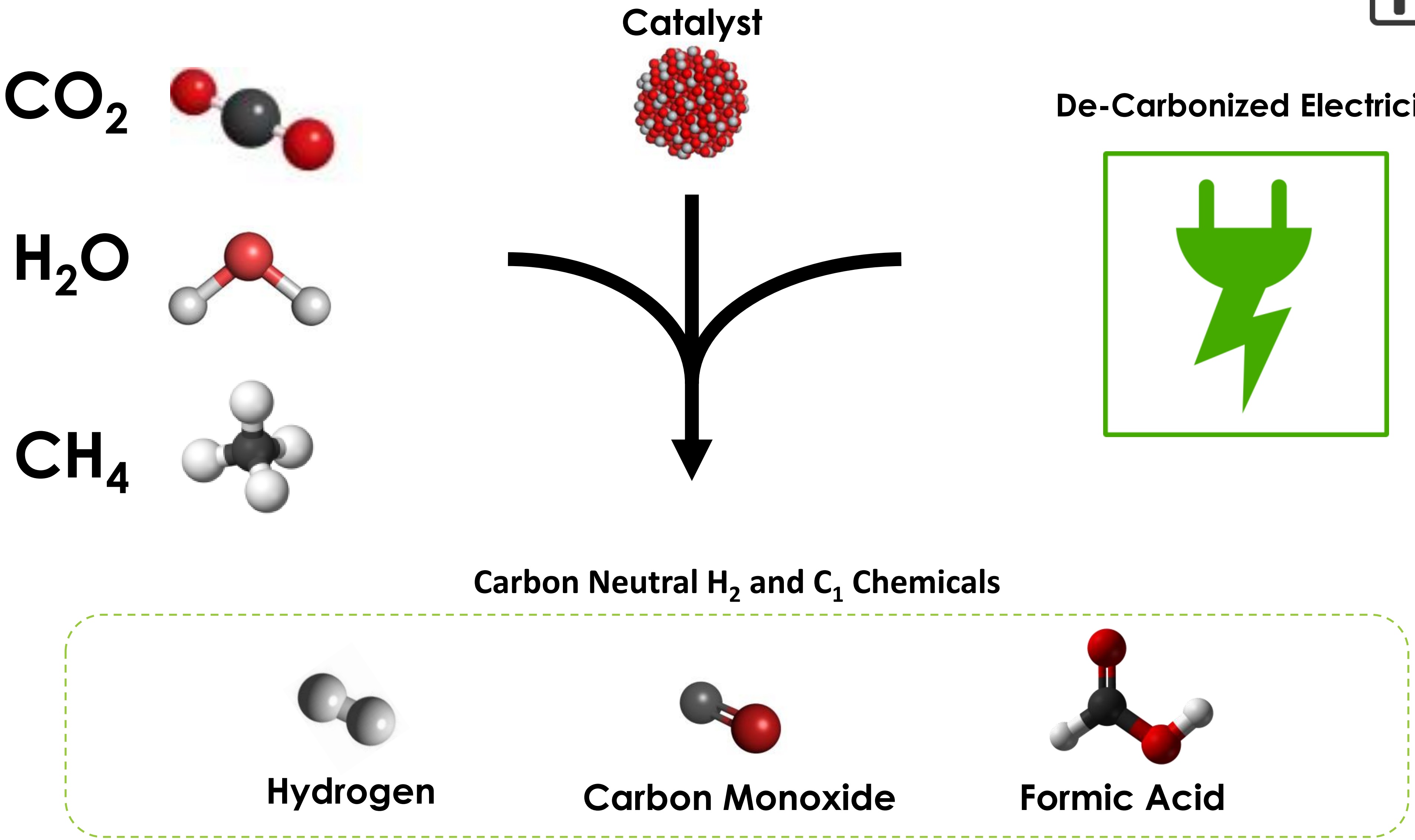
Electrochemical CO_2 Conversion at NETL

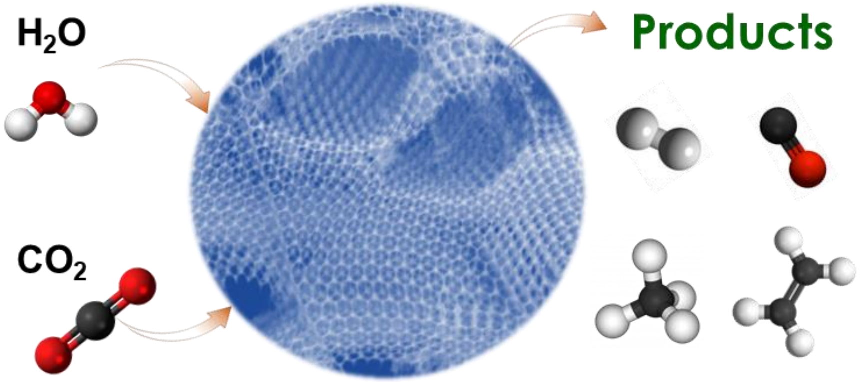
Douglas R. Kauffman

Catalytic CO_2 Conversion at NETL



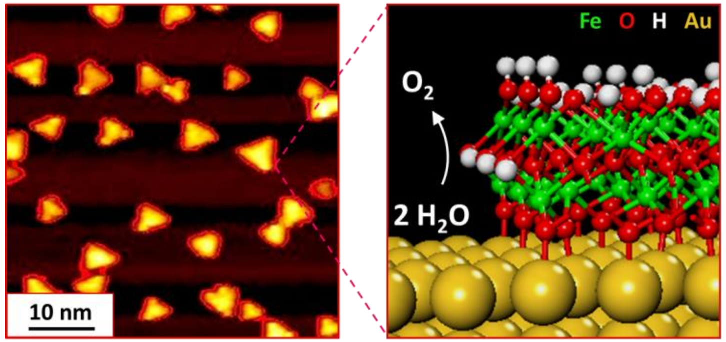
Electrochemical Catalyst Design

Structure-controlled product selectivity

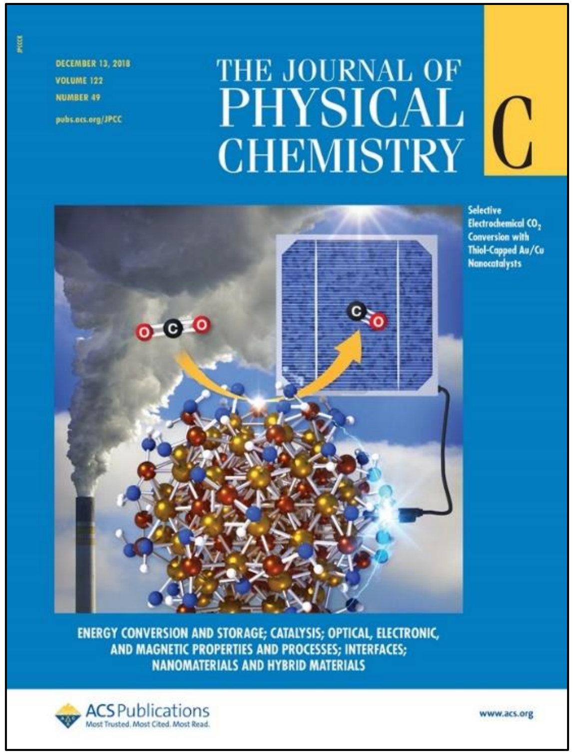


J. Mater Chem. A, 2019, 7, 27576

Surface-science enabled electrocatalysis



"Atomically Precise" nanocatalysts



JPCC, 2018, 122, 49, 27991

ACS Catalysis, 2020, 10, 12011

Angew. Chem. Int. Ed., 2021, 133, 6421

ACS Catalysis, 2019, 9, 5375

ACS Catalysis, 2020, 10, 11768

3D Structured SnO_2 Catalysts

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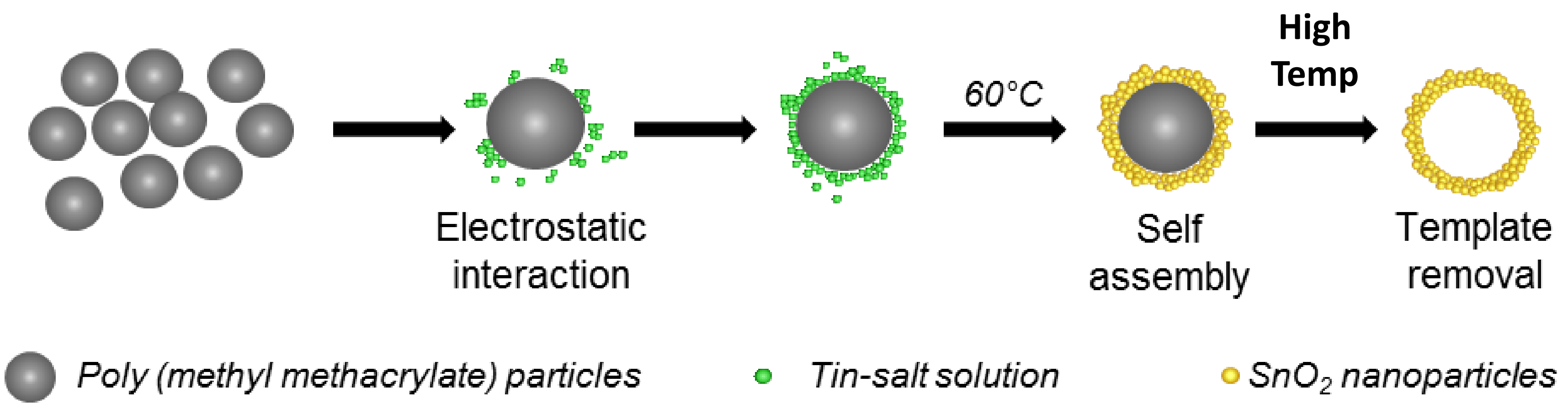
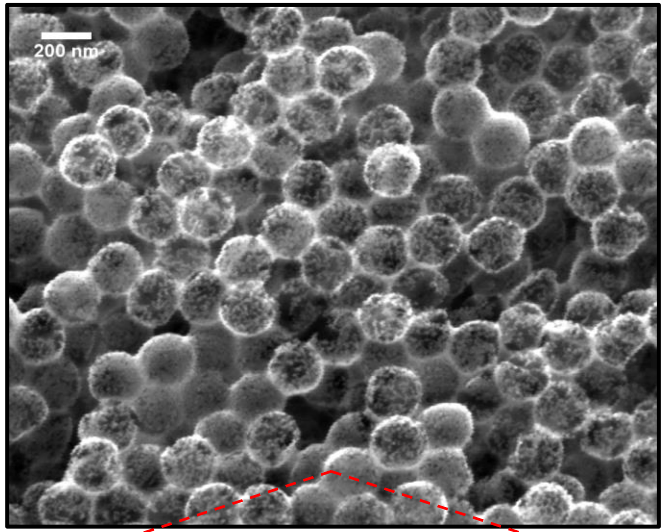
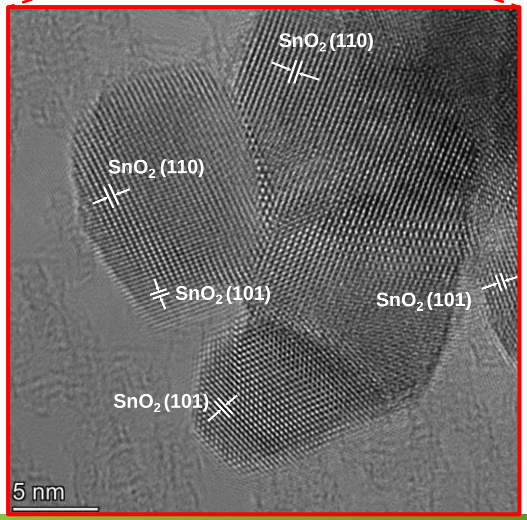
