UCONN

Metal Oxide Nano-Array Catalysts for Low Temperature Diesel Oxidation

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& Institute of Materials Science
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Washington D.C.

Project ID #: ACE095

Project Overview

Overall objective:

Develop a unique class of cost-effective and high performance metal oxide based nano-array catalysts for low temperature CO and HC oxidation, 90% conversion at 150 °C or lower

Timeline

- Project start date: 10/01/2014
- Project end date: 8/31/2017
- Percent complete: ~50%

Budget

- Total project funding
  - DOE share: $1,450,000
  - Contractor share: $380,139

Barriers

- Barriers addressed
  - From DOE Vehicle Technologies Multi-Year Program Plan
    - 2.3.1.B: Lack of cost-effective emission control
    - 2.3.1.D: Durability
  - Responsive to USDRIVE ACEC Tech Team Roadmap, Low Temperature Aftertreatment Workshop Report

Team Partners

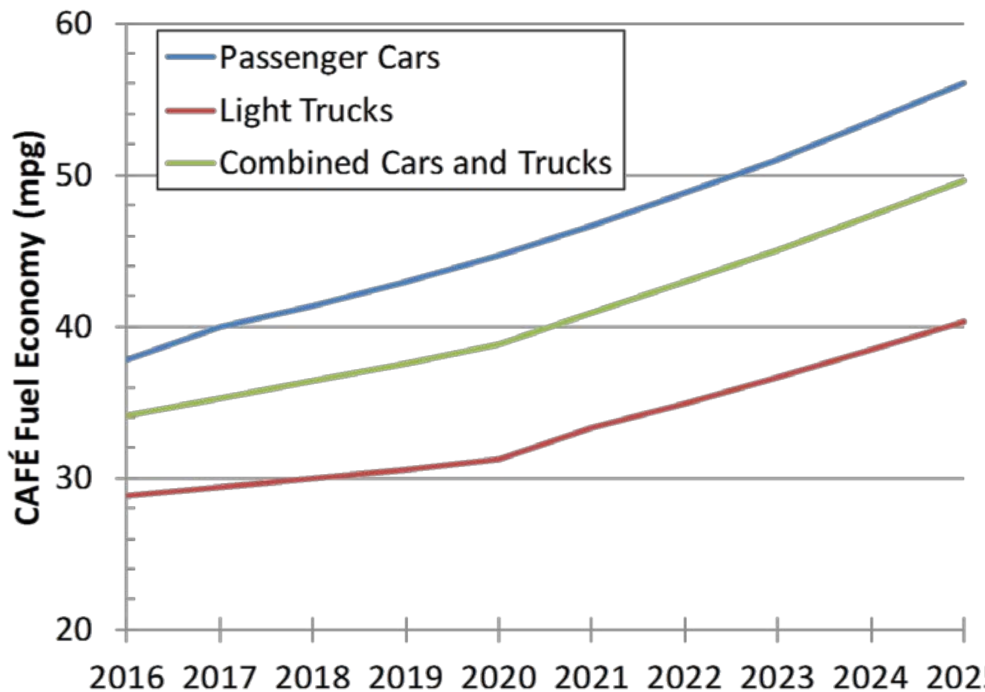
- ORNL, Umicore, and 3D Array Technology LLC

Project Relevance

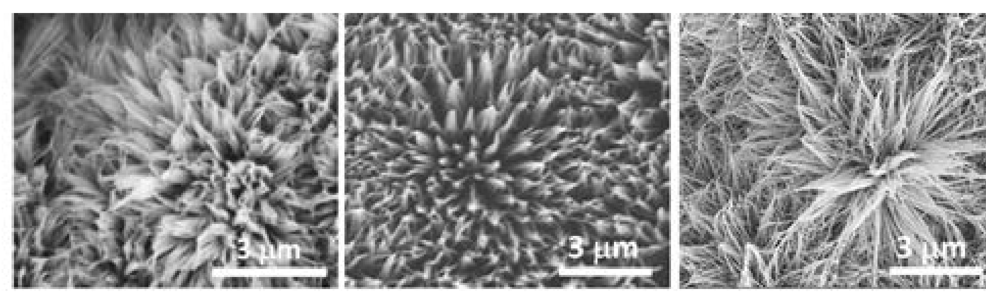
- Improved fuel economy standards will require advanced combustion engines with greater fuel efficiency and consequently **low exhaust temperatures**
- Challenges:
  - Stricter emissions standards
  - Greater HC + CO emissions
  - Low reactivity at 150°C

