Electrochemical CO_2 Conversion at NETL

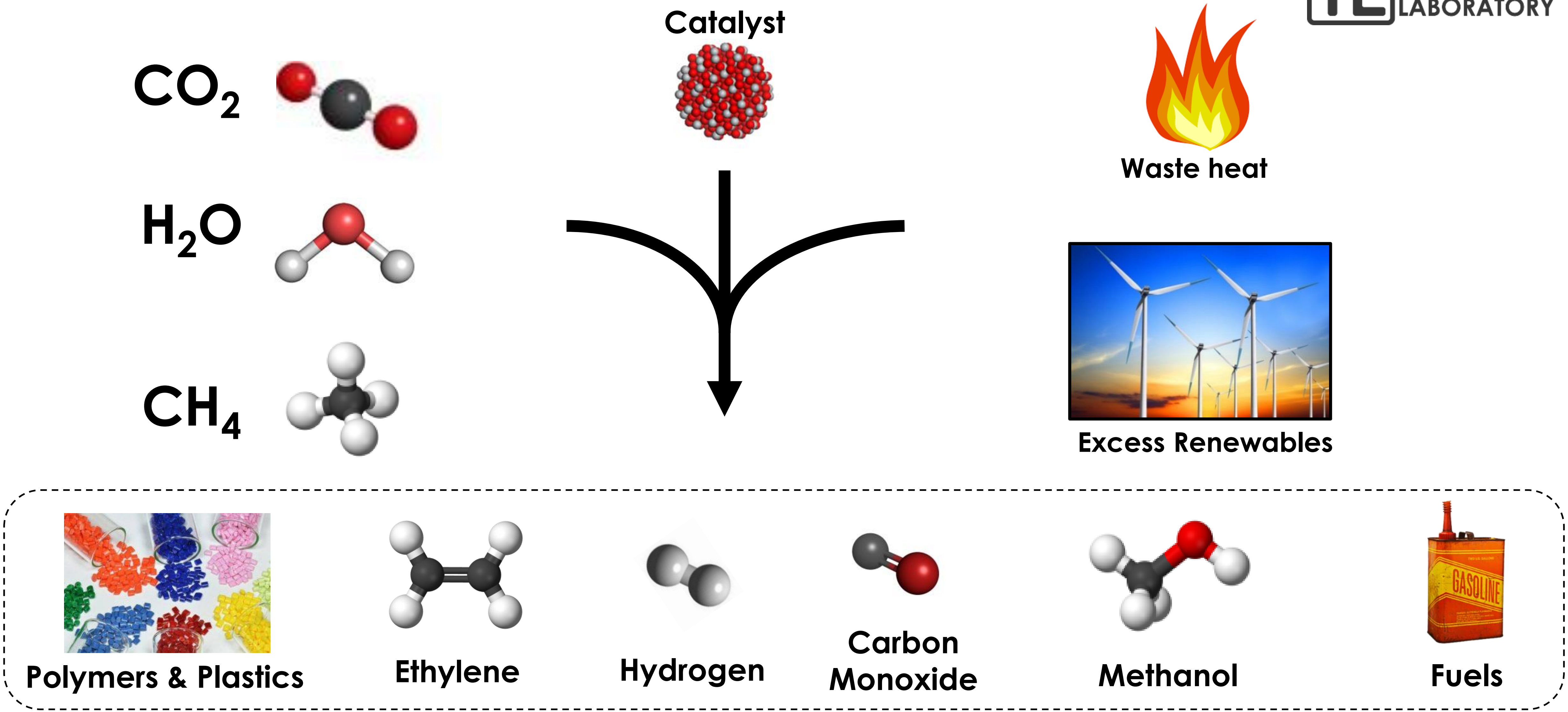
NATIONAL ENERGY TECHNOLOGY LABORATORY

Douglas R. Kauffman (NETL / DOE)

Solutions for Today | Options for Tomorrow

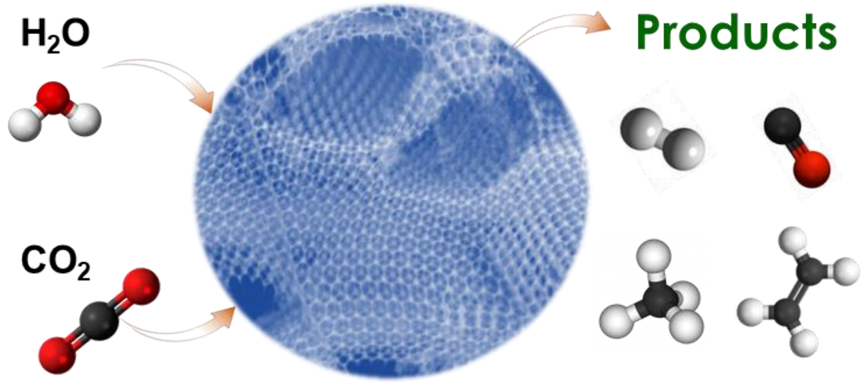
U.S. DEPARTMENT OF ENERGY

Catalytic CO_2 conversion at NETL



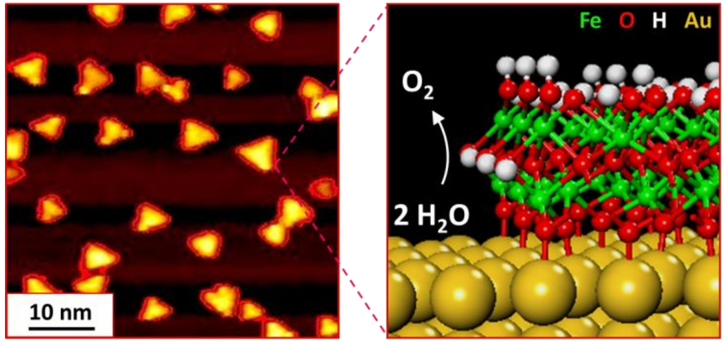
Electrochemical catalyst design

Structure-controlled product selectivity

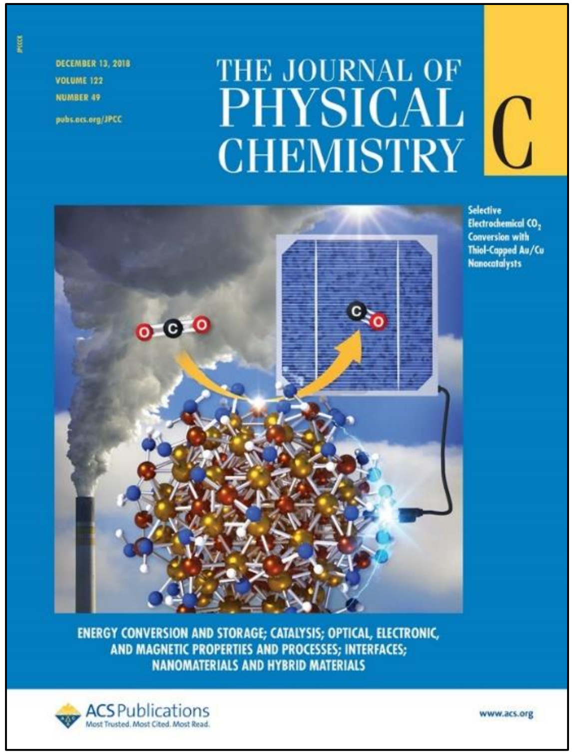


J. Mater Chem. A, 2019, 7, 27576

Surface-science enabled electrocatalysis



"Atomically Precise" nanocatalysts



JPCC, 2018, 122, 49, 27991

ACS Catalysis, 2020, 10, 12011

ACS Catalysis, 2019, 9, 5375
ACS Catalysis, 2020, 10, 11768

3D Structured SnO_2 Catalysts

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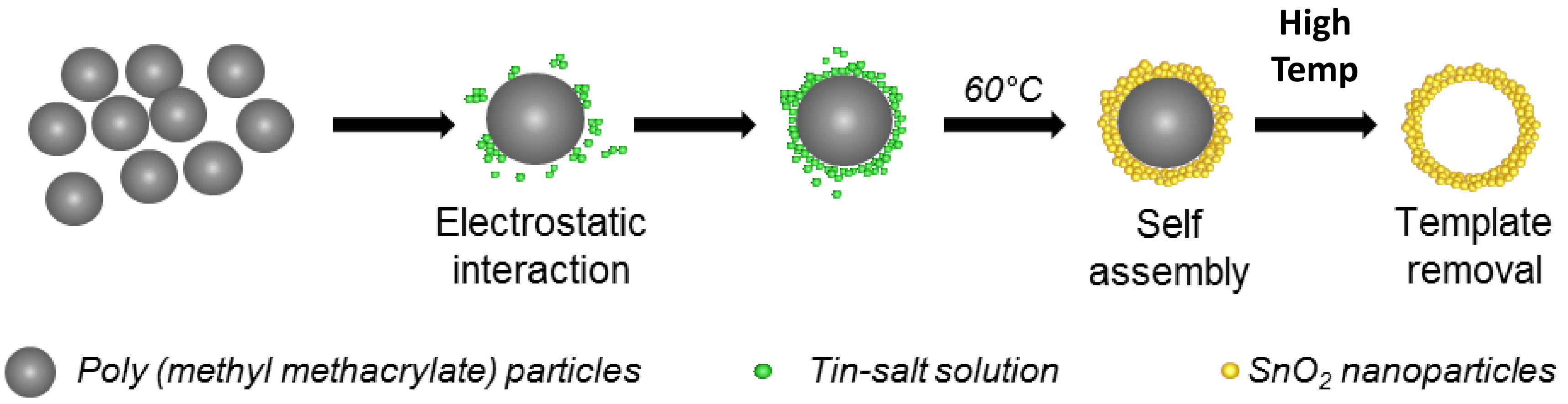
- Electrochemically reduce CO_2 to formate/formic acid ($HCOO^-$ / HCOOH).

