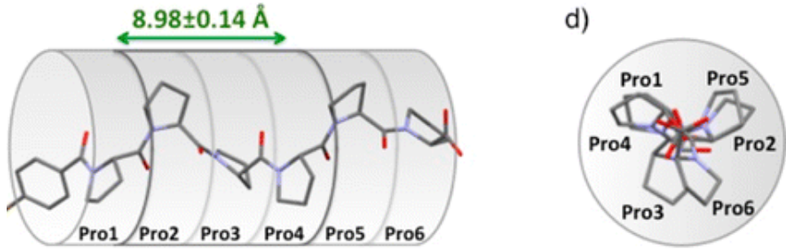
  Theranostics **2013,** *3* (12), 986-1003; *Future Med Chem* **2010,** *2* (3), 427-49.

- PPII helices have unique structures (no H-bonds; consistent length every 4 AAs) and are involved in self-assembly processes.

  J. Mol. Biol. (2013) 425, 2100–2132

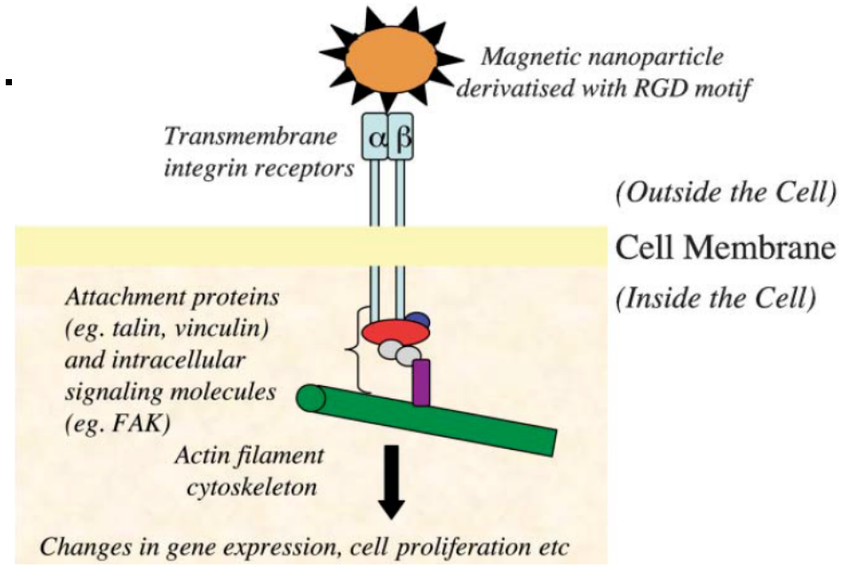
- While various peptide systems have been attached to iron oxide, none have attached PPII peptides specifically.





Poly-L-Proline: 3 fold symmetry

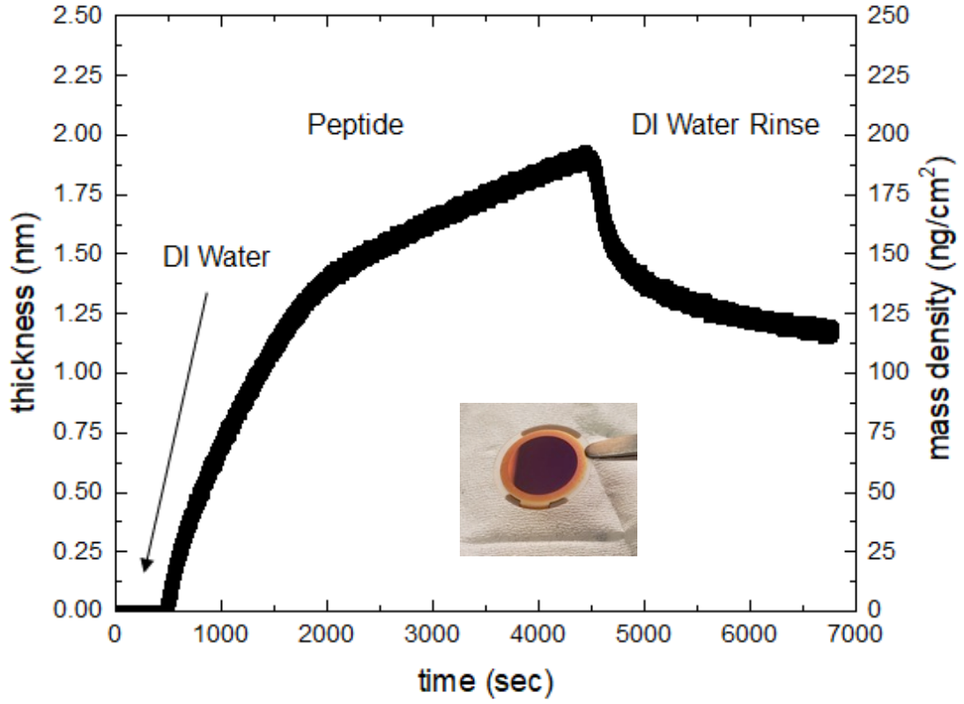
Wilhelm et al. *J. Am. Chem. Soc.*, **2014**,*136*(45), pp 15829–15832