→ **New technology needed**

→ Investigate nano-array catalysts for low-cost pathway to 90% conversion of HC + CO at 150°C

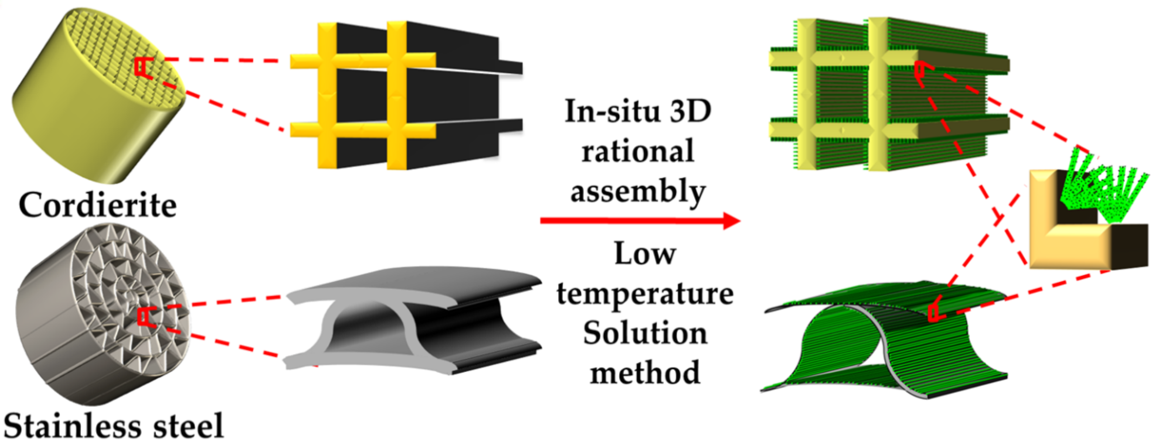


C. DiMaggio, "ACEC Low Temperature Aftertreatment Program", 6/21/12.

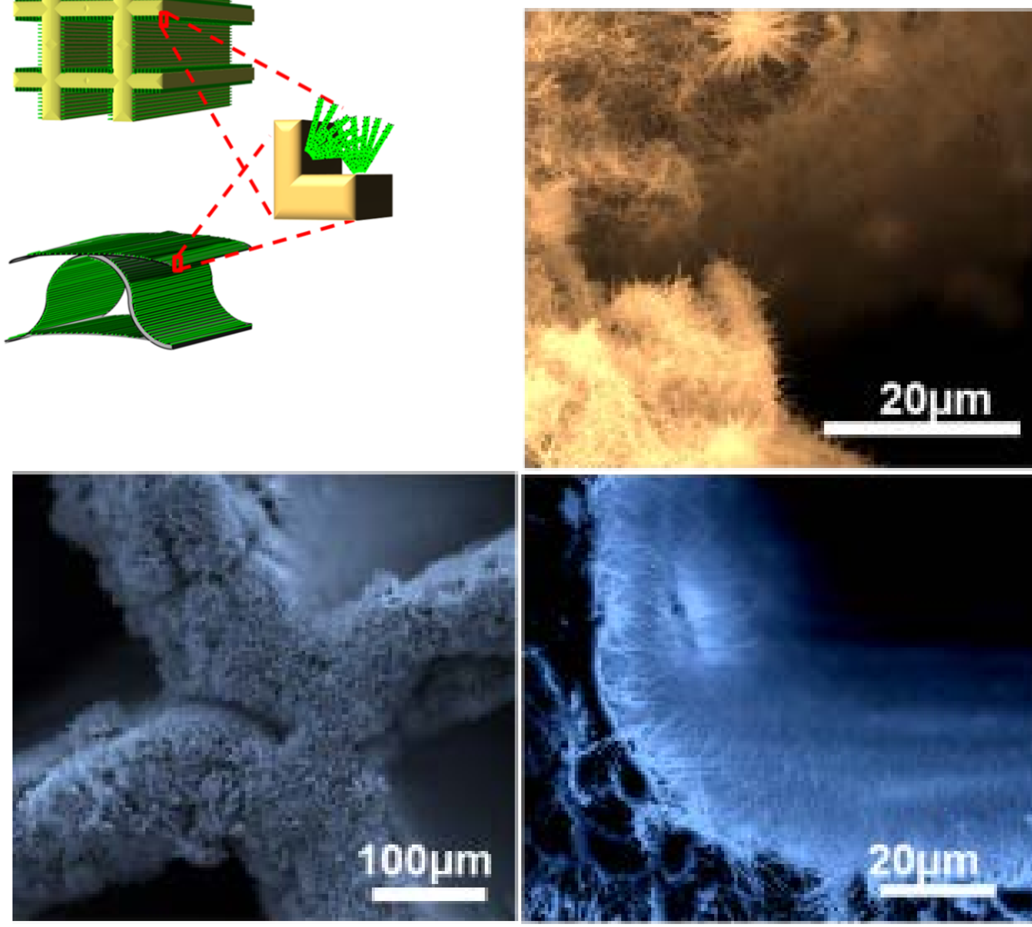


$Ni_xCo_{3-x}O_4$ $Zn_xCo_{3-x}O_4$ $Mn_xCo_{3-x}O_4$

In-situ Growth of Nano-arrays onto Honeycomb Monoliths



- In-situ solution-based growth of (nanostructure array) nano-array on monolith