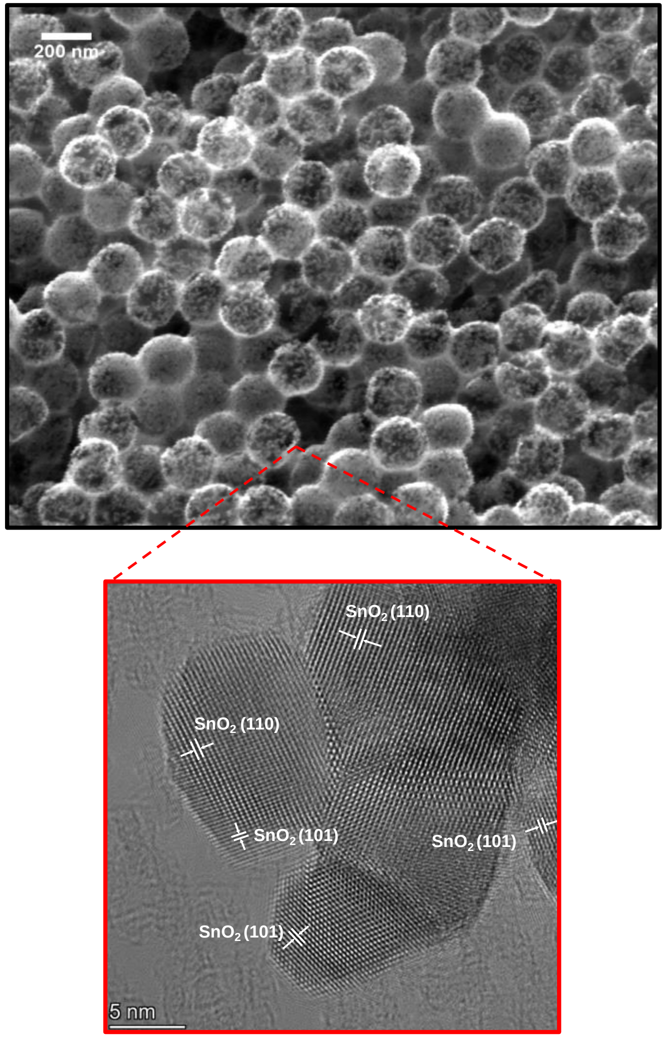
- Formic acid has agricultural and industrial uses.
  - Currently produced via NG reforming and methanol processing.
  - Extremely carbon intensive.

- Formic acid is also an emerging energy carrier (53 g H_2 / L)

- Key Challenges:
  - Current density
  - Stability / durability
  - Scalable catalyst synthetic procedure.

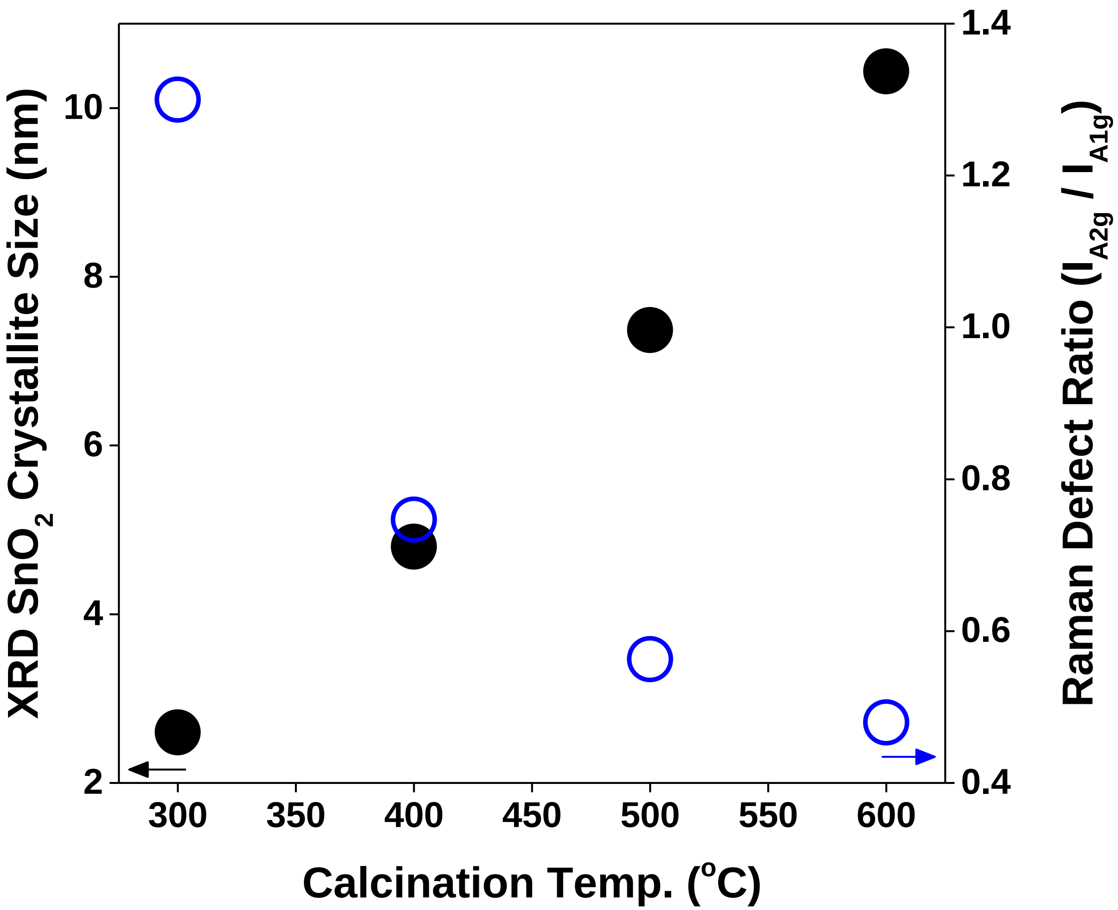
Catalyst synthesis approach





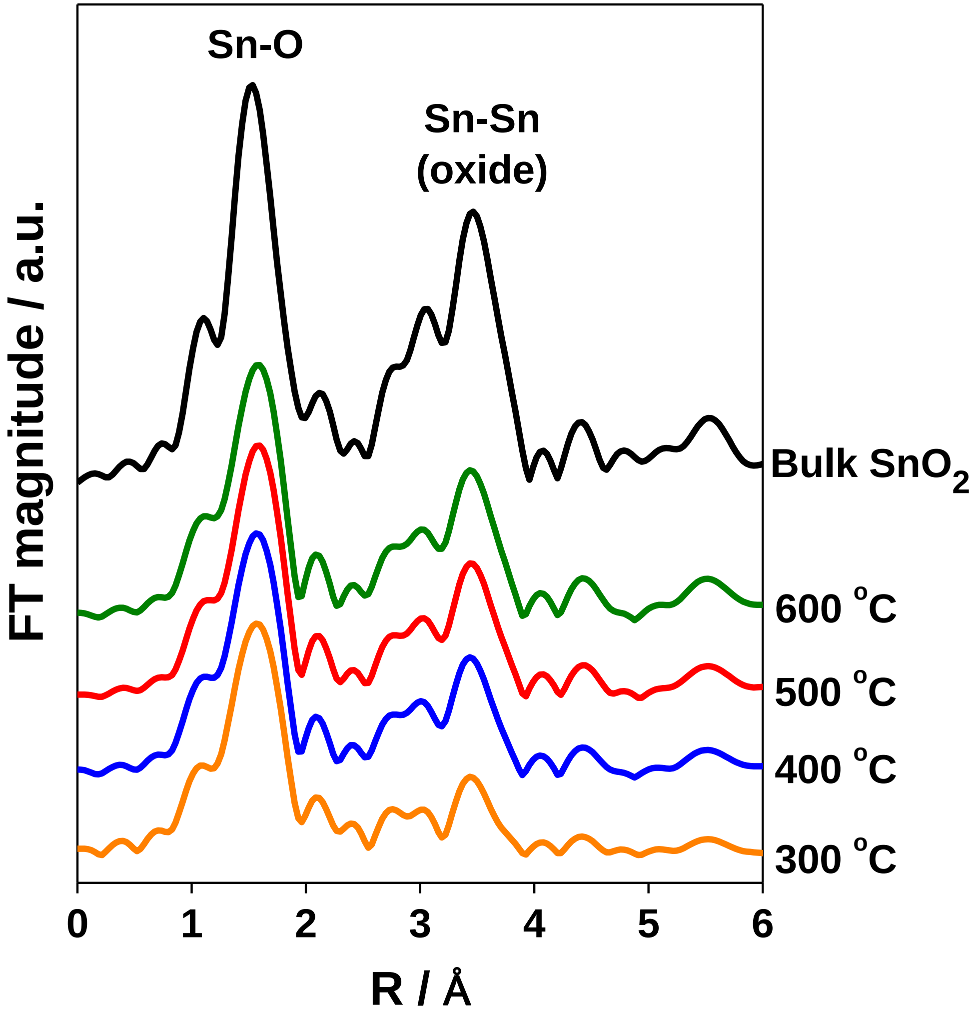
- **Sphere size is fixed at ~200 nm based on PMMA template.**
- **Constituent SnO_2 nanoparticles are controlled between 2-10 nm with calcination in air between 300-600°C.**
- **Simple solution-phase synthesis and thermal processing**

Characterization Results and Echem Details



- **XRD, XPS and Raman showed increased calcination temperature produced larger, more crystalline SnO_2 NPs.**

Characterization Results and Echem Details



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- XRD, XPS, EXAFS and Raman all confirmed SnO_2 oxidation state.