- **Electrochemically reduce CO_2 to formate/formic acid (HCOO^{-} / HCOOH).**
- **Formic acid has agricultural and industrial uses.**
  - Currently produced via natural gas reforming and methanol processing.
  - Extremely carbon intensive.
- **Formic acid is also an emerging energy carrier (53 g H_2 / L)**
- **Key Challenges:**
  - Current density
  - Stability / durability
  - Scalable catalyst synthetic procedure.

Catalyst Synthesis Approach



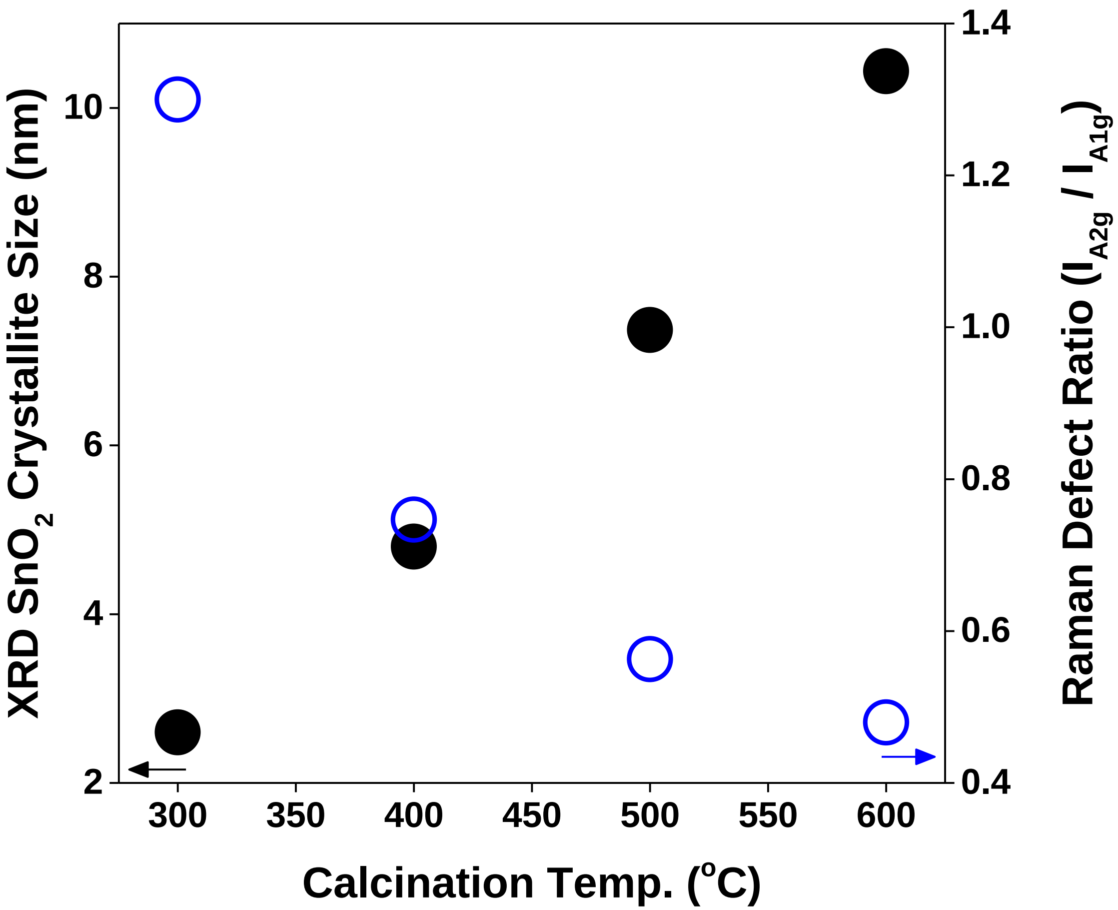




- **PMMA template produces sphere diameter at ~200 nm.**
- **Control the size and crystallinity of constituent SnO_2 nanoparticle by air calcination temperature (300-600ºC.)**
- **Simple solution-phase synthesis and thermal processing**

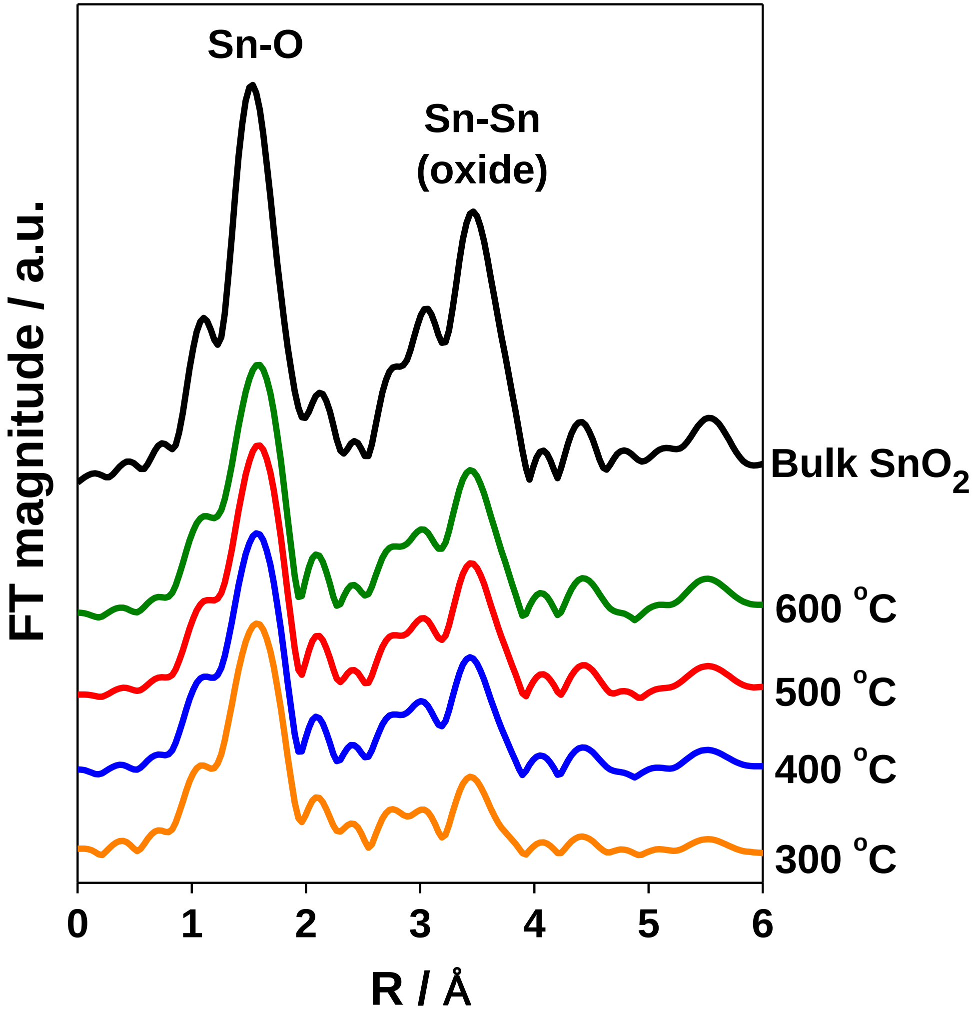
US patent application submitted and manuscript in preparation