- Free of binders, robustness due to the strong substrate-array adhesion after in-situ growth
- Reduced PGM and other materials
- Improved efficiency due to size, shape, and structure



Ren, Gao et al., *Angew. Chem. Int. Ed.*, **2014** , 53(28), 7223–7227.
Guo, Ren, Gao et al., *Nano Energy*, **2013,** 2, 873-881.
Ren, Gao et al., *J. Mater. Chem. A.*, **2013** , 1, 9897-9906 **.**

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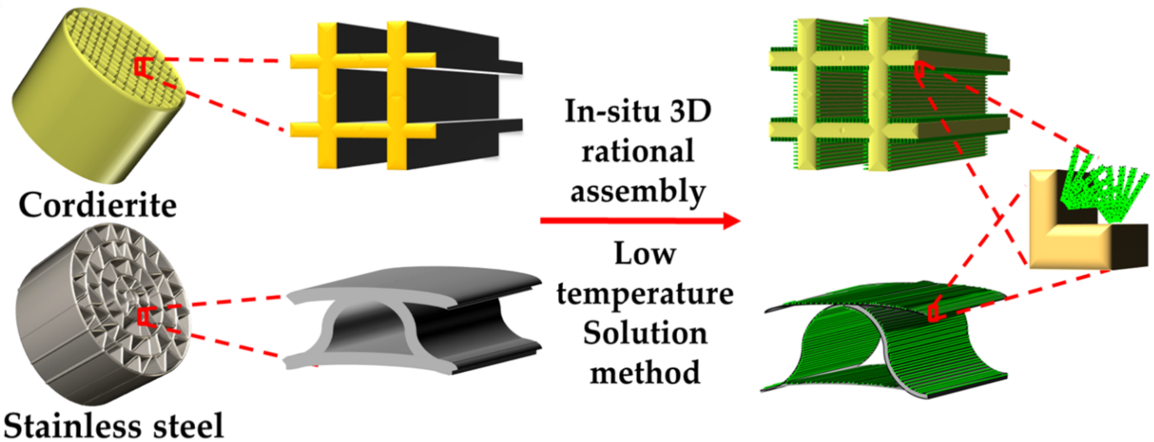