Characterization Results and Echem Details

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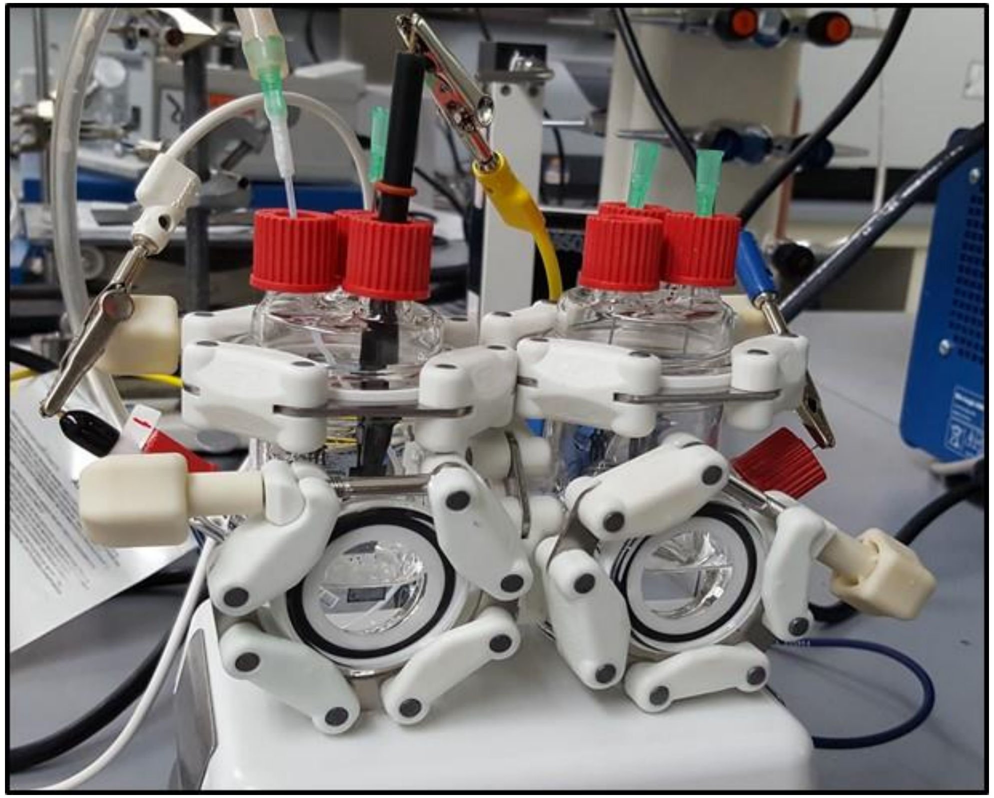


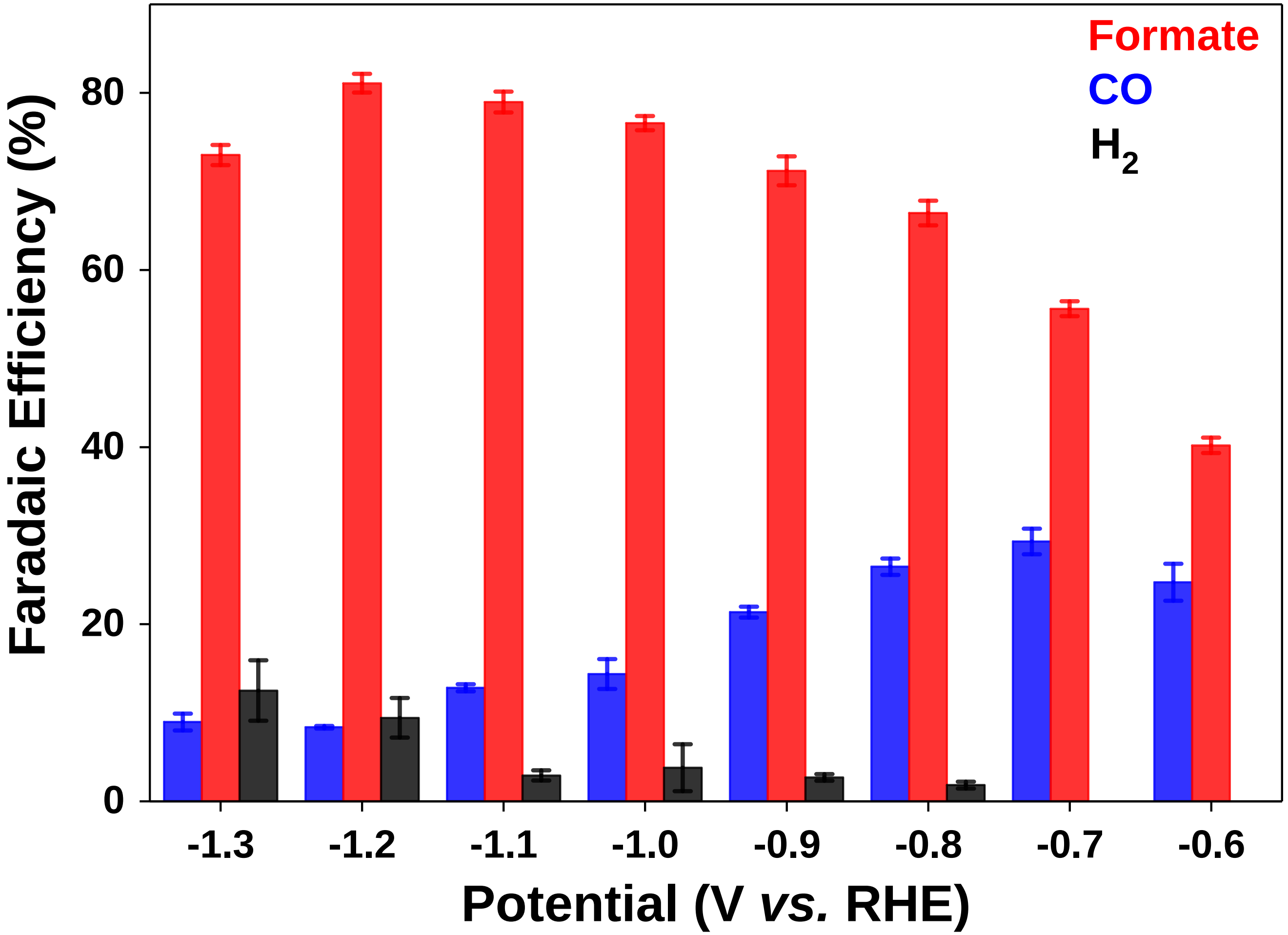
Cathode Chamber

Anode Chamber

- **XRD, XPS and Raman showed increased calcination temperature produced larger, more crystalline SnO_2 NPs.**
- **XRD, XPS, EXAFS and Raman all confirmed SnO_2 oxidation state.**
- **SnO_2 catalysts mixed w/ 10 wt% carbon black, Nafion binder and deposited onto PTFE-coated carbon paper electrodes at 5.4 mg_{SnO2}/cm_{geo}^2.**
- **All electrochemical experiments conducted in H-Cell reactor with CO_2 saturated 0.1M $KHCO_3$**