Berry., *J. Mater. Chem.*, 2005, 15, 543–547

PPII Monolayer on Fe_2O_3 via QCM-D

- A **monolayer** of PPII peptide on the metal surface is calculated based on QCM-D measurements.
- Mass density and thickness measurements found to be **108 ± 22 ng/cm²** and **1.08 ± 0.23 nm**, respectively.
  - Leads to a packing density of **6.98** molecules AA / nm² iron oxide

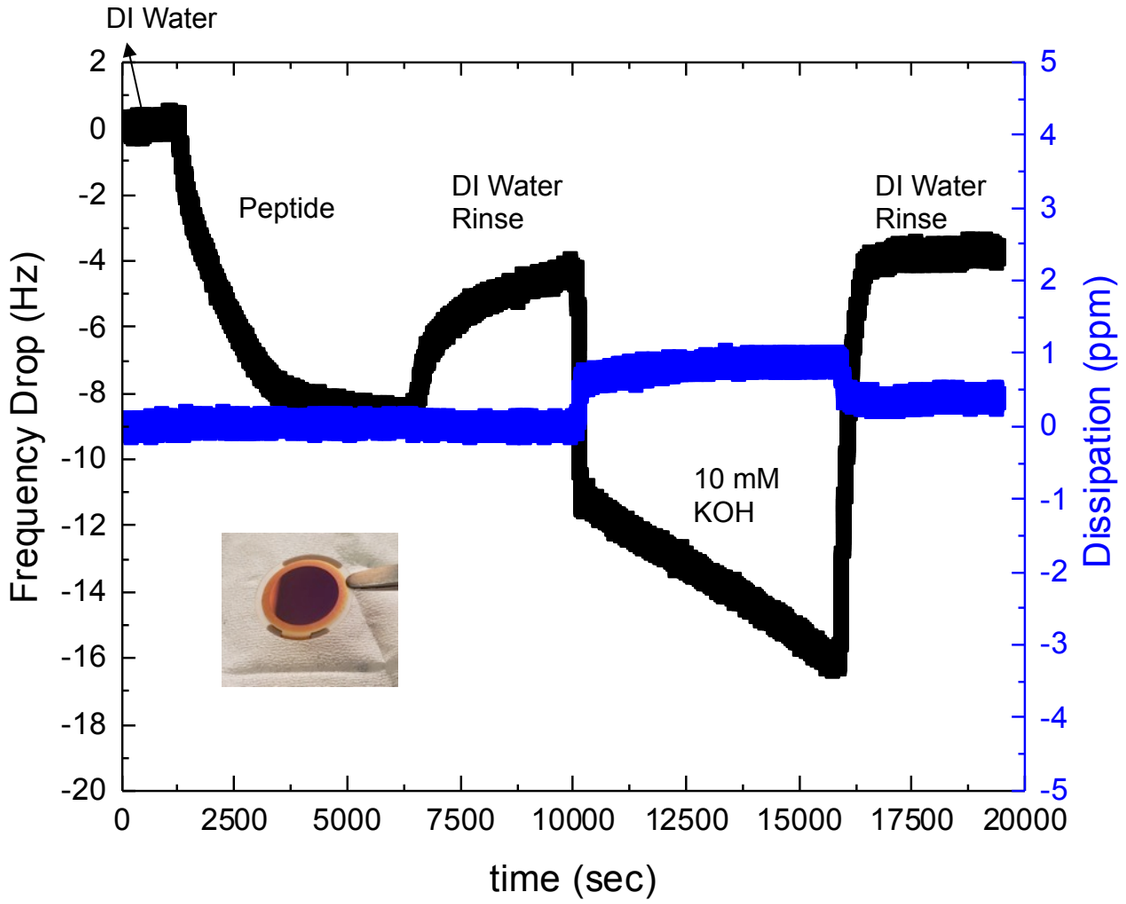


Coverage (%)	Reference
~68	Schwaminger et al., *J. Phys. C* 2015, 119, 23032-23041