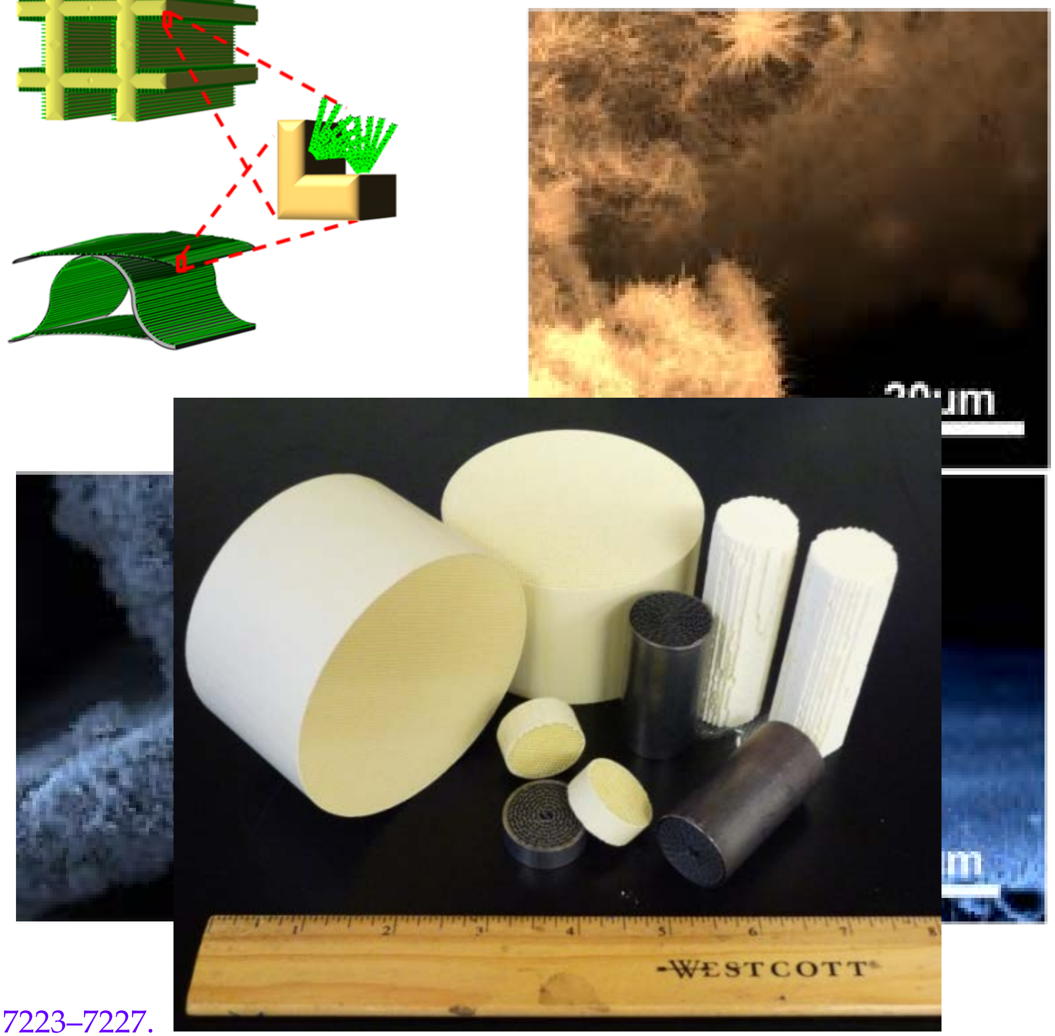

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- ➢ Free of binders, robustness due to the strong substrate-array adhesion after in-situ growth
- ➢ Reduced PGM and other materials
- ➢ Improved efficiency due to size, shape, and structure
- ➢ **Demonstrated on a range of scales**

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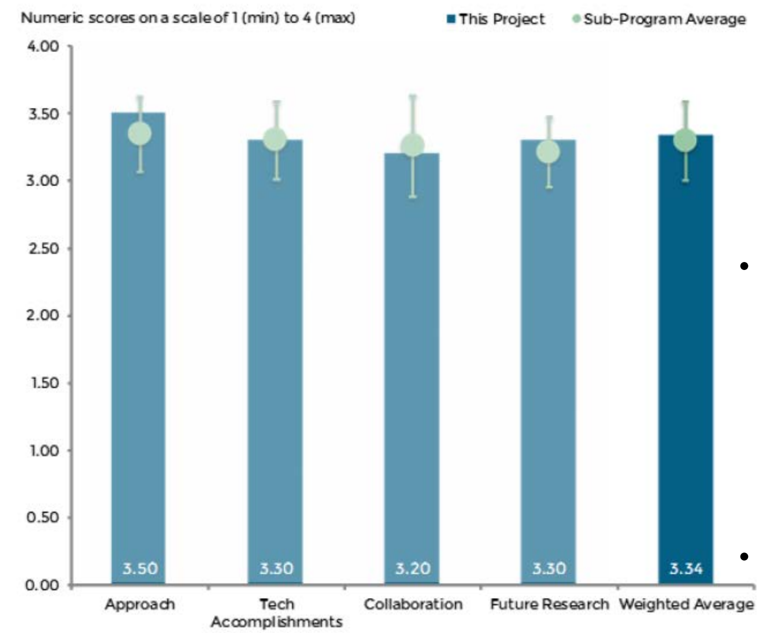
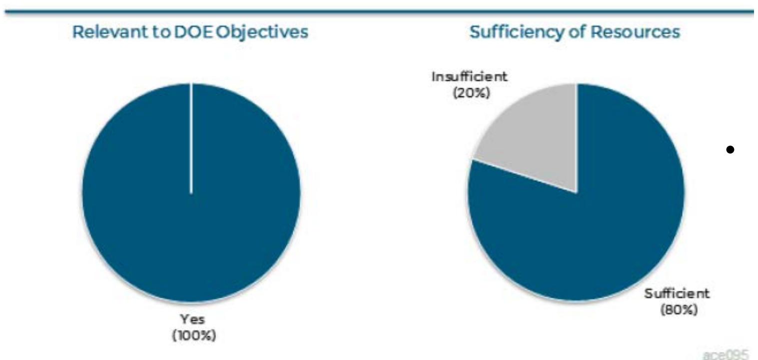
Responses to 2015 Reviewers (5)