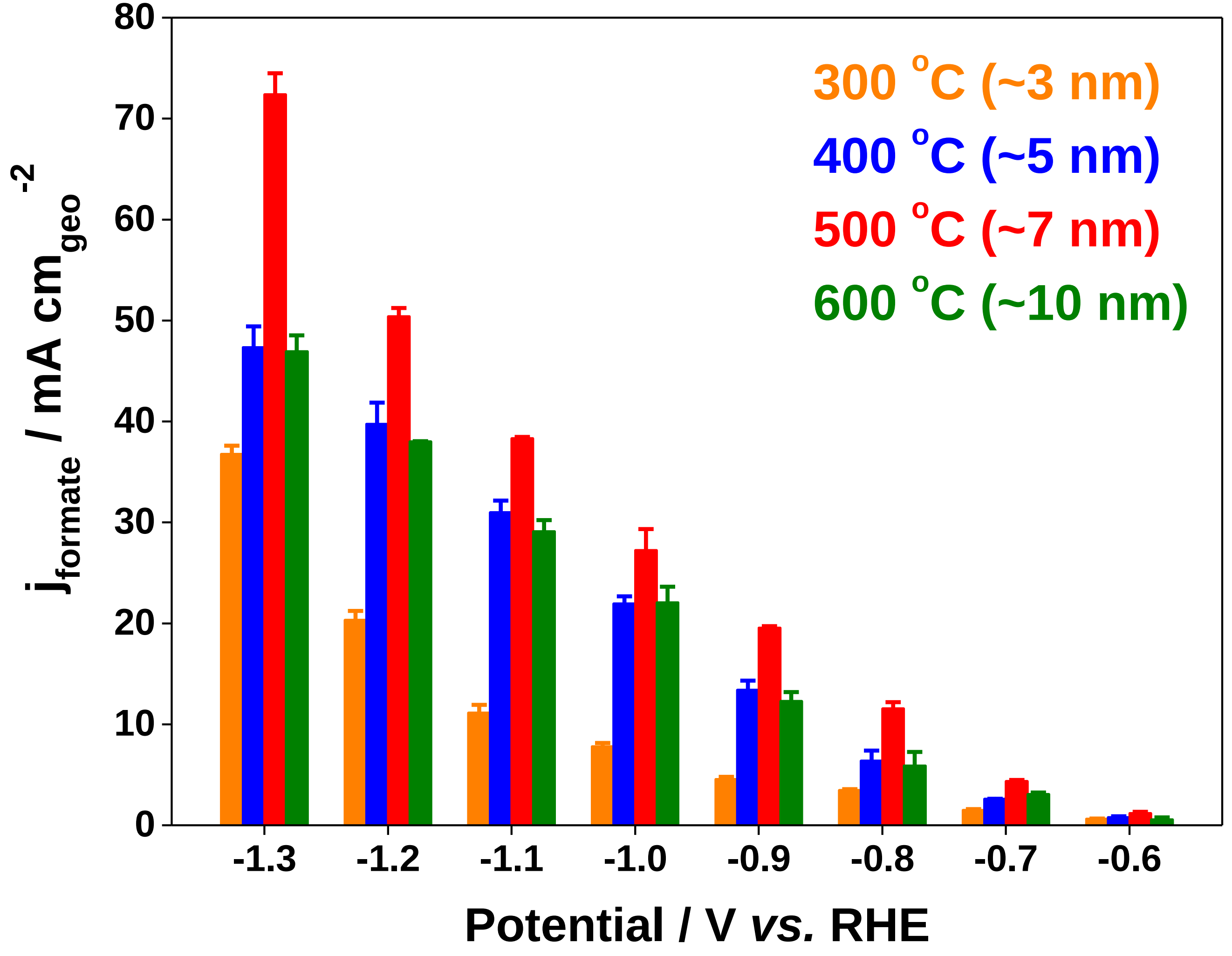
Catalyst Performance (Formate Selectivity)

500 °C calcined SnO_2 Nanosphere



- All catalyst synthesis temperatures selectively produced formate w/ 60-80% FE between -0.7V to -1.3V.
- 500 C calcination temperature produced highest overall formate FE.
- CO and H_2 were the only other products detected.

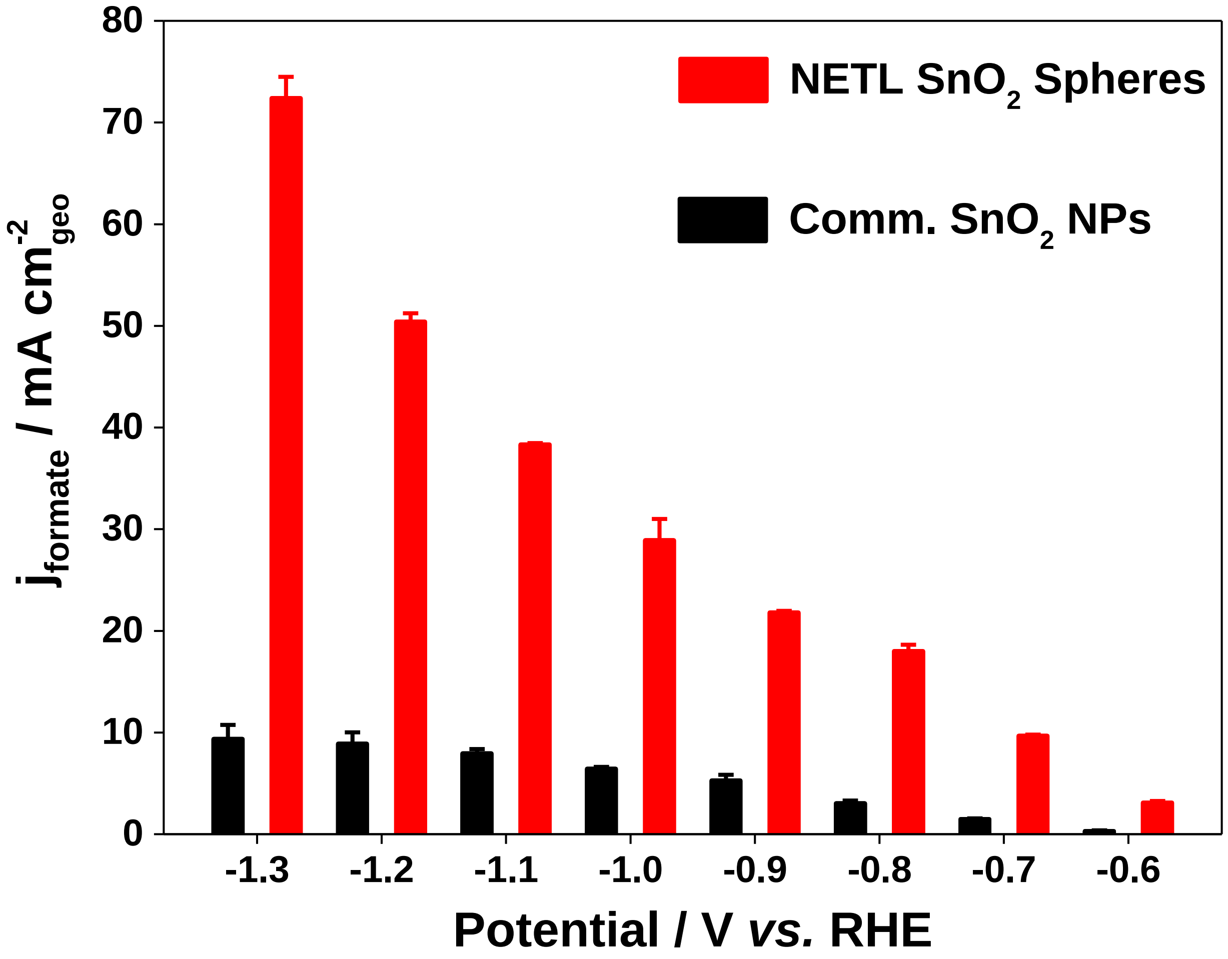
Catalyst Activity vs Calcination Temperature