Characterization Results



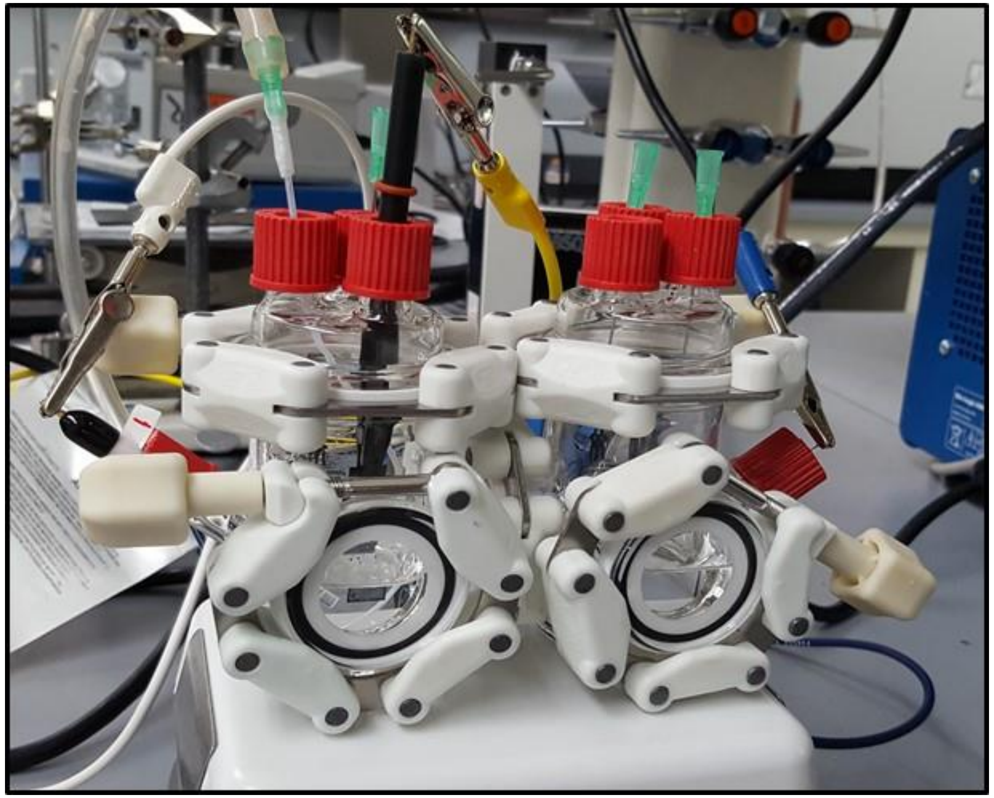
- **XRD, XPS and Raman showed higher calcination temperatures produced larger, more crystalline SnO_2 NPs.**

Characterization Results



- XRD, XPS and Raman showed higher calcination temperatures produced larger, more crystalline SnO_2 NPs.
- XRD, XPS, EXAFS and Raman all confirmed SnO_2 oxidation state.
- Performance differences stem from the size and crystallinity of constituent nanocrystals.

Electrochemical Details

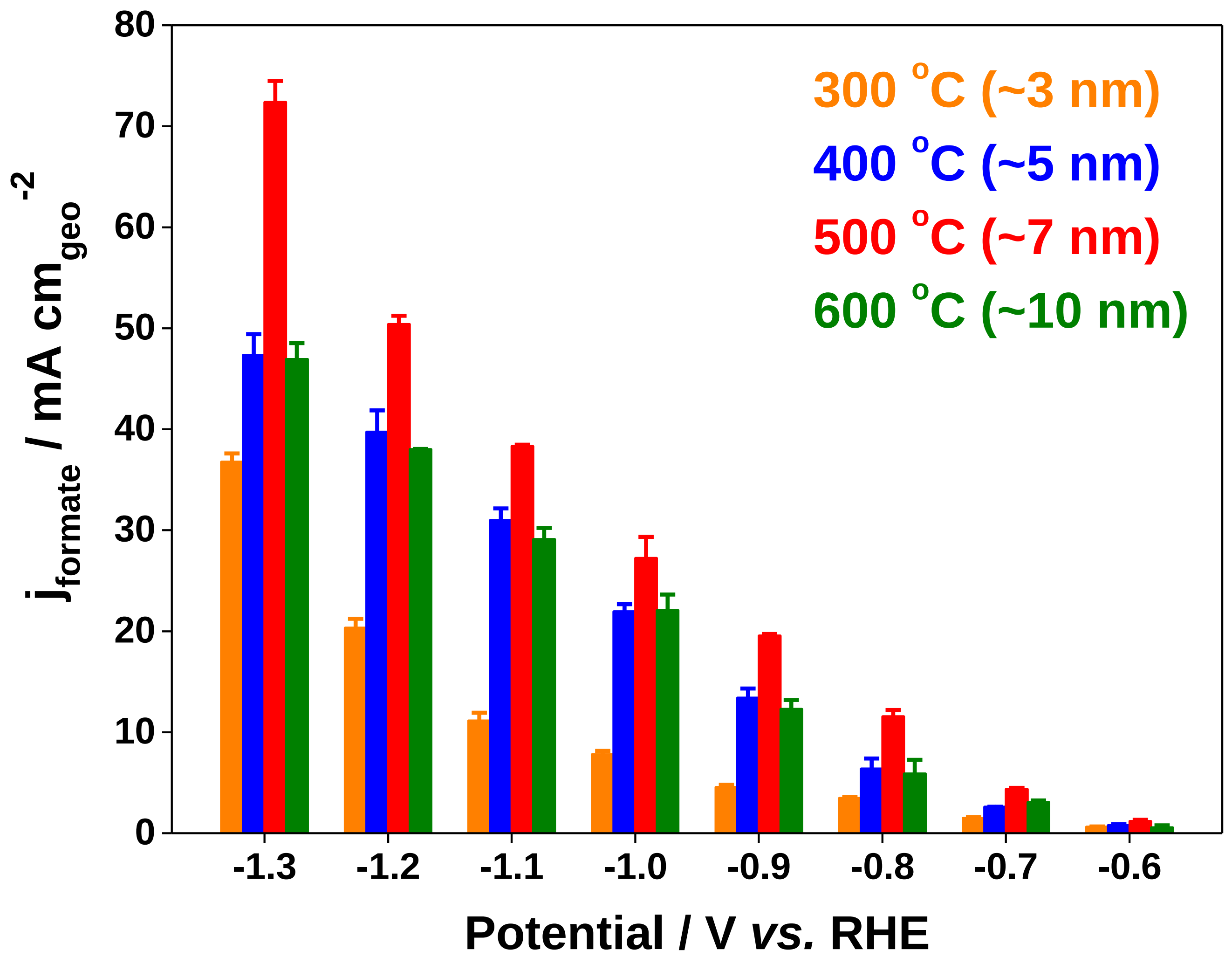


Cathode Chamber

Anode Chamber

- SnO_2 catalysts mixed w/ ~10 wt% carbon black powder to increase conductivity & Nafion binder.
- Deposited onto PTFE-coated carbon paper electrodes at 5.4 mg_{SnO2}/cm_{geo}^2.
- Electrochemical H-Cell screening conducted in CO_2 saturated 0.1M $KHCO_3$