67.3	Ma et al. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 212 (2003) 219-226
4 – 35	*Peelle et al., *Langmuir*, Vol. 21, No. 15, 2005
27 – 67	Qu et al., *Inorganica Chimica Acta* 389 (2012) 60–65
85	**This work.**

100 µg/mL PPII peptide in solution; 150 µL/min; 18°C; composite Sauerbrey model (constant dissipation); hydrated protein density assumption

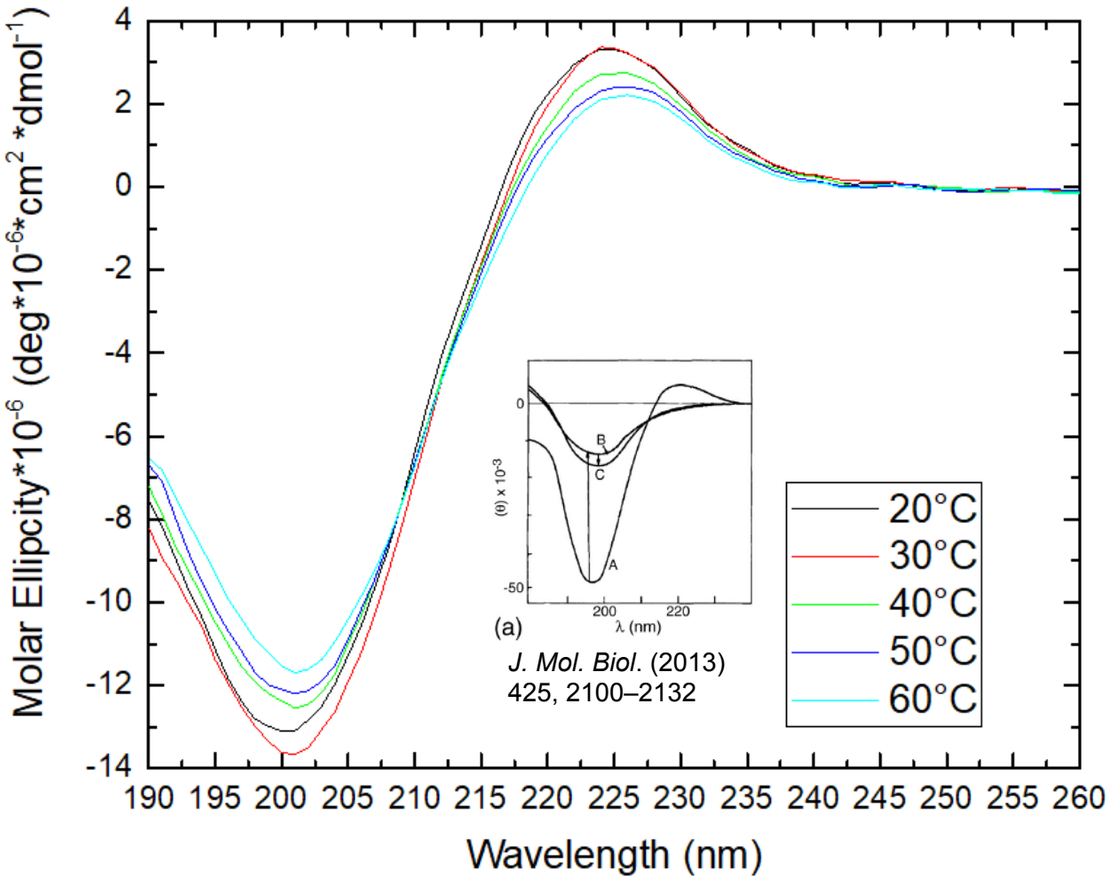
PPII Peptide: Stable in Heat; Stable Fe_2O_3 Bond in 10 mM KOH