- **Approach (3.5/4.0):** outstanding novel approach to grow and characterize nano-arrays on monolith with and without PGM using potentially scalable methods including solution and gas phase approaches.... Inclusion of ORNL team in project is also a key to the approach being kept focused on what may work in real catalyst systems....**the appropriate test conditions that include known CO and HC reaction inhibitors at low-temperature were not used in the screening process**...use of rare-earth and base metals as a substitute for precious metals is a novel approach **...it is very important for this approach to show that there is sufficient surface area to carry out the reaction in real exhaust.**... Need to show effects of thermal aging on the activity for all of the catalysts,.
- **Technical Accomplishments (3.3/4.0):** excellent accomplishments demonstrating capability to grow and test PGM-free nano-array catalysts such as spinel MxCo3 -xO4...coating on a monolith and doing the activity measurements are great accomplishments... **the team needs to define the test conditions better, in regards to gas concentrations, space velocity, aging**...The number of systems on the to-do list is large. It could be **better to focus on the most promising and needed materials, even if others are easier to work with**.
- **Collaborations (3.2/4.0):** excellent collaboration with national laboratories, a catalyst manufacturer, and novel nano-structure company... **inclusion of an OEM or wash coat supplier to help determine the viability of the material and production process at an early stage would have benefited this project**...collaborations are sufficiently broad, with a full ORNL and Umicore involvement. These, particularly Umicore, should be useful, again to keep the evaluations realistic.
- **Future plans (3.3/4.0):** there was an excellent map for future with metal oxide nano-array catalysts designed forfor: performance at 150°C or lower, optimized PGM loading with perovskite nano-particles, CO and HCs oxidation tests under simulated exhaust atmosphere, and engine testing in FY 2016.... project team is proceeding down this pathway; however, **there is no specific approach to mitigate the water and sulfur problems**.... **Down selection, as mentioned already, should be considered, because of the breadth of catalyst families in the program**. ... **project team needs to explore sulfur tolerance and desulfation capability of the more promising candidates**. **2016 is probably premature for engine testing.**
- **Relevance (100%):** this low-temperature catalyst project would be extremely important

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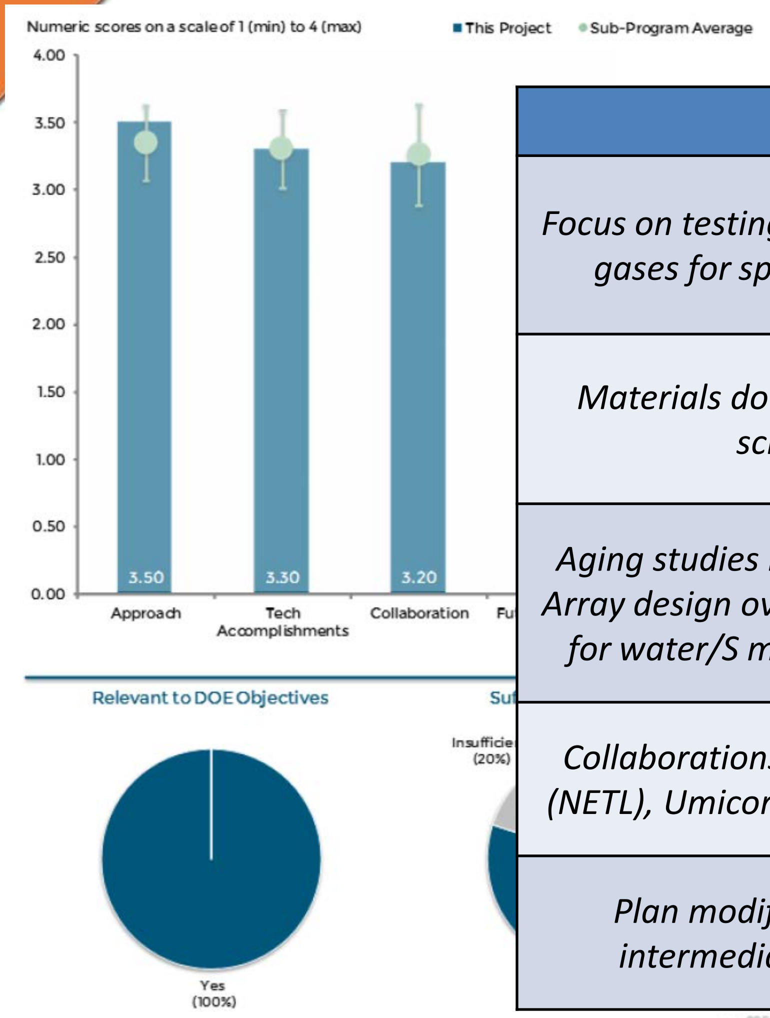