Catalyst Activity vs Calcination Temperature

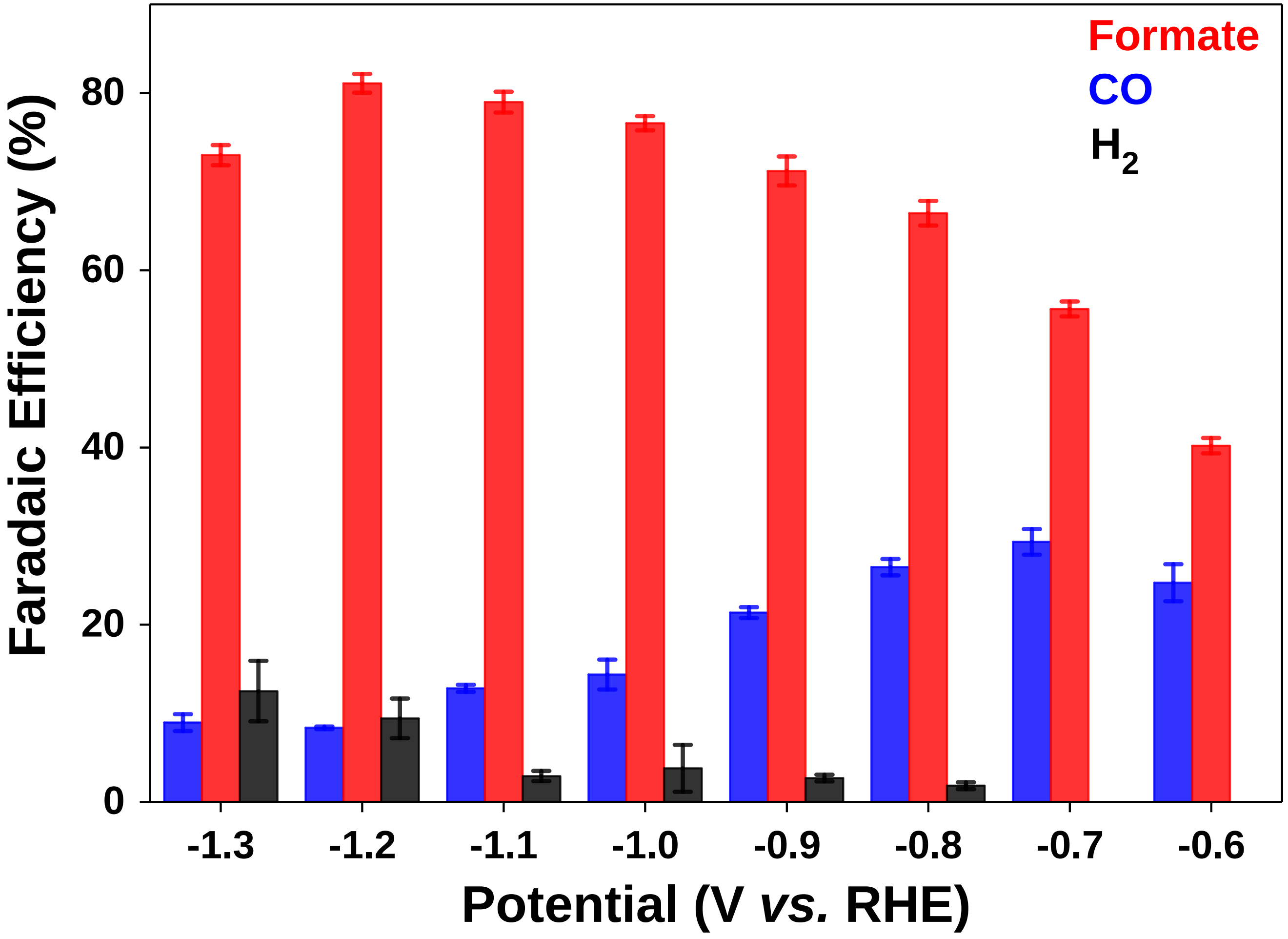


Balance between crystallinity and particle size

- **<500 °C the SnO_2 formed smaller, less crystalline NPs.**
  - Lower formate partial current density.
  - Increased HER (~20% FE).
- **>500 °C produced larger SnO_2 particles with lower activity.**
  - Reduced active surface area