Balance between crystallinity and particle size

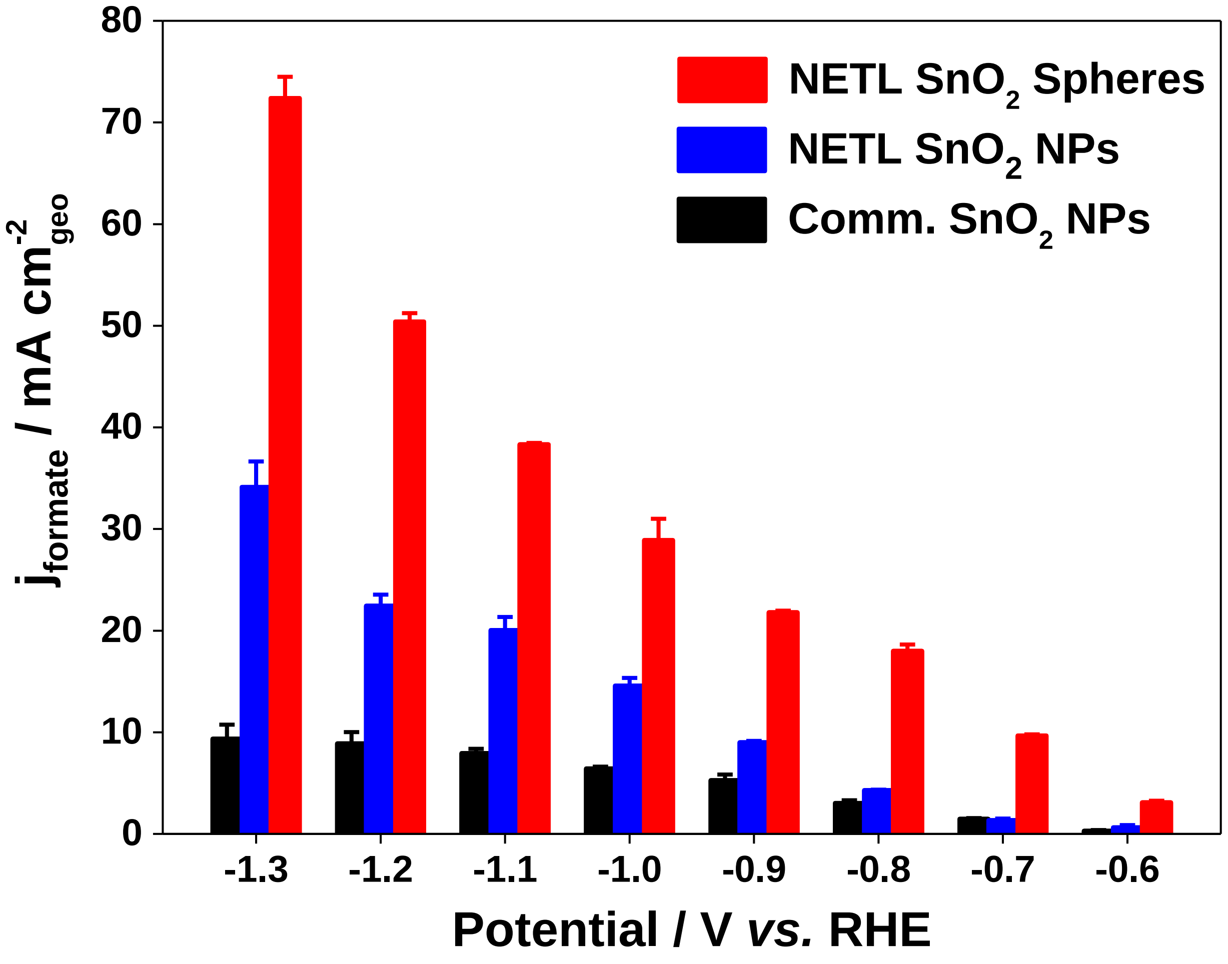
- Below 500 °C the SnO_2 formed smaller and less crystalline NPs.
- Above 500 °C larger SnO_2 particle sizes formed: reduced catalyst surface area
- 500 °C was the optimum calcination temperature

Benchmarking Catalyst Performance



- **Benchmarked against commercially available SnO_2 catalyst particles (Sigma Aldrich; ~28 nm diameter NPs)**
- **Substantially higher formate current density at all potentials.**
- **Approximately 3 times larger electrochemical surface area and number of electrochemically active Sn atoms at equivalent catalyst loading.**

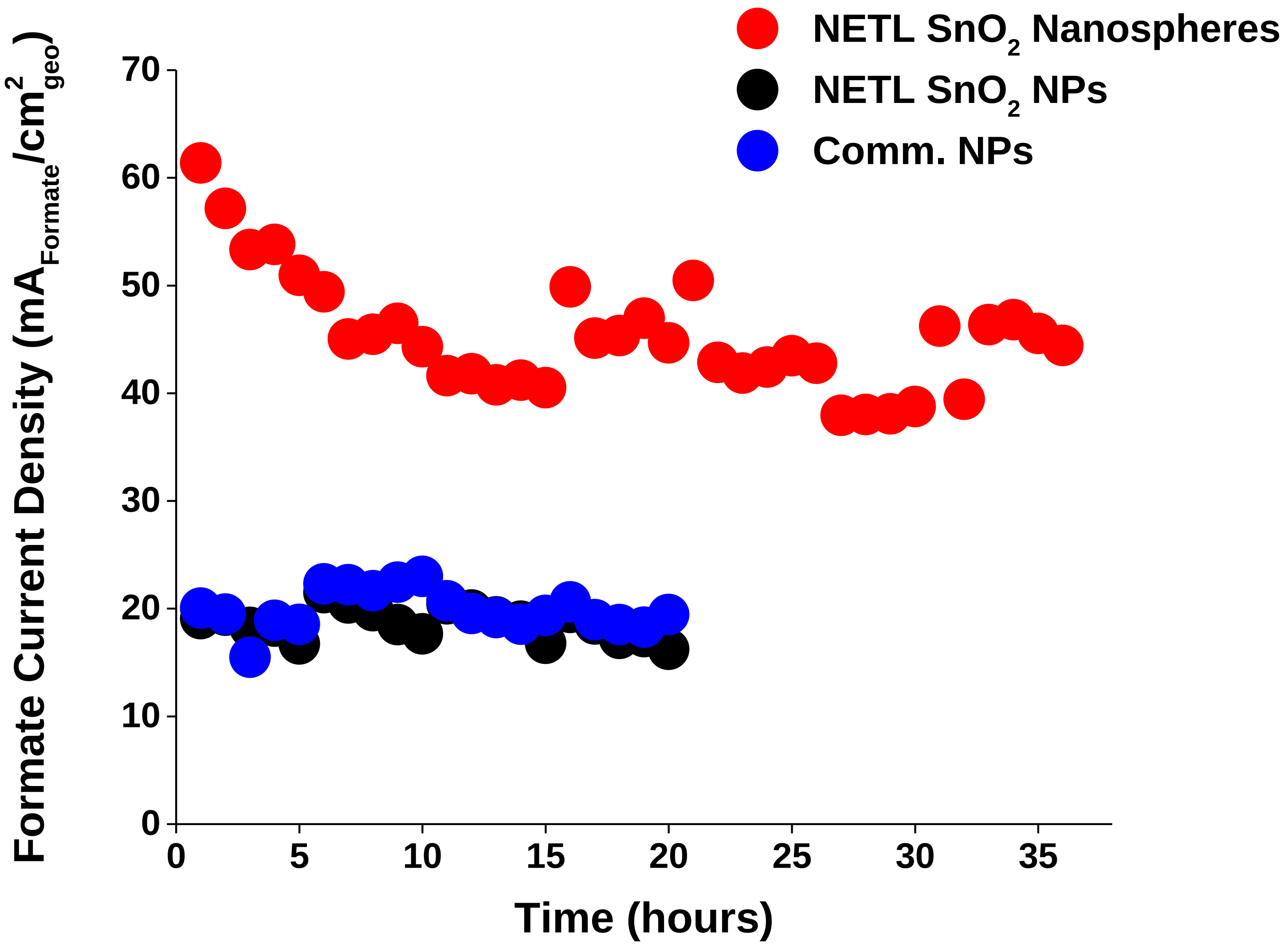
3D morphology Boosts Surface Area and Performance



SnO2 Nanospheres also outperformed *non-templated* SnO_2 NPs of identical size.

	Electrochemical Surface Area (cm^2/ mg_{SnO2})
NETL SnO_2 Nanospheres	134
NETL SnO_2 NPs	84
Comm. SnO_2 NPs	45

Long-Term Performance at -1.2V *vs.* RHE



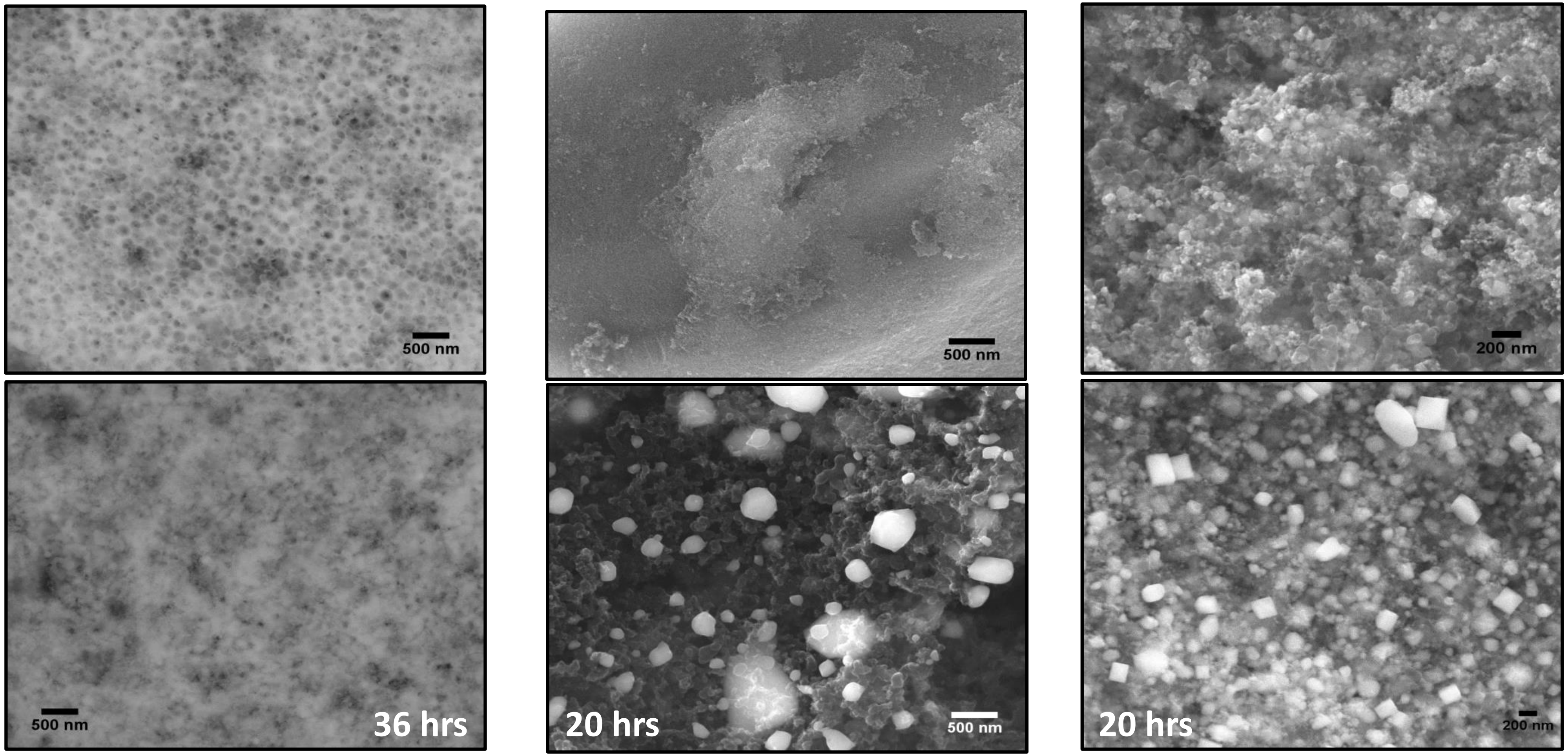
- NETL SnO_2 Nanospheres demonstrated ≥2x performance increase over SnO_2 NPs.
- All catalysts demonstrated ~70% Formate FE during long-term runs.
- Currently being translated into high-performance electrolyzer.