Responsive Actions
Focus on testing under realistic simulated gases and mixture gases for species inhibition/promotion understanding
Materials down selection through literature review, test screening and team brainstorming
Aging studies being performed (including sulfur exposure); Array design over PGM doping and CeO_2 or Al_2O_3 decoration for water/S mitigation; Surface area tracked for catalysts
Collaborations grow: national labs besides ORNL and BNL (NETL), Umicore, and Universities (Georgia Tech, UT Dallas)
Plan modified: engine test in June-July FY16-FY 17, intermediate transient test conducted at Umicore.

- **<u>Relevance (100%):</u>** this low-temperature catalyst project would be extremely important

Technical Accomplishments

(Project period: 4/1/2015-03/31/2016)

1) Demonstration of doped **Co_3O_4 nano-array** based catalysts with very good low temperature propane oxidation performance
   a) Doping agents: Ni, Mn and Cu

2) Demonstration of **ZnO/perovskite/Pt core-shell** metal oxide nano-array catalysts with tunable propane oxidation activities
   a) Pt-doping in perovskite, H_2 and acid treatment

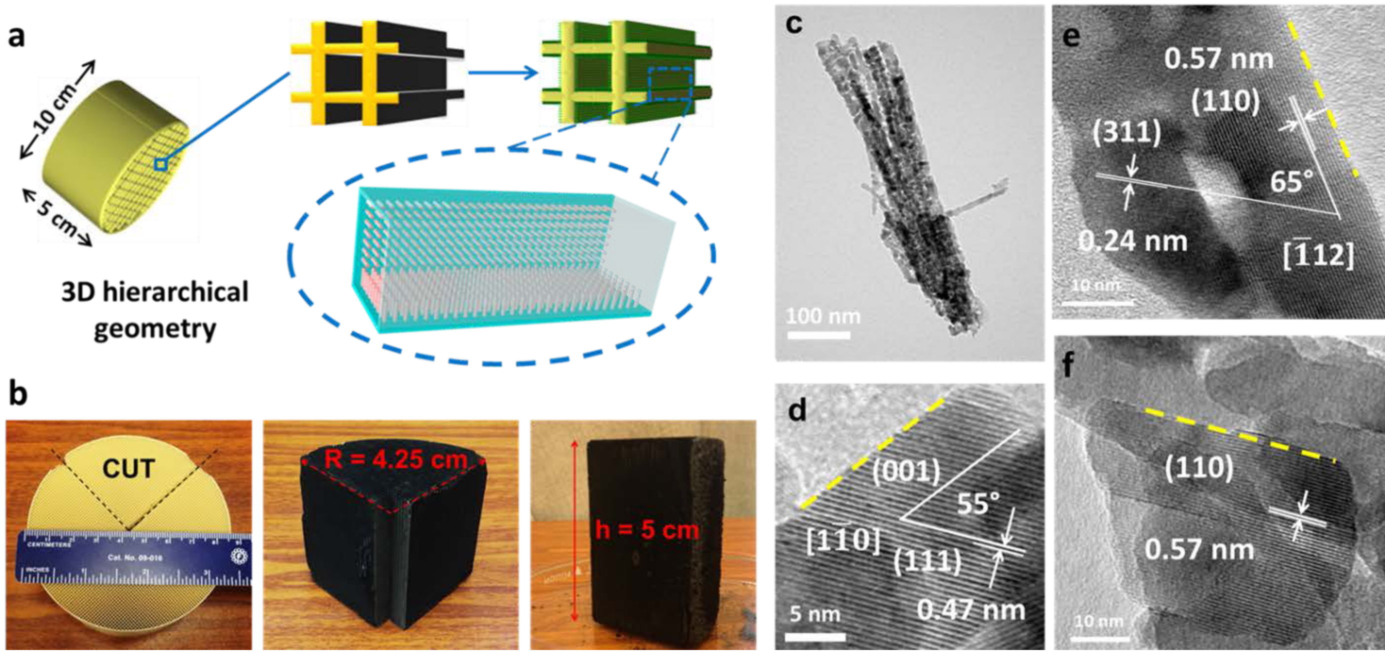
3) Demonstration of **TiO_2/Pt nano-array** catalysts with superb low temperature C_3H_8 oxidation performance at dry condition and high HC content