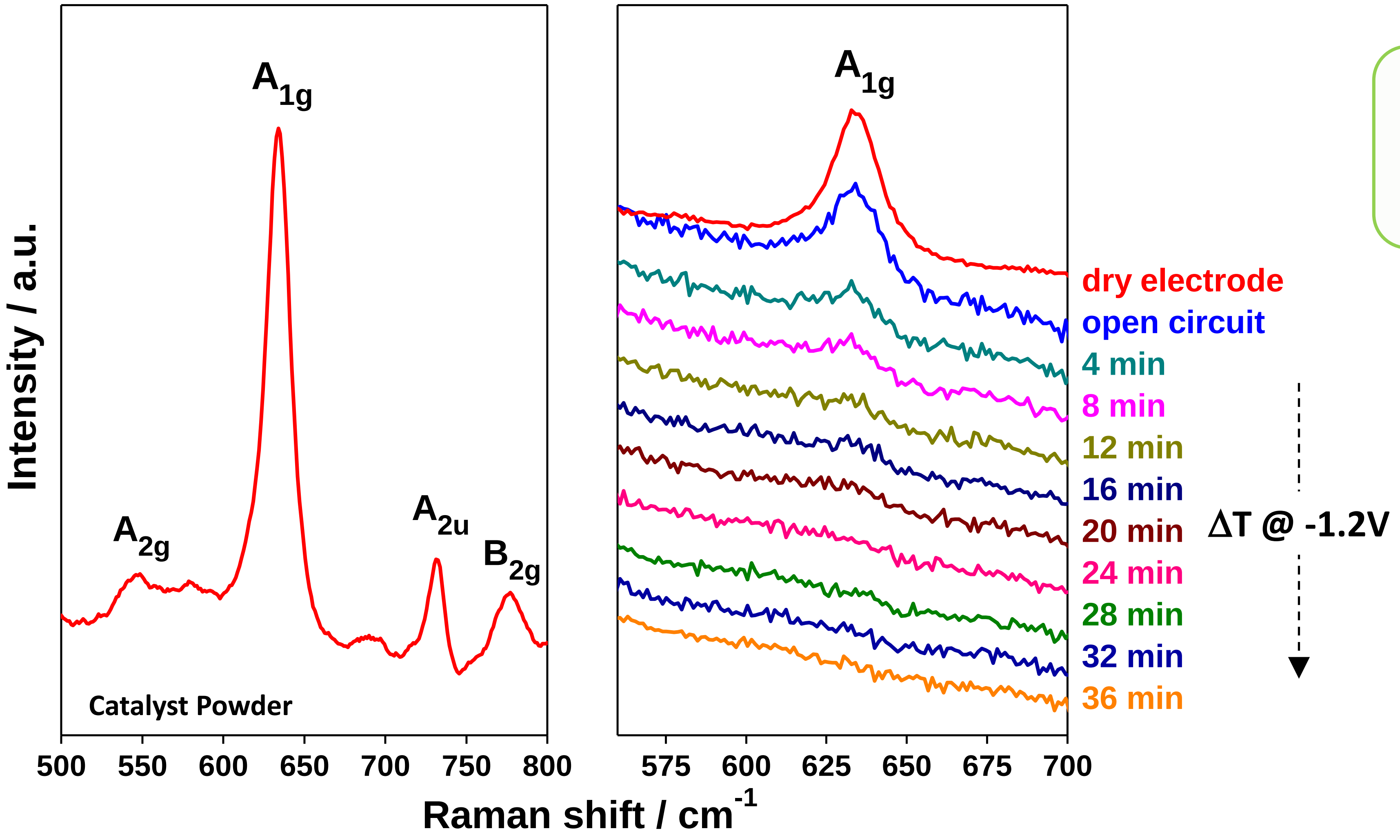
Product Selectivity

500 °C calcined SnO_2 Nanosphere



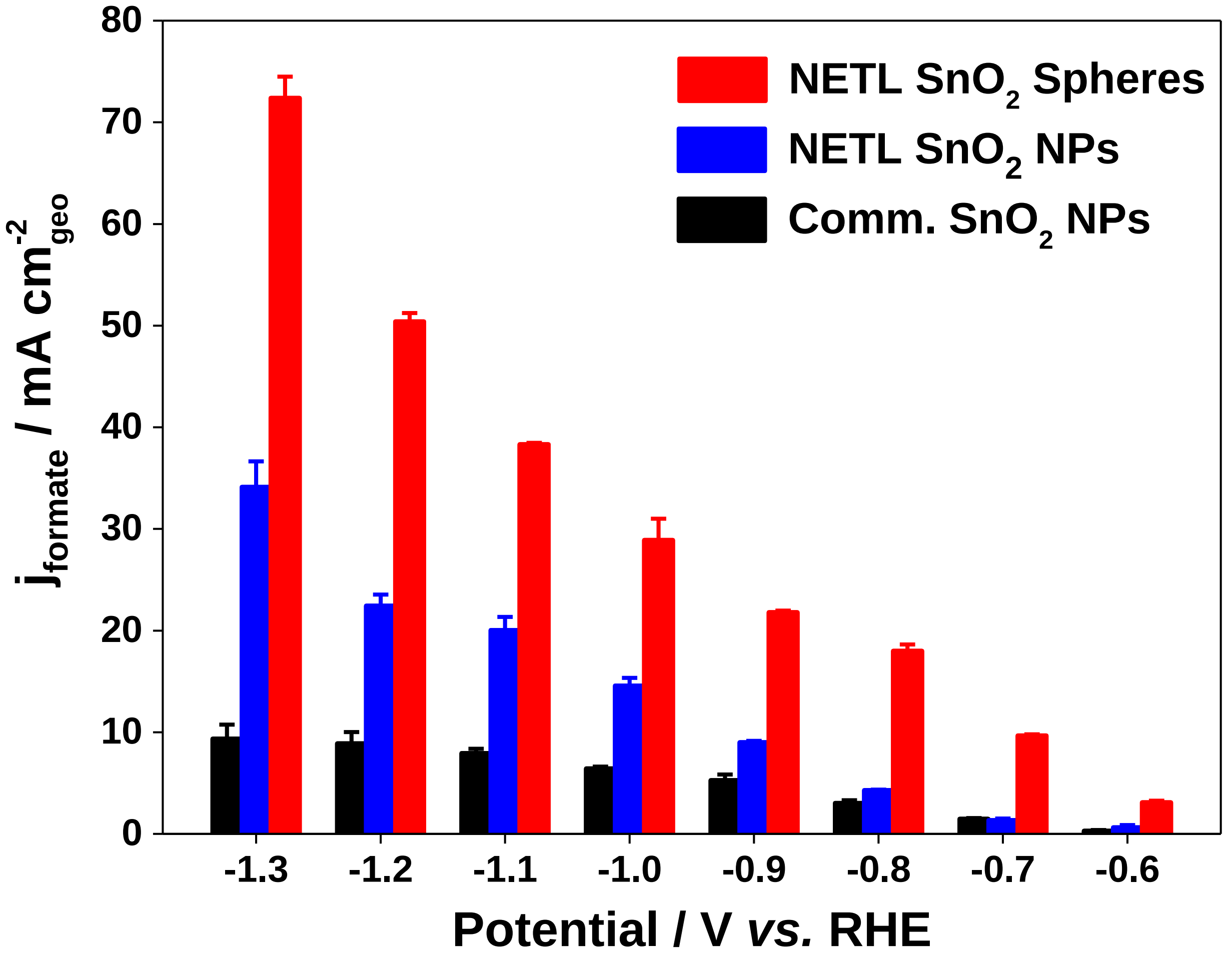
- **500 C calcination temperature produced highest activity and formate FE.**
- **CO and H_2 were the only other products detected.**

In situ Raman Spectroscopy



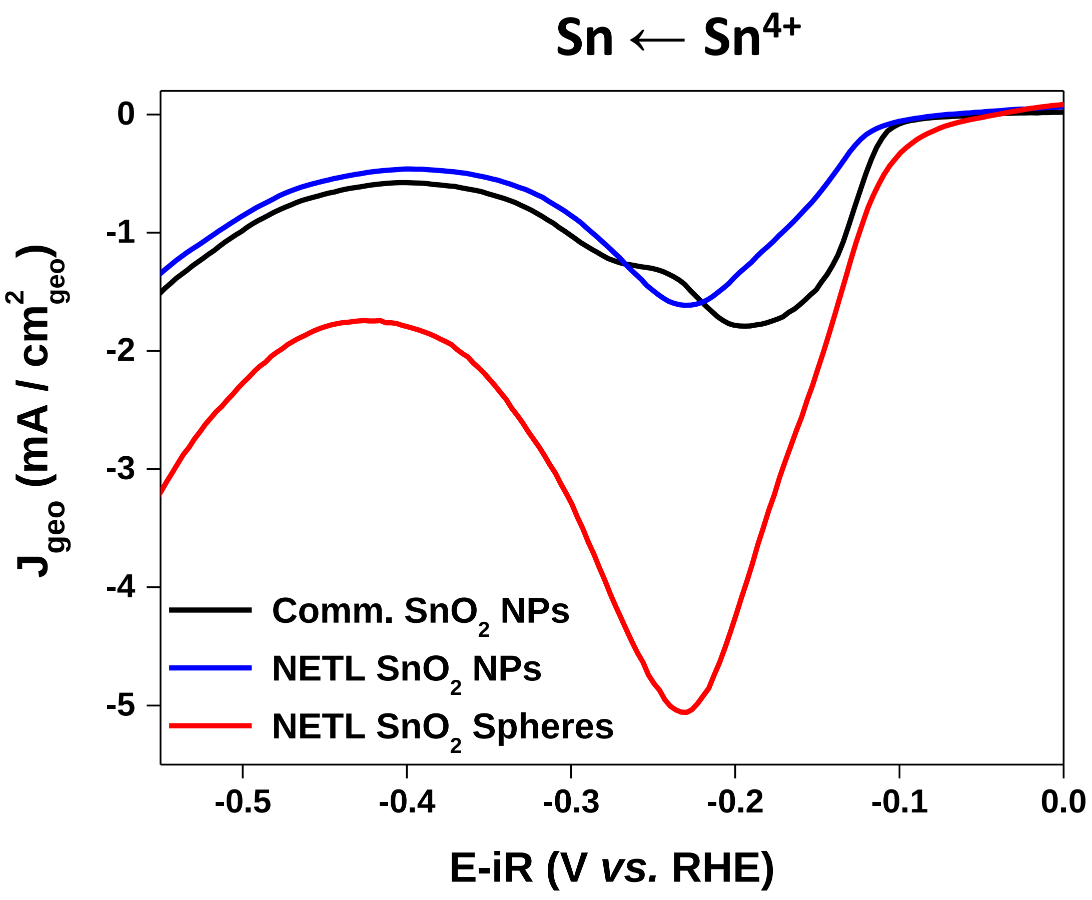
Rapid reduction of SnO_2 to metallic Sn during CO_2RR.

Benchmarking Catalyst Performance



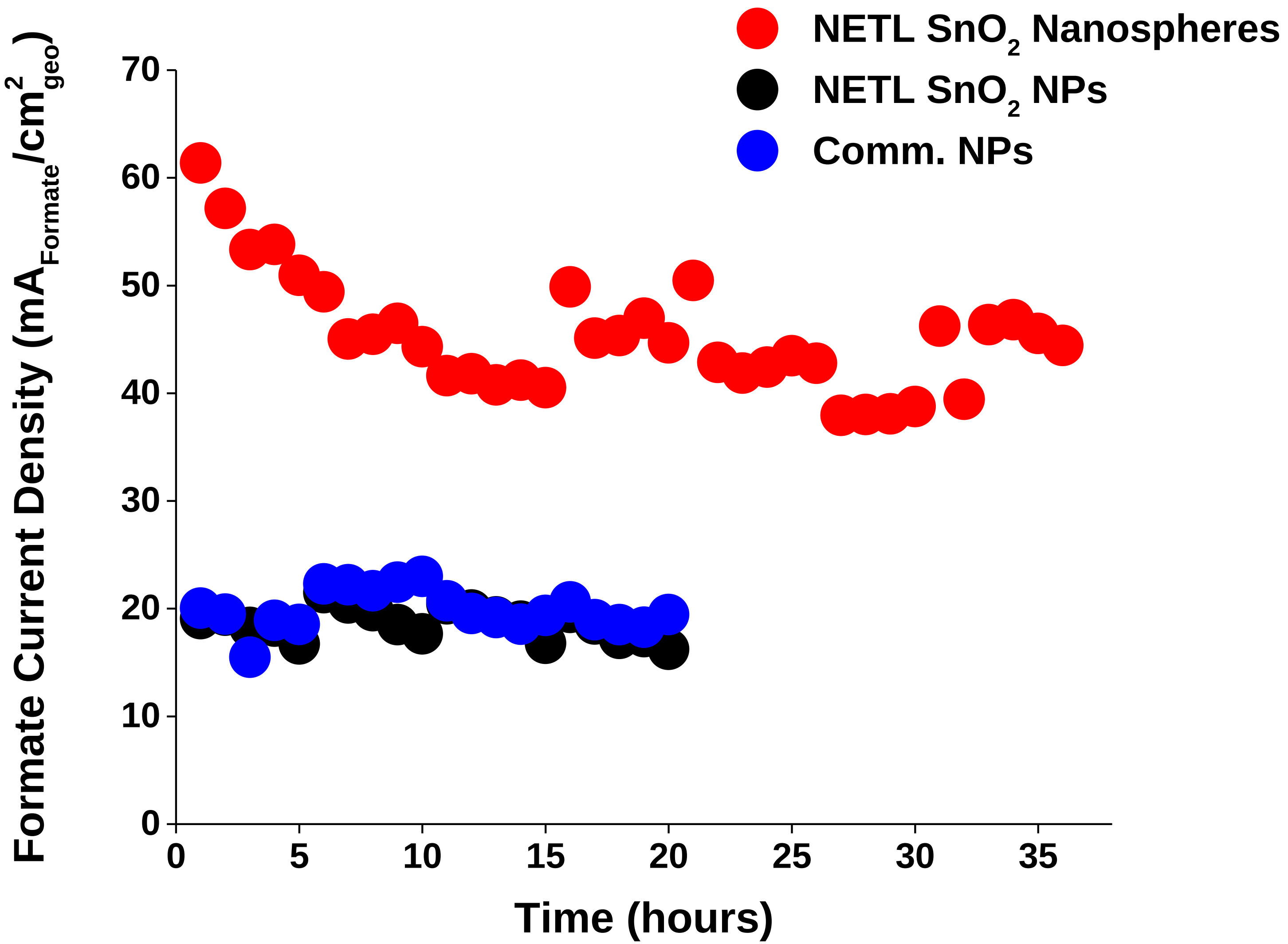
- Benchmarked against commercially available SnO_2 catalyst particles (Sigma Aldrich; ~28 nm diameter NPs)
- Benchmarked against identically synthesized non-templated SnO_2 nanoparticles (~8 nm diameter)
- Substantially higher formate partial current density at all potentials.