Post-Reaction Morphology

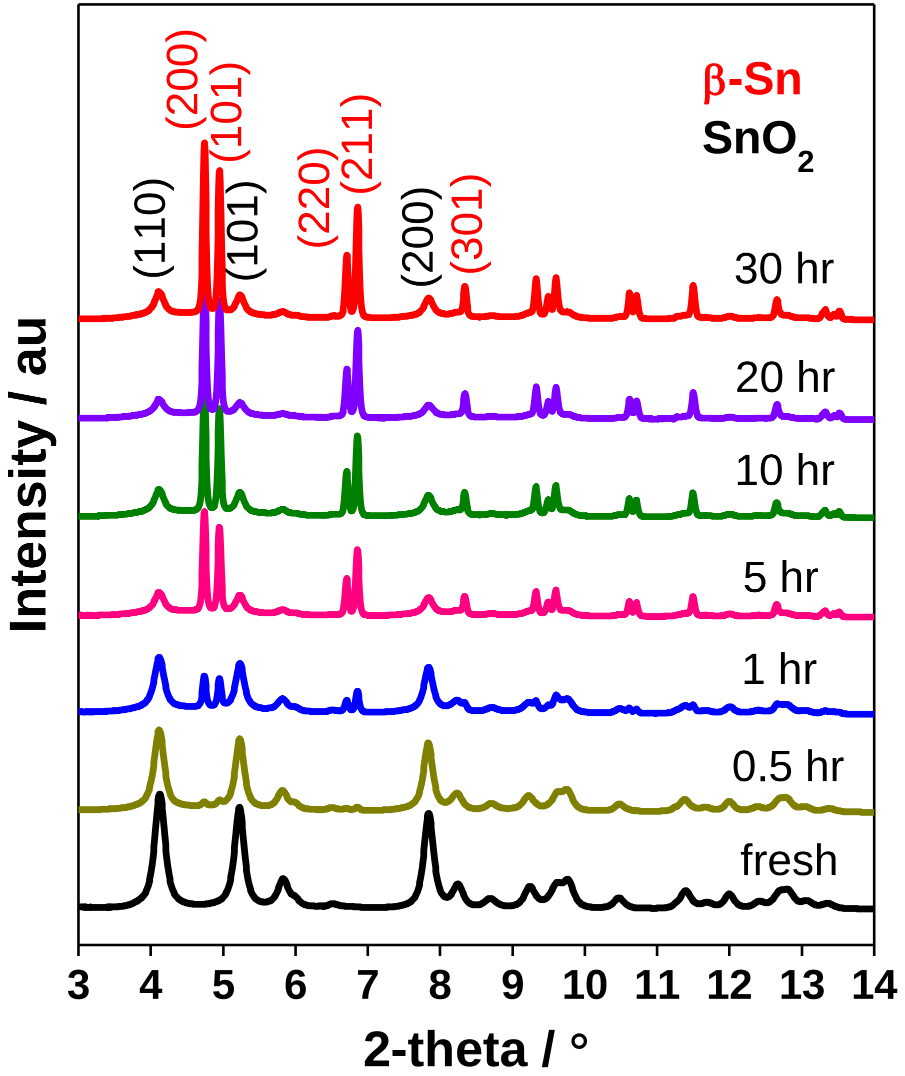
NETL SnO_2 Nanospheres | NETL SnO_2 NPs | Commercial SnO_2

Before CO_2 Reduction

After CO_2 Reduction

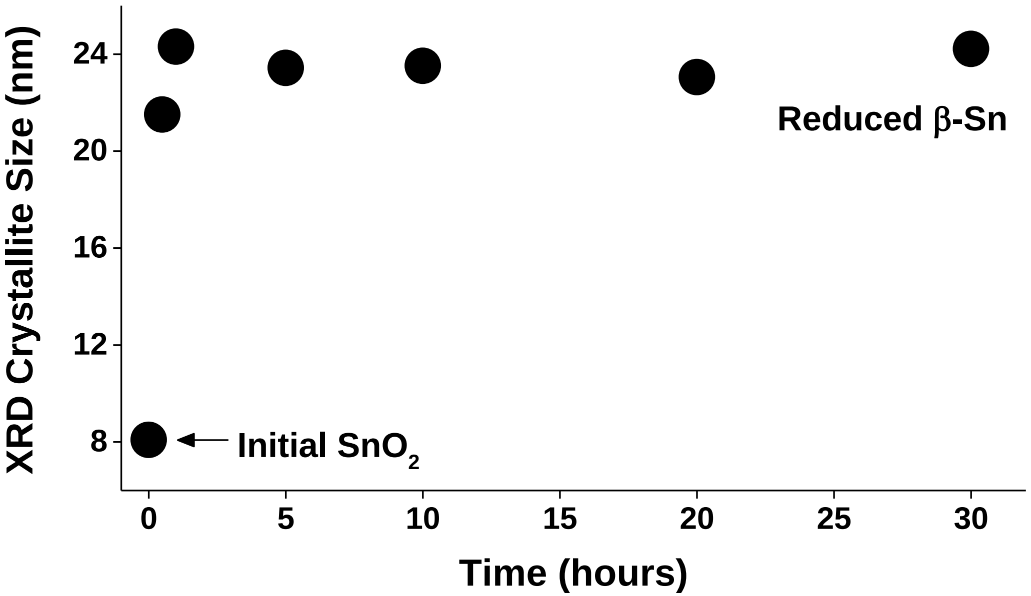


Time Dependent X-ray Diffraction



Time Dependent synchrotron X-Ray Diffraction shows:

- Rapid formation of ~25 nm metallic Sn nanoparticles with β-Sn crystallographic orientation.
- No further particle growth after initial reduction.
- In situ Raman spectroscopy confirms SnO_2 transforms into metallic Sn at operating voltages.



SnO_2 Nanosphere Conclusions

1. **NETL SnO_2 Nanospheres out-perform SnO_2 NPs and commercially available SnO_2.**
    - Unique shape with extremely high surface area
    - Optimized synthetic process to maximize formate current density
    - High formate FE and selectivity
    - Stable ~25 nm nanoparticle size under steady state operation

2. **In situ Raman and time dependent XRD show SnO_2 is quickly reduced to metallic Sn**

3. **Ongoing work: Collaboration with NREL to evaluate NETL SnO_2 Nanospheres in recently reported formate electrolyzer**
    - Reach industrially relevant current densities (100s mA/cm^2).

Acknowledgements

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Synchrotron XAS: Brookhaven NSLS-II, beamline 8-ID (ISS); Eli Stavitski.

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Questions or Comments?

Thank you for your attention!