- QCM-D measurements of peptide attachment onto Fe_2O_3, followed by a **KOH** step, imply the **peptide is stably-bound onto the Fe_2O_3 sensor.**



100 µg/mL PPII peptide in solution; 150 µL/min; 18°C

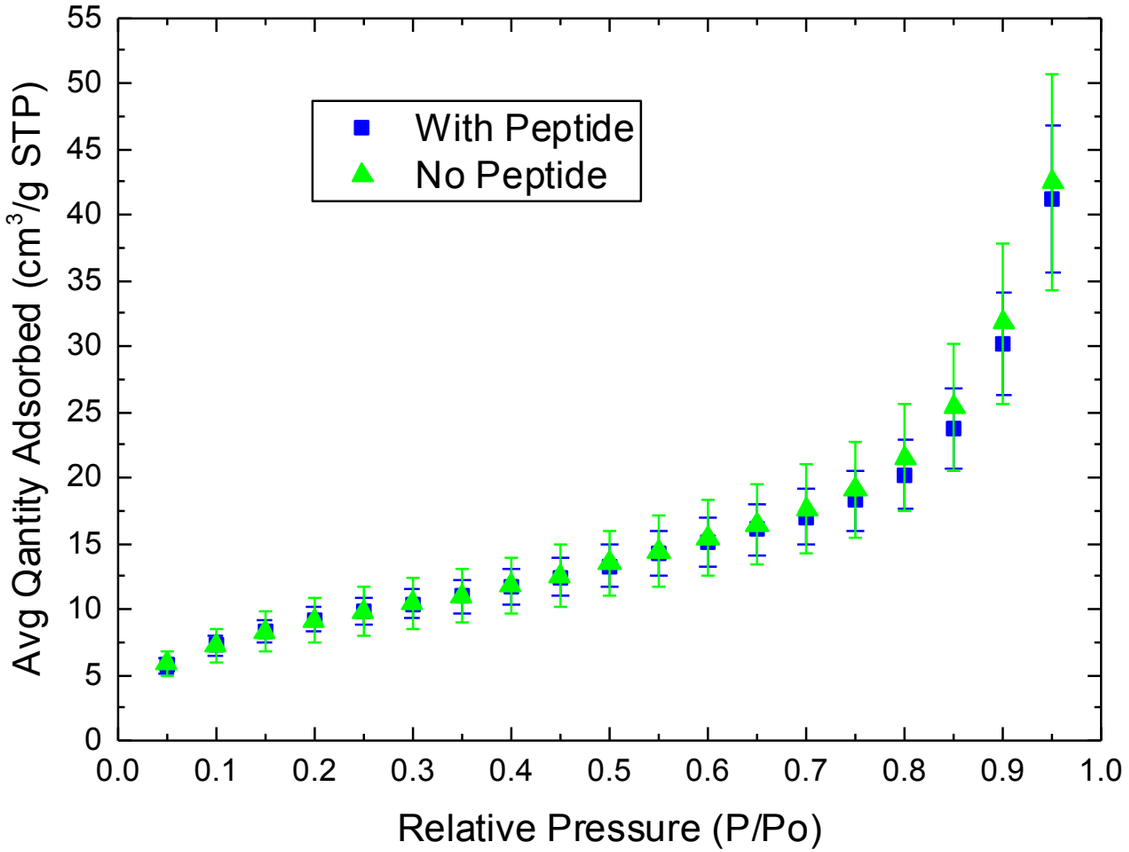
- Circular dichroism measurements up to **60°C** depict **peptide's PPII behavior is stable** up until that point.