Estimating Active Site Density



- SnO_2 has characteristic redox peaks.
- SnO_2 reduced to metallic Sn during cathodic-going sweep.
  - Confirmed with *in situ* Raman
  - Overall 4 electron process.
- We can use the cathodic reduction peak to estimate active site density.
  - Integrated peak area (Coulombs; C)
  - C / (F*ne^-) = mol Sn sites
- NETL SnO_2 nanospheres have ~2-4 times higher active site density and ~2-3 times higher electrochemical surface area.

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



- NETL SnO_2 Nanospheres demonstrated ≥2x performance increase over SnO_2 NPs.
- Average 68±8% formate FE during 36 hour electrolysis
  - Multiple start/stop cycles

Post-Reaction Morphology

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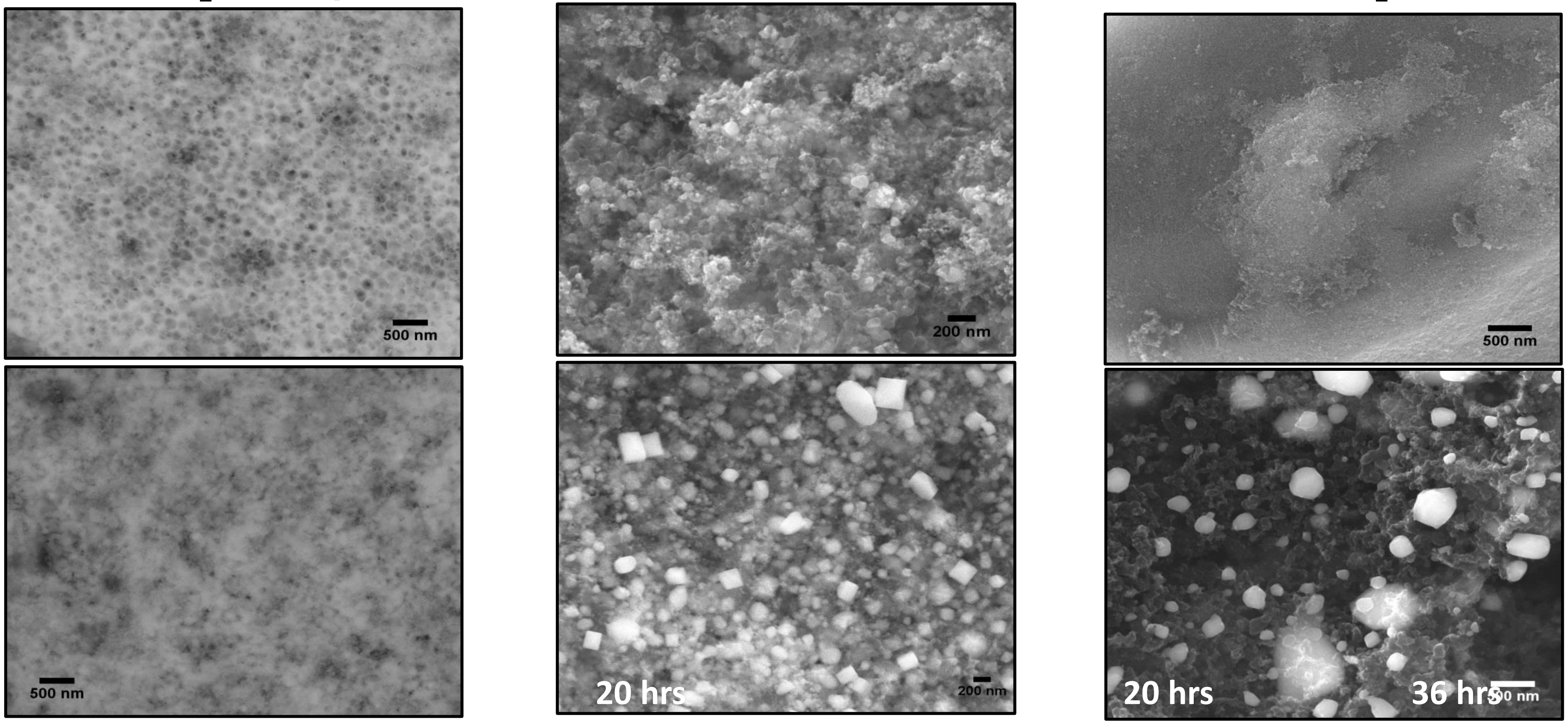
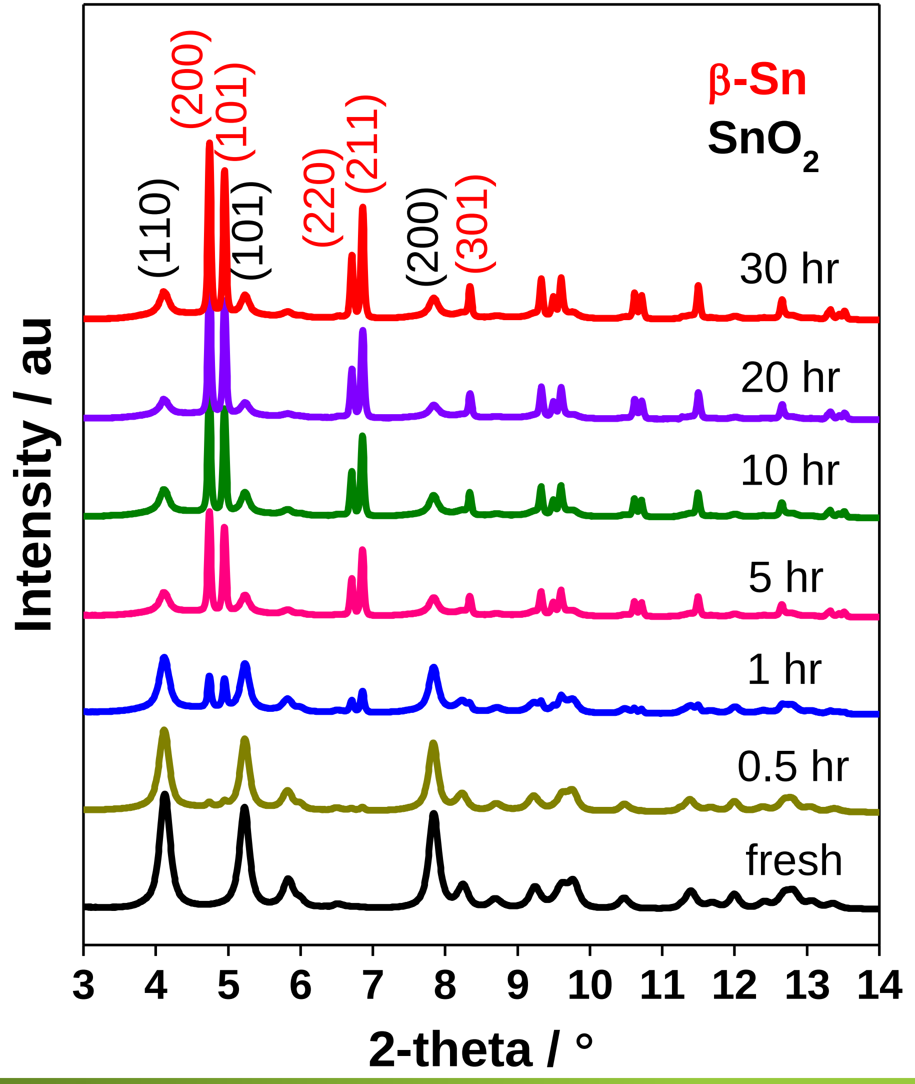
	NETL SnO_2 Nanospheres	Commercial SnO_2	NETL SnO_2 NPs
Before CO_2 Reduction			
After CO_2 Reduction			