4) Demonstration of **TiO_2/Pt nano-array** catalysts with superb low temperature CO, C_2H_4, and C_3H_6 oxidation performance in US-DRIVE protocoled CDC simulated exhaust gas conditions

5) **Hydrothermal durability** evaluation of various metal oxide based nano-array based monolithic catalysts

Successfully synthesized PGM-free doped Co-oxide Nano-array Catalysts:

Spinel $M_xCo_{3-x}O_4$ (M=Co, Cu, Ni and Mn)



a) Monolithic integration of nano-arrays on commercialized honeycomb supports; b) Photographs of a piece of monolithic nano-arrays catalyst; c) TEM characterization of the Co_3O_4 nanorrays; HRTEM investigation of d) Co_3O_4, e) $Ni_{0.5}Co_{2.5}O_4$ and f) $Zn_{0.5}Co_{2.5}O_4$ nano-arrays.

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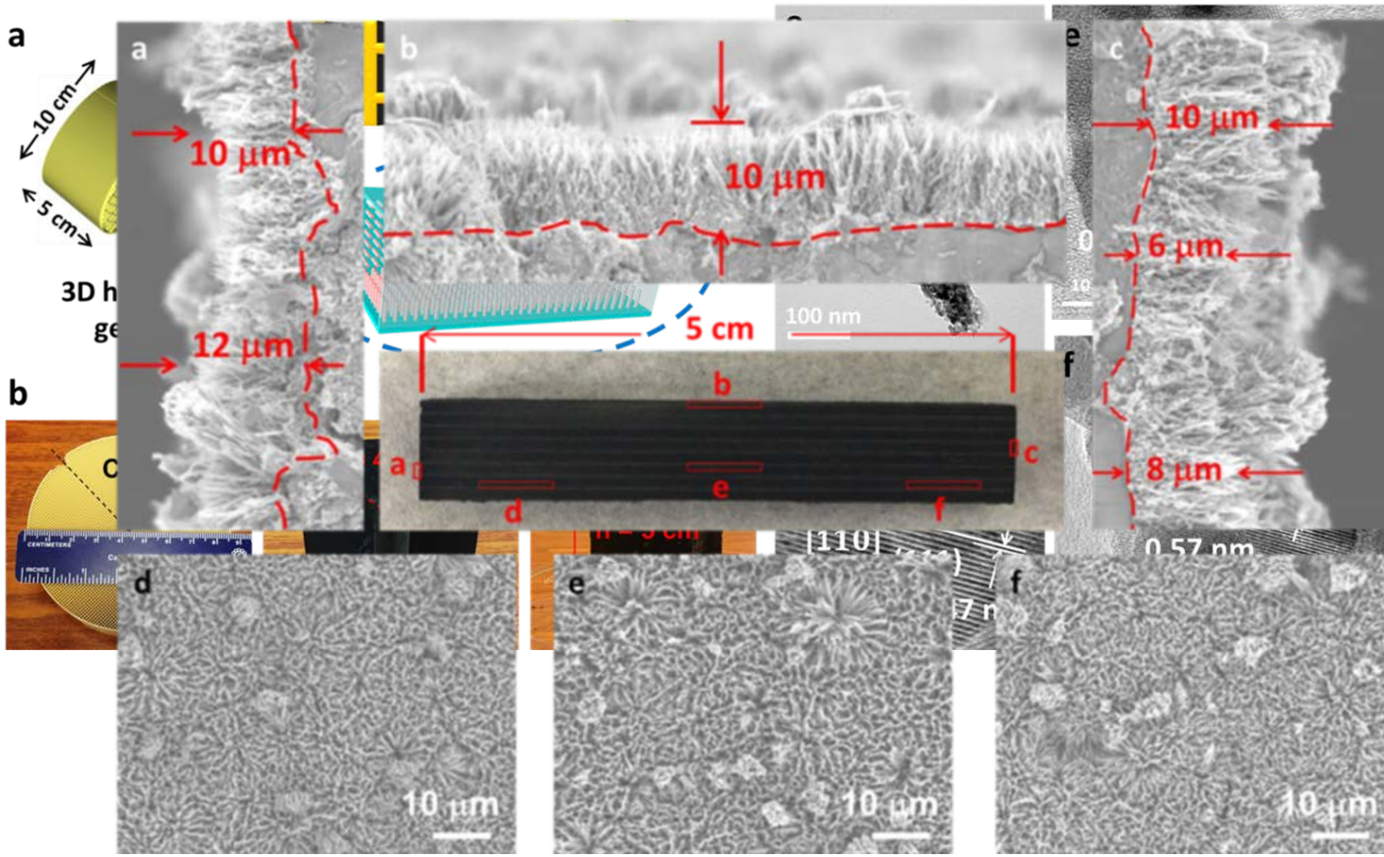