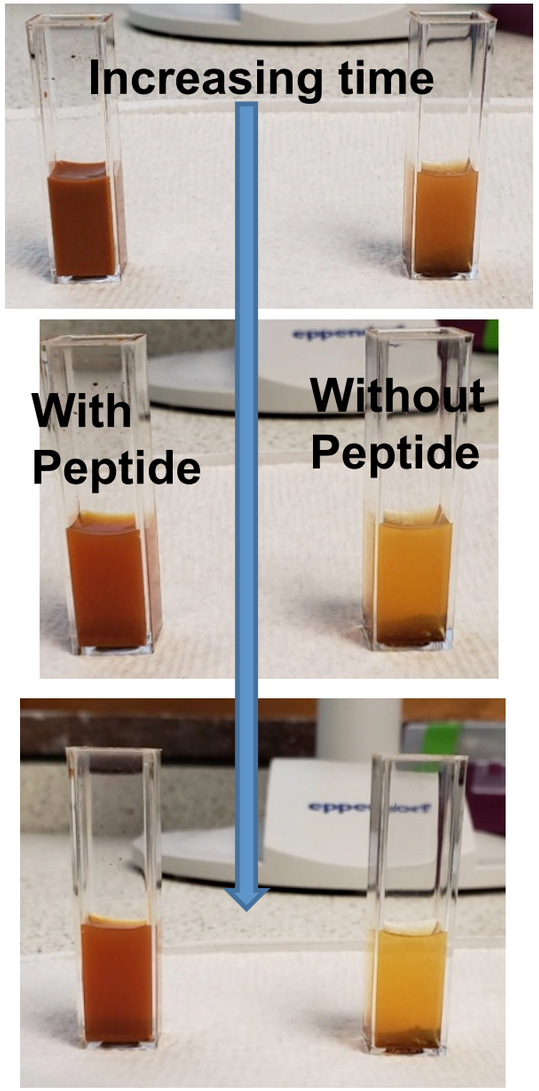


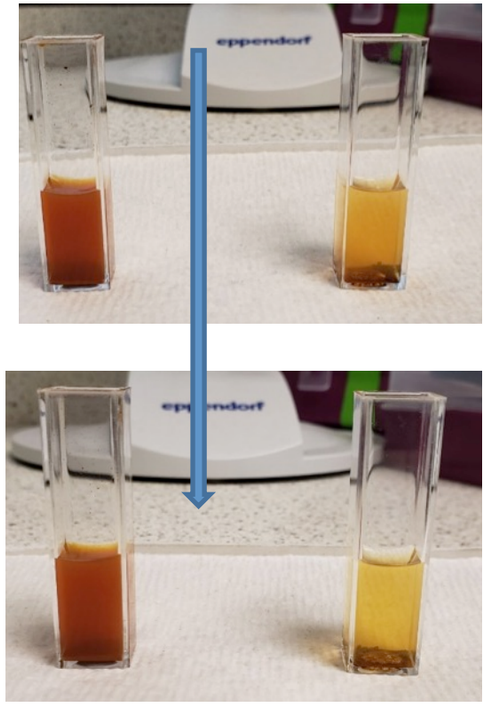
150 µg/mL PPII peptide in solution; 200 nm/min; 5 accumulations

PPII Peptide Doesn't Affect N_2 Adsorption, but Does Affect Settling

- Brunauer–Emmett–Teller (BET) analysis determined that there is **no significant difference of N_2 adsorption** on the functionalized versus the bare Fe_2O_3 nanoparticles.







- Clearly **distinct settling behaviors** despite being at the same concentration.

Appx 200 mg Fe_2O_3/run; degassed overnight with N_2 at 100°C; run overnight with liquid N_2

200 µL of 1 mg/mL Fe_2O_3; PPII-functionlized Fe_2O_3 (left); bare Fe_2O_3 (right).

Conclusions

- PPII helices are interesting for ammonia generation as well as other applications related to the biomedical field.
- Well-packed PPII peptide SAMS on Fe_2O_3 surface (useful for control of surface).
- PPII peptide on Fe_2O_3 is stable in KOH (useful for electrochemistry applications).
- PPII peptide signature secondary structure is preserved at temperatures up to at least 60°C (useful for moderate-temperature electrochemical applications).
- N_2 adsorption sites are not blocked (useful for desired N_2 to NH_3 reduction).
- Dispersion of Fe_2O_3 in PPII-functionlized Fe_2O_3 solution (may be useful for biomedical applications).