U.S. DEPARTMENT OF ENERGY

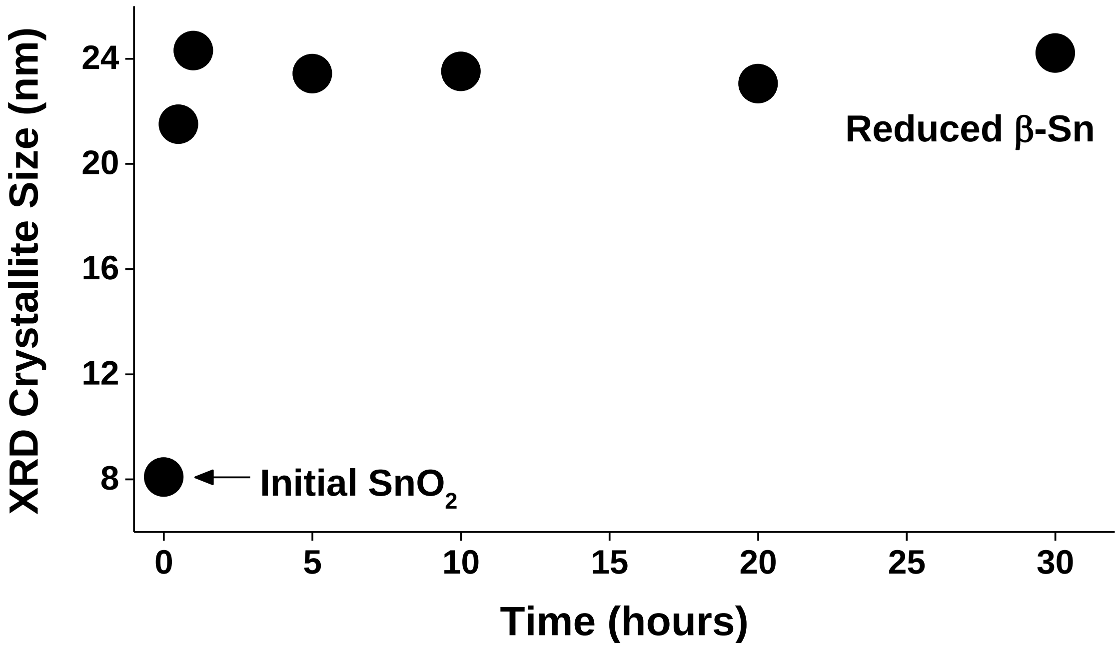
NETL SnO_2 Nanospheres resist large-scale particle agglomeration

Time Dependent X-Ray Diffraction

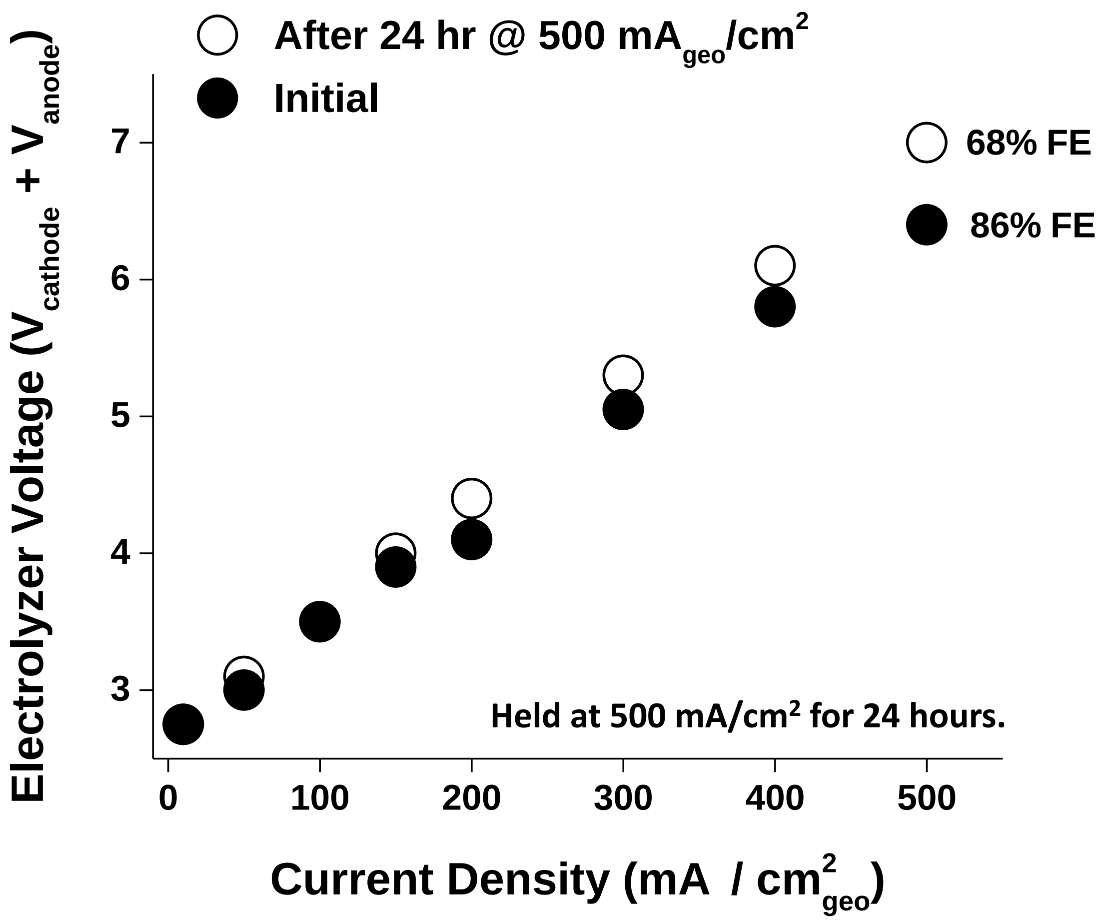


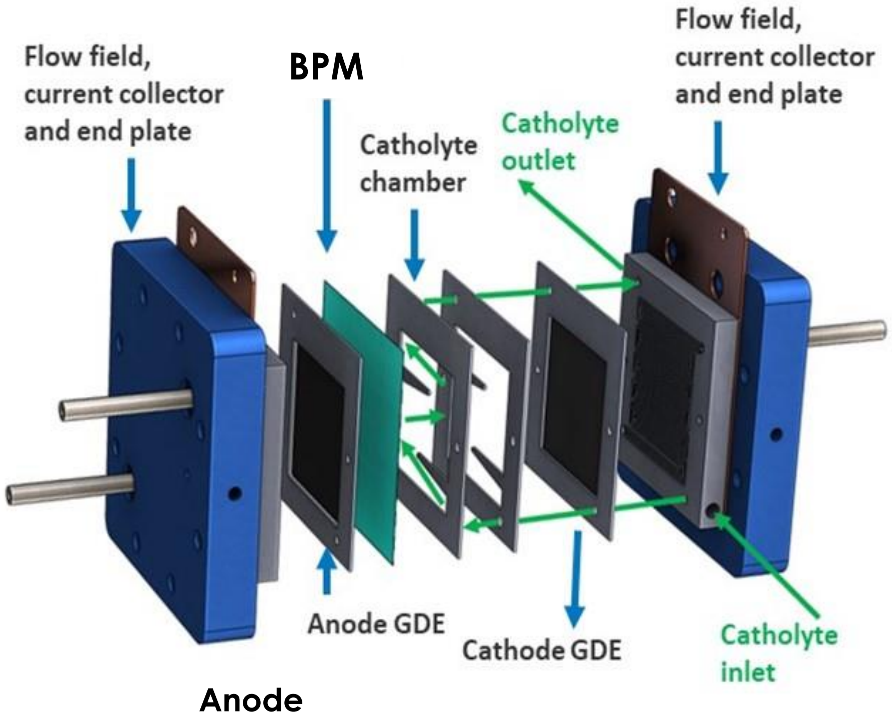
Time Dependent synchrotron X-Ray Diffraction shows:

- Rapid formation of ~25 nm metallic Sn nanoparticles with β-Sn crystallographic orientation.
- No further particle growth after initial reduction.
- Metallic Sn consistent with *in situ* Raman spectroscopy.