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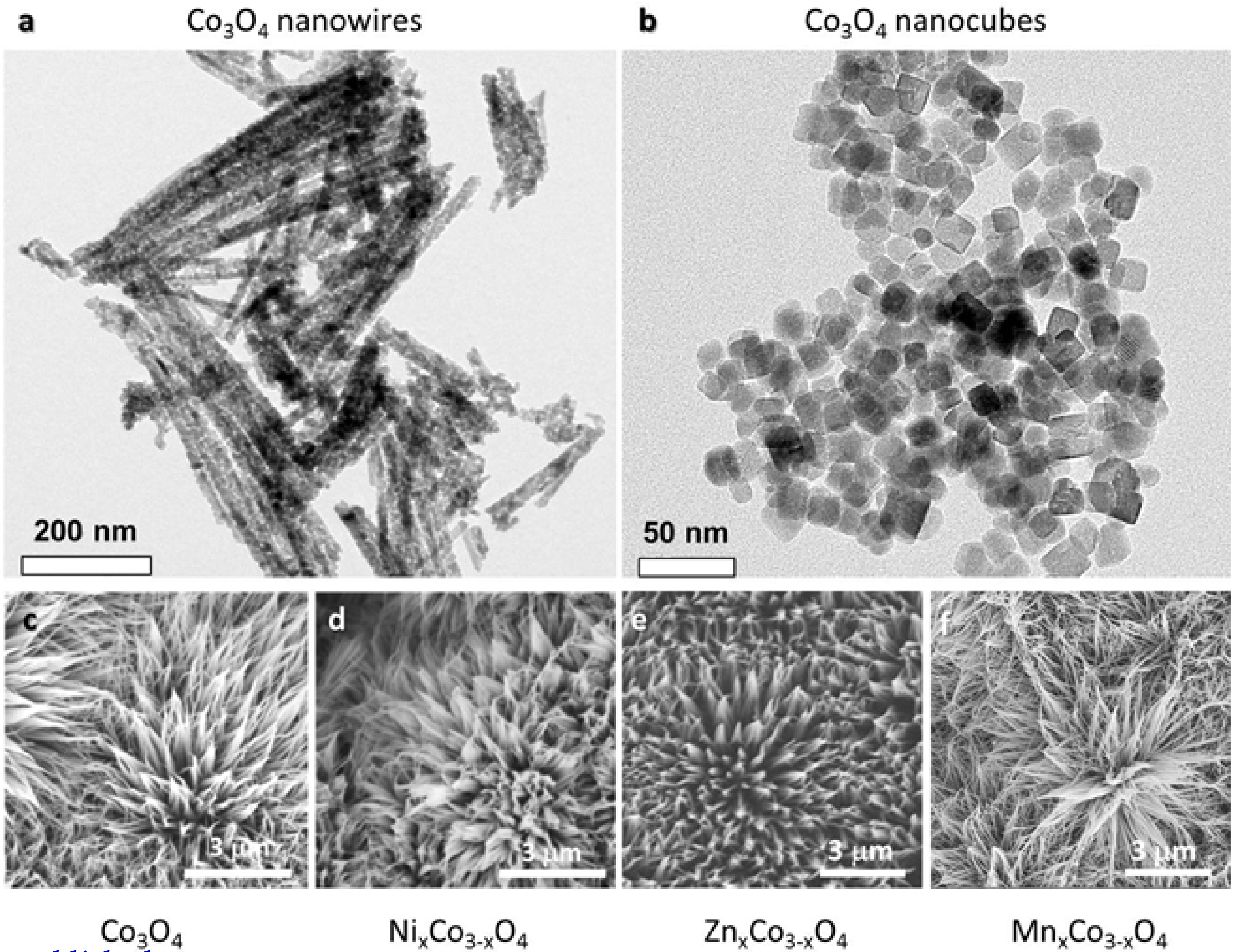