Acknowledgements

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- David Suttmiller

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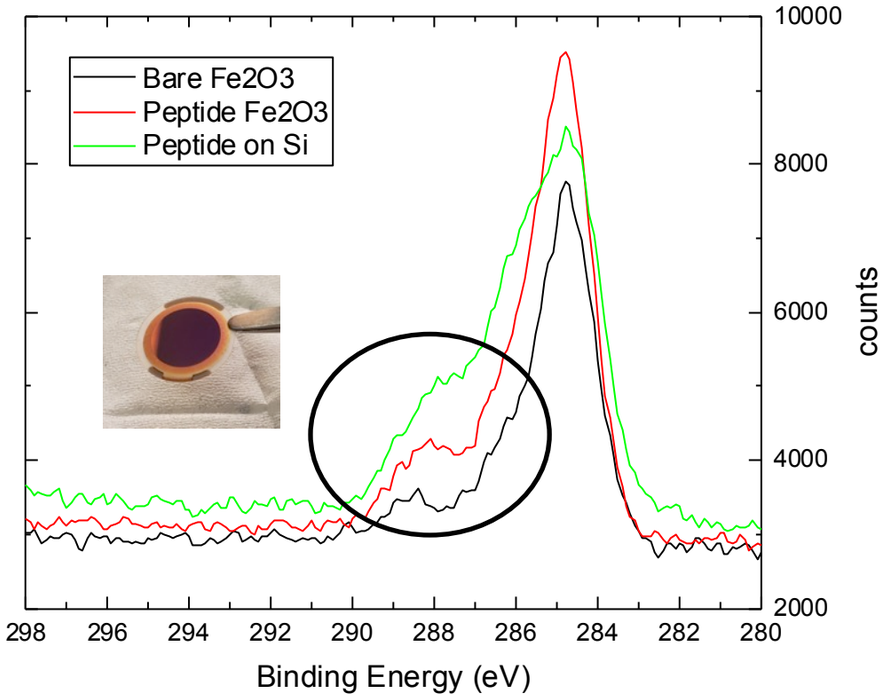
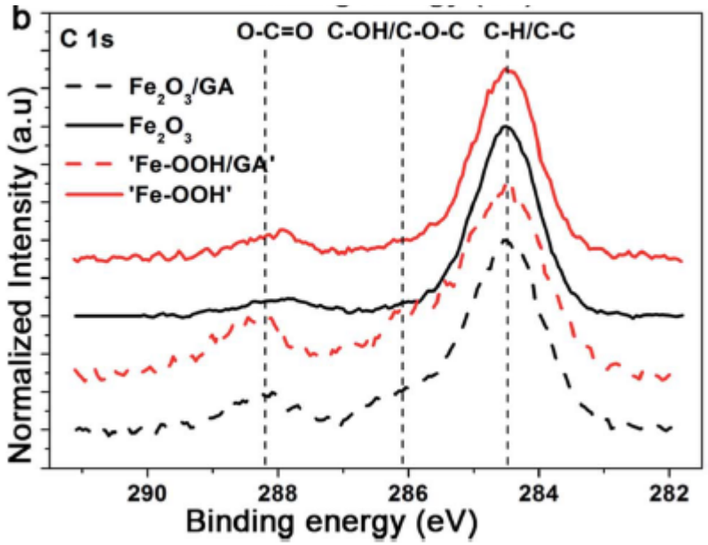
- DOE BES DESC0016529

Supplemental: XPS

- We don't see Fe-O-Metal interaction via O1s (right), but C1s (below) implies such an interaction.