Electrolyzer Performance





- Collaboration with NREL
- 25 cm^2 electrode; 0.5 mg/cm^2 catalyst loading
- 0.4 M K_2SO_4 catholyte (40 mL/min)
- 1M NaOH anolyte (50 mL/min)
- Ni mesh anode

NREL Electrolyzer Design: *ACS Energy Lett*. 2020, *5*, 1825−1833

NETL SnO_2 Nanosphere Conclusions

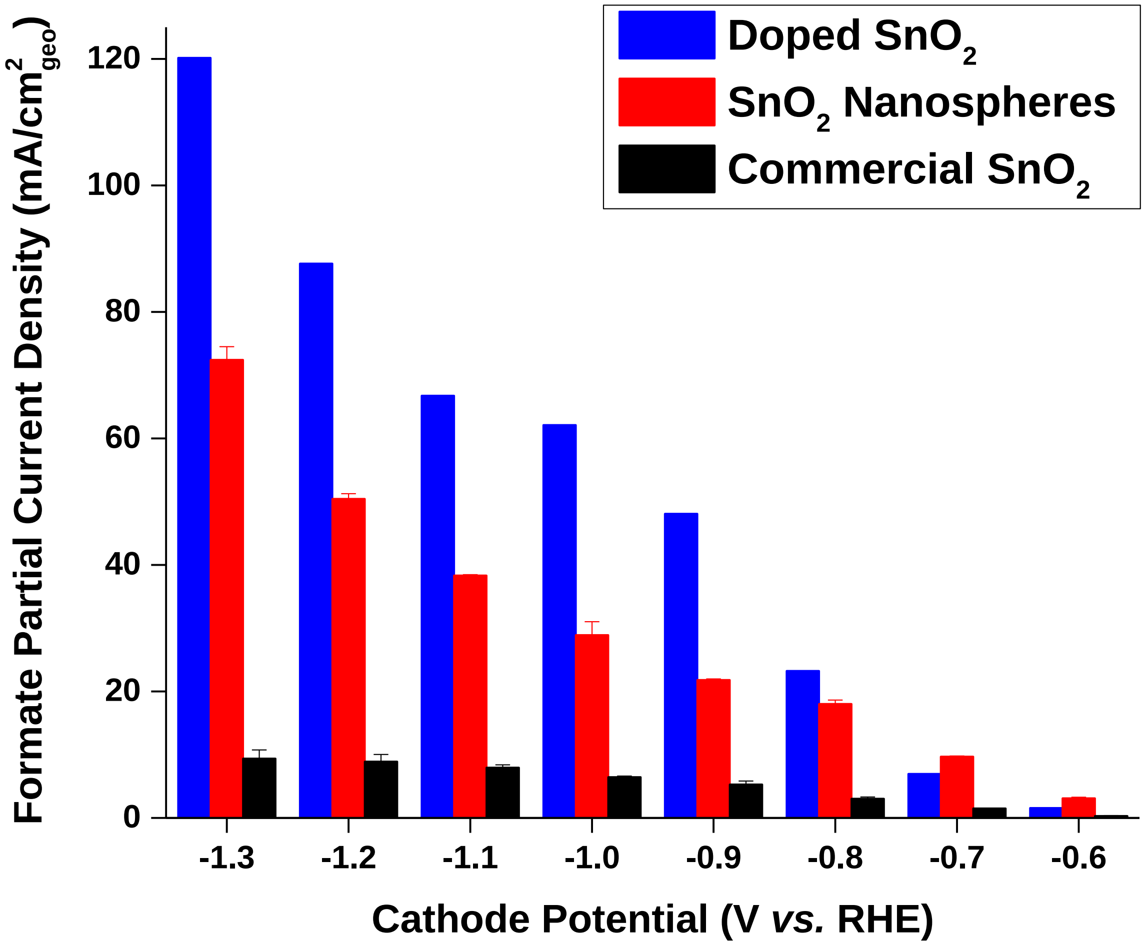
NATIONAL ENERGY TECHNOLOGY LABORATORY

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 under steady state H-Cell operation

2. **Raman and synchrotron-XRD show SnO_2 was quickly reduced to metallic Sn**

3. **Collaboration with NREL to evaluate NETL SnO_2 Nanospheres in electrolyzer**
   - Sustained 24 hour performance at industrially relevant current densities (~500 mA/cm^2).
   - Ongoing efforts to minimize component level losses (BPM degradation, overpotentials, etc.)

Moving Forward: Doped SnO_2 for Improved Performance

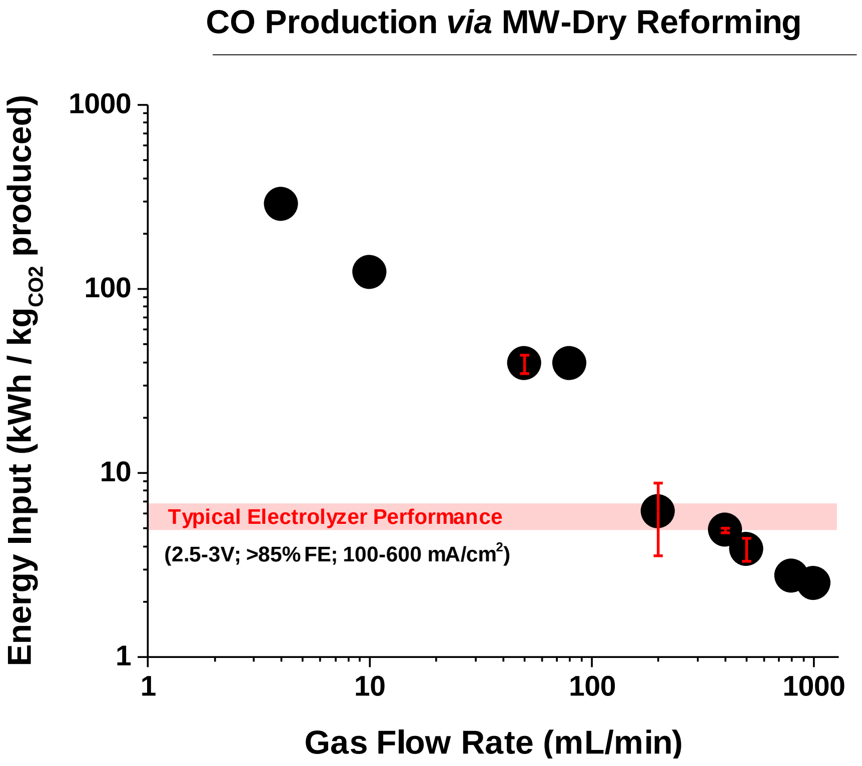


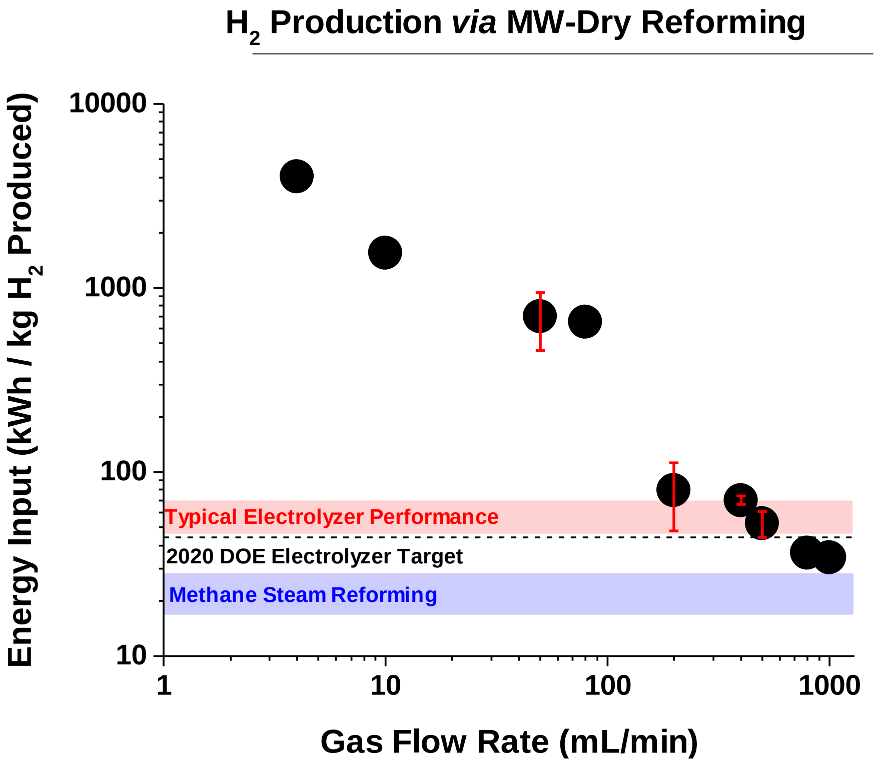
- **Doping Strategies to improve performance.**
- **Scalable synthetic strategy.**
- **Preliminary H-Cell data shows excellent activity and good stability.**
- **Initiating in-house electrolyzer testing.**

***Patent application and manuscript in preparation.**

Alternative CO_2 Utilization Technology: Microwave Catalysis

- Microwave-assisted Dry Reforming of Methane: $CO_2 + CH_4 \rightarrow 2CO + 2H_2$
- Electrically-driven process; microwaves selectively and rapidly heat catalyst bed to ~900C.
- Ultra-efficient production of CO and H_2; >80% single pass conversion.
- Kilogram-scale catalyst production.





Patent application and *Appl. Catal. B,* 2021, 284, 119711

Key Contributors

Catalyst Design, Characterization, and Electrochemistry: Thuy-Duong Nguyen-Phan and Douglas Kauffman (NETL).

Electrolyzer Validation: Leiming Hu and K. C. Neyerlin (NREL).

Synchrotron XRD : Wenqian Xu; beamline 17-BM-B (ANL; APS).

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

Acknowledgement and Disclaimer

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Questions or Comments?

Thank you for your attention!

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