We have an open post-doc / early career position for electrolyzer testing

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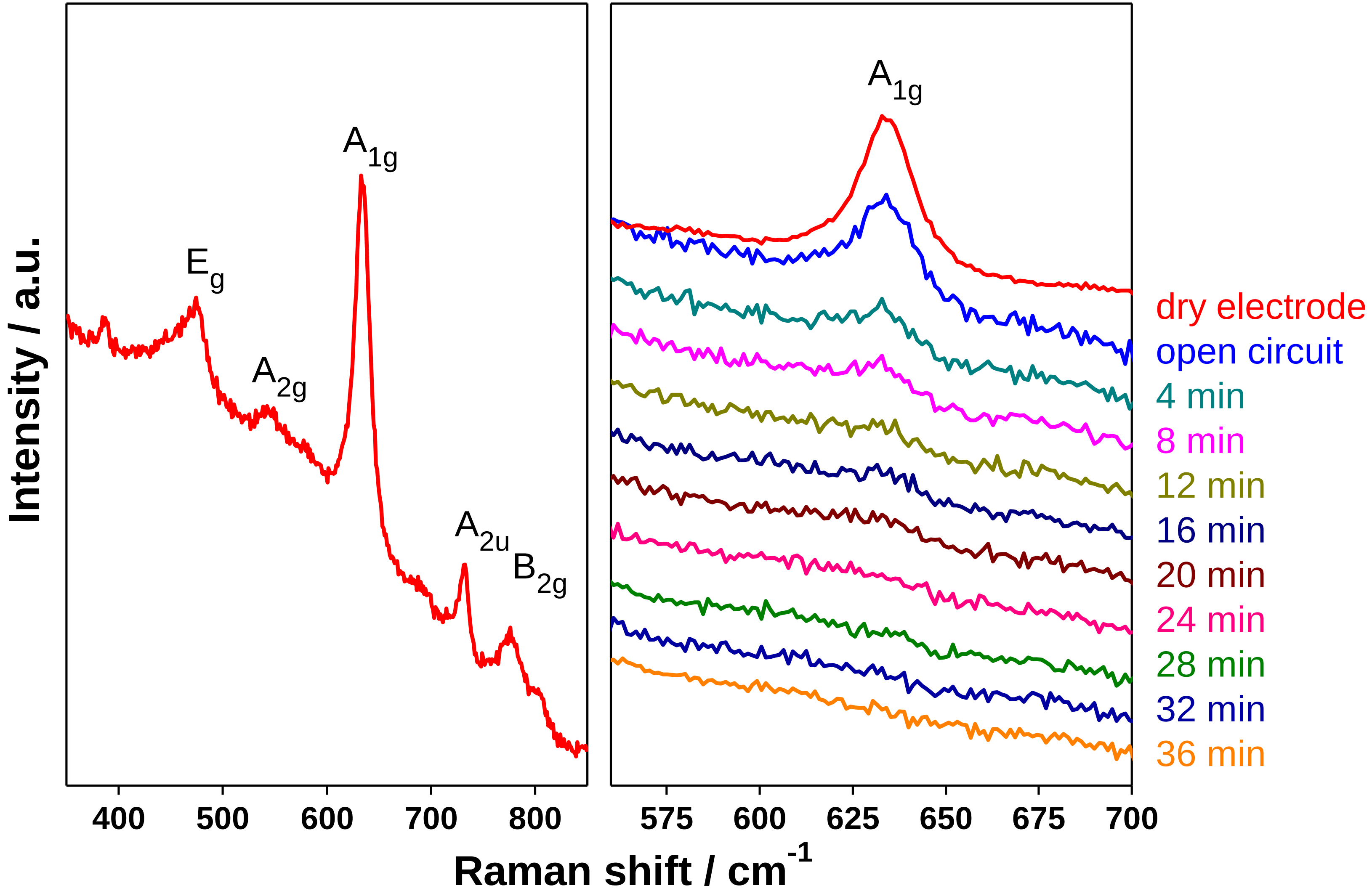
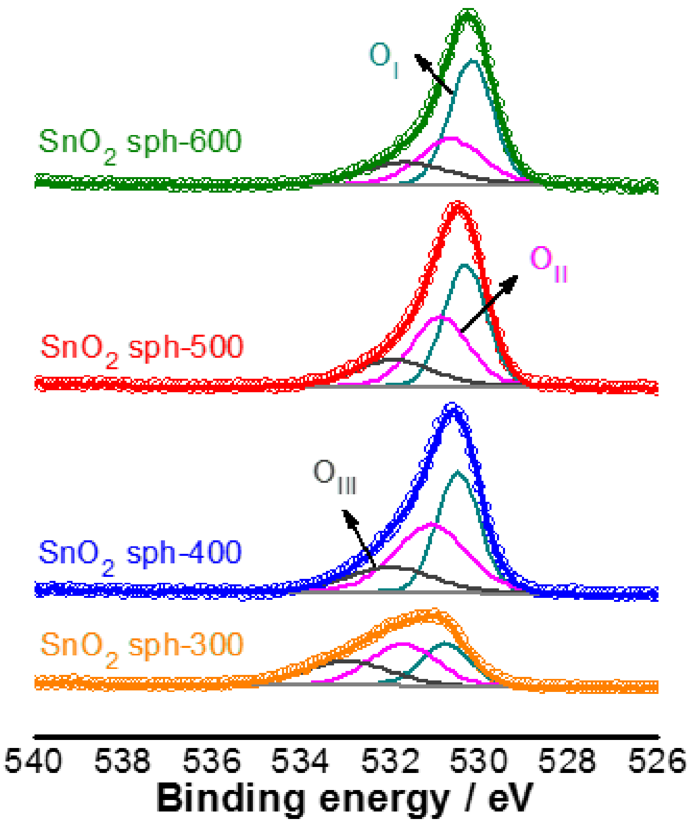
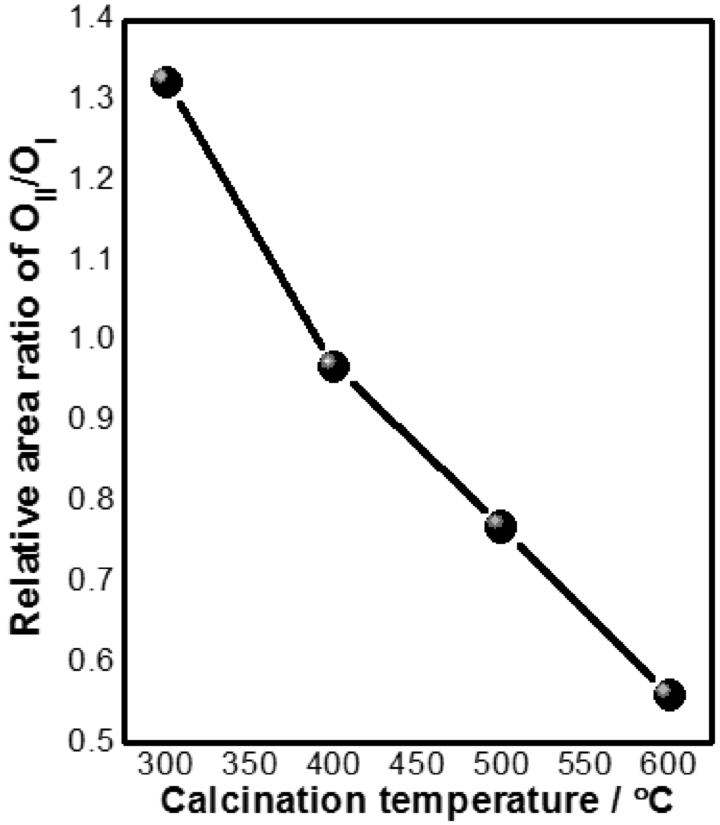
In situ Raman Data