Taffa *et al.* RSC Adv., 2015, 5, 103512–103522

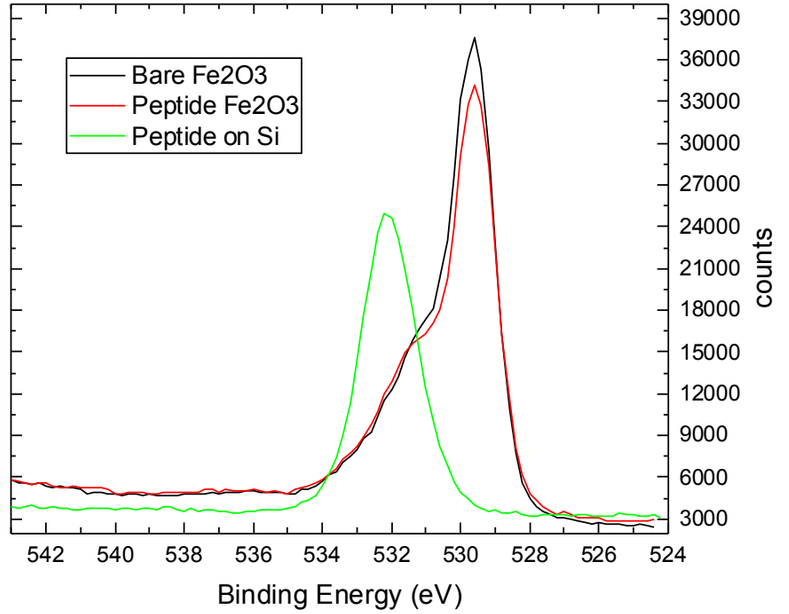


Table 1 | Binding energy (B.E.) of metal–O–C bonds in O 1s spectra

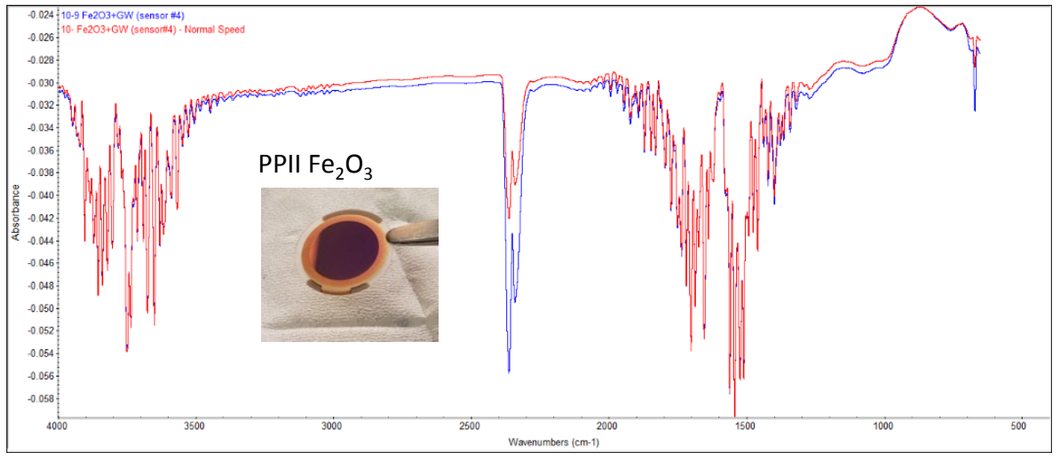
Metal–O bond	B.E. (eV)	Metal–O–C bond	B.E. (eV)	Refs.
Fe–O	530.3	Fe–O–C	531.7	28
		Fe–O–C	533.0	33
Fe–O	529.8	Fe–O–C	531.2	This work
Ni–O	529.3	Ni–O–C	530.2	32
Cu–O	530.5	Cu–O–C	532.8	34

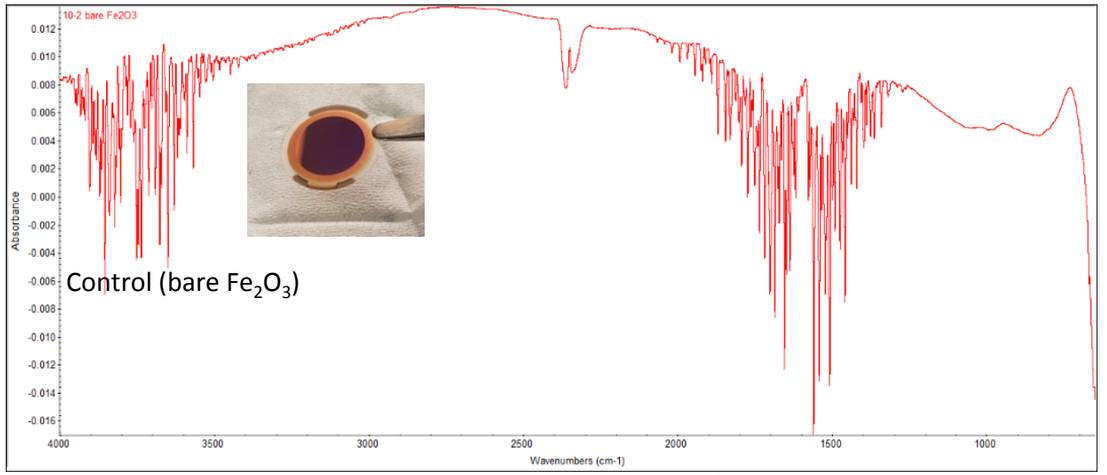
Zubir *et al. SCIENTIFIC REPORTS* | 4 : 4594 | DOI: 10.1038/srep04594

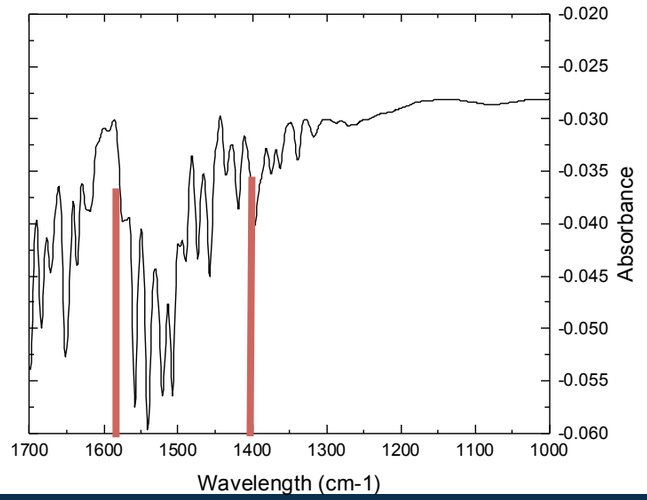
Step size 0.2 eV for O1s and 0.1 eV for C1s

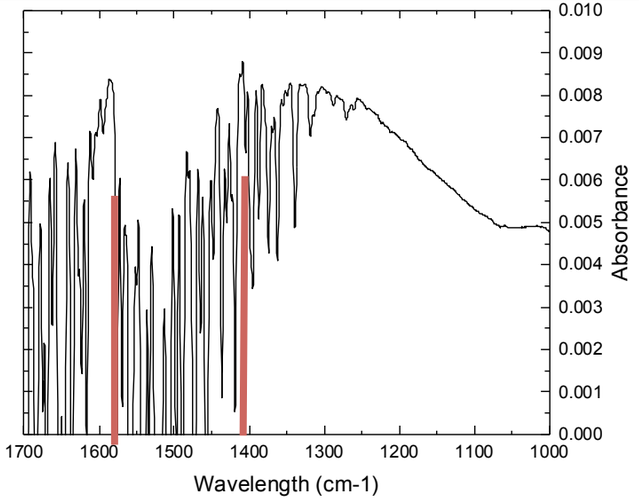
Supplemental: FTIR

“. . .the characteristic vibrations of the carboxylic groups are located at 1410 and 1580 cm^{-1}, which are assigned to the symmetric and asymmetric COO– stretching. The difference between these two peaks is about 170 cm^{-1}, implying a bridging structure between the surface iron ions and carboxylic groups” H. Qu et al. / *Inorganica Chimica Acta* 389 (2012) 60–65









8.000 cm^{-1} resolution; 2000 scans; ZnSe polarizer at 90°; Veemax III accessory at 80°

Supplemental: PPII Monolayer Calculation for on Fe_2O_3 via QCM-D

$$Coverage: (\mathbf{108} ng/cm\uparrow 2\ ) * (10\uparrow -7\ cm/nm\ )\uparrow 2 * (1\ nmol/1211.33\ ng\ ) * (10\uparrow -9\ mol/nmol\ ) * (6.022 * 10\uparrow 23\ peptides/1\ mol\ ) = 0.537 peptides/nm\uparrow 2\ \ or\ \mathbf{1.86} nm\uparrow 2\ /peptide$$

$$Total\ peptide\ \#: (0.537\ peptide/nm\uparrow 2\ ) * (0.7 cm\uparrow 2\ ) * (10\uparrow 7\ nm/1 cm\ )\uparrow 2 * \pi = \mathbf{8.27} * \mathbf{10\uparrow 13}\ peptides/Fe2O3\ QCM\ Sensor$$

$$Theortical\ peptide\ \# = (SAfe2o3/SApeptide\ ) = [(0.7 cm)\uparrow 2 * (10\uparrow 7\ cm)\uparrow 2\ * \pi]/[13 * (0.35 nm)\uparrow 2\ ] = \mathbf{9.67} * \mathbf{10\uparrow 13}\ \ peptide/Fe2O3\ QCM\ sensor$$

Supplemental: Overnight QCM-D, KOH Run