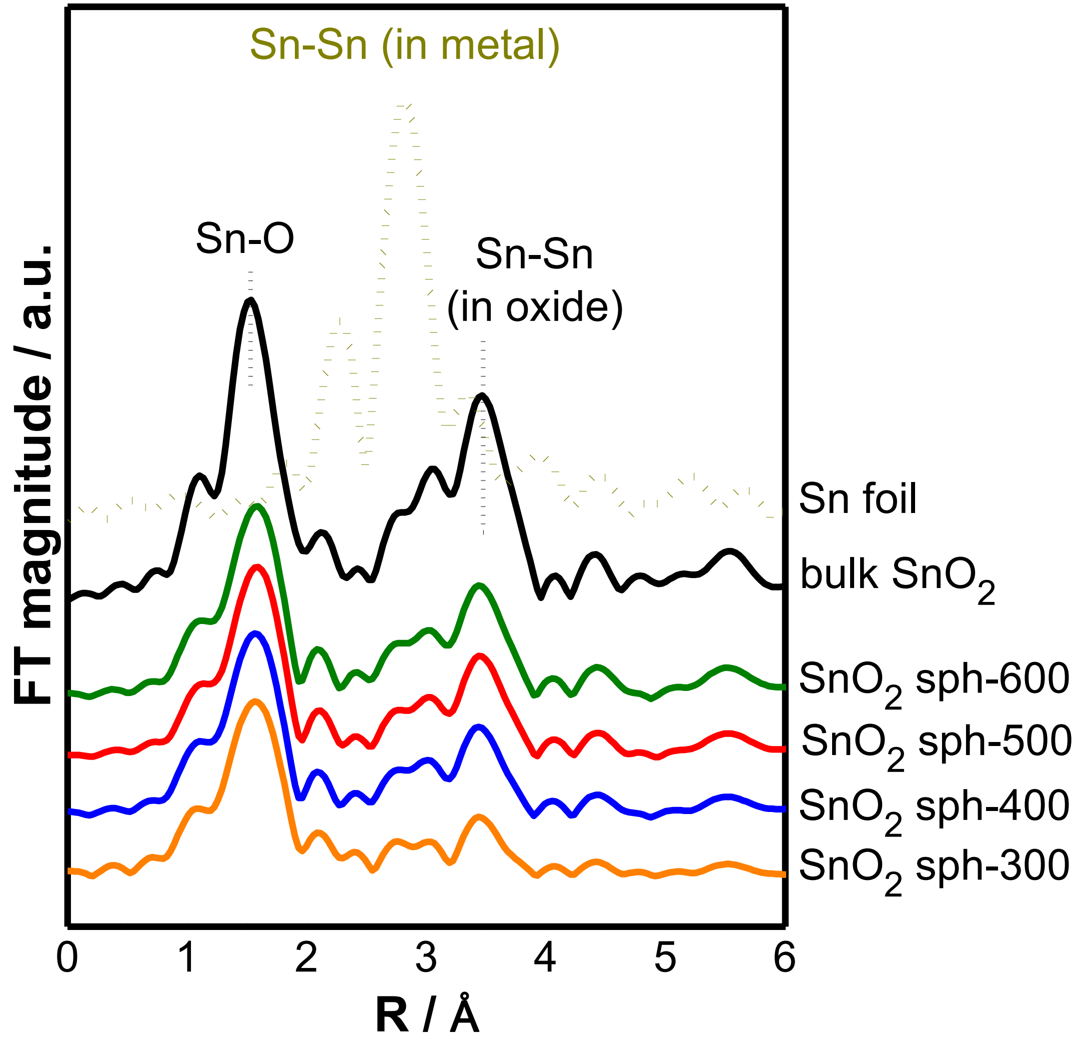


Temp Dependent O1s XPS and Raman data

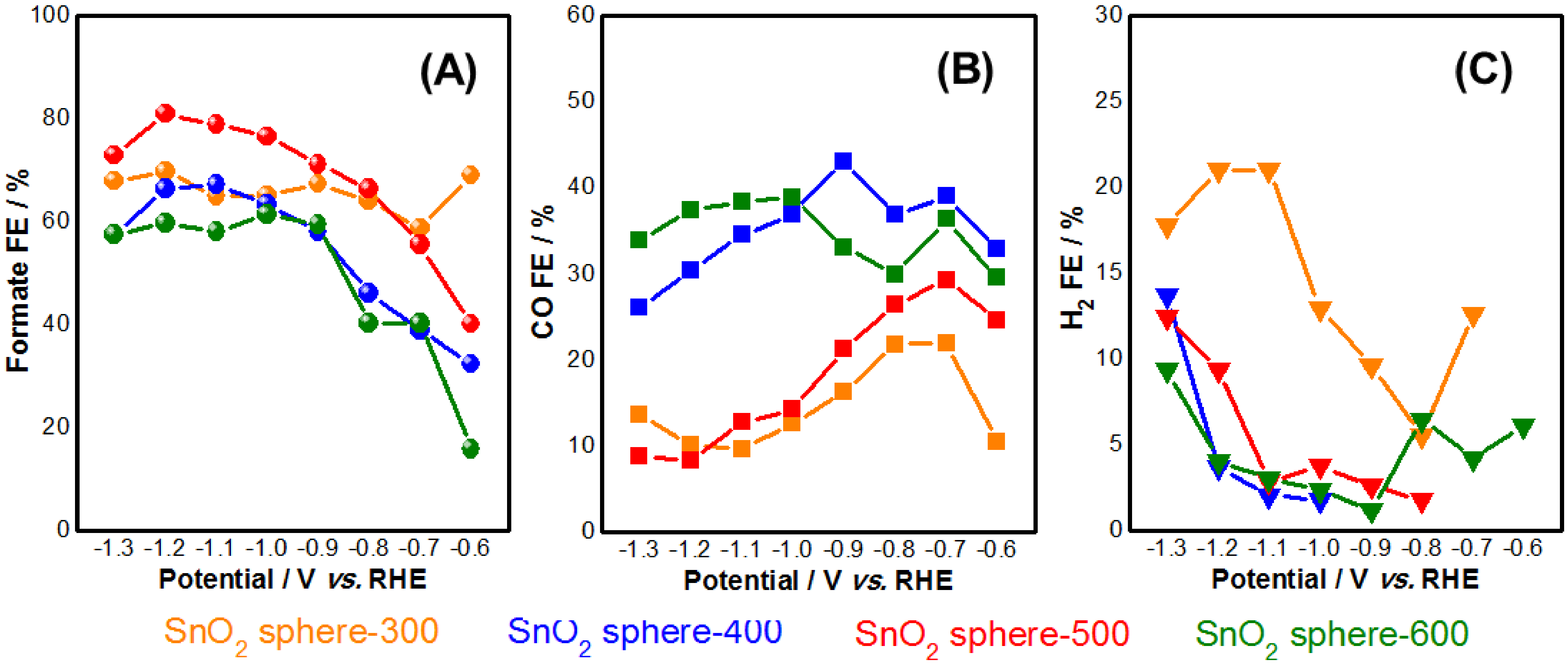




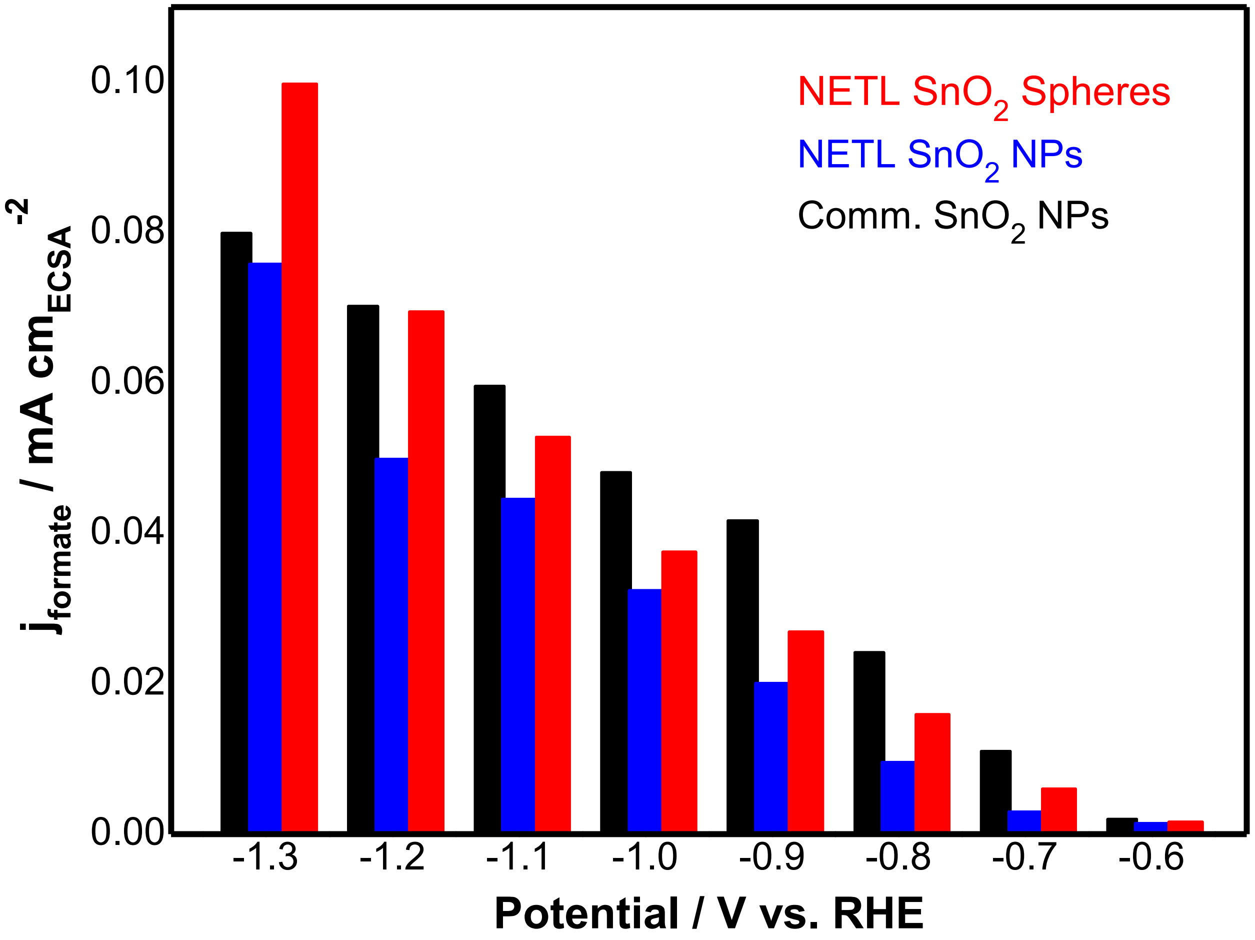
Temp Dependent Sn K-Edge EXAFS data



Potential Dependent Product FE



Current normalized to Electrochemical Surface Area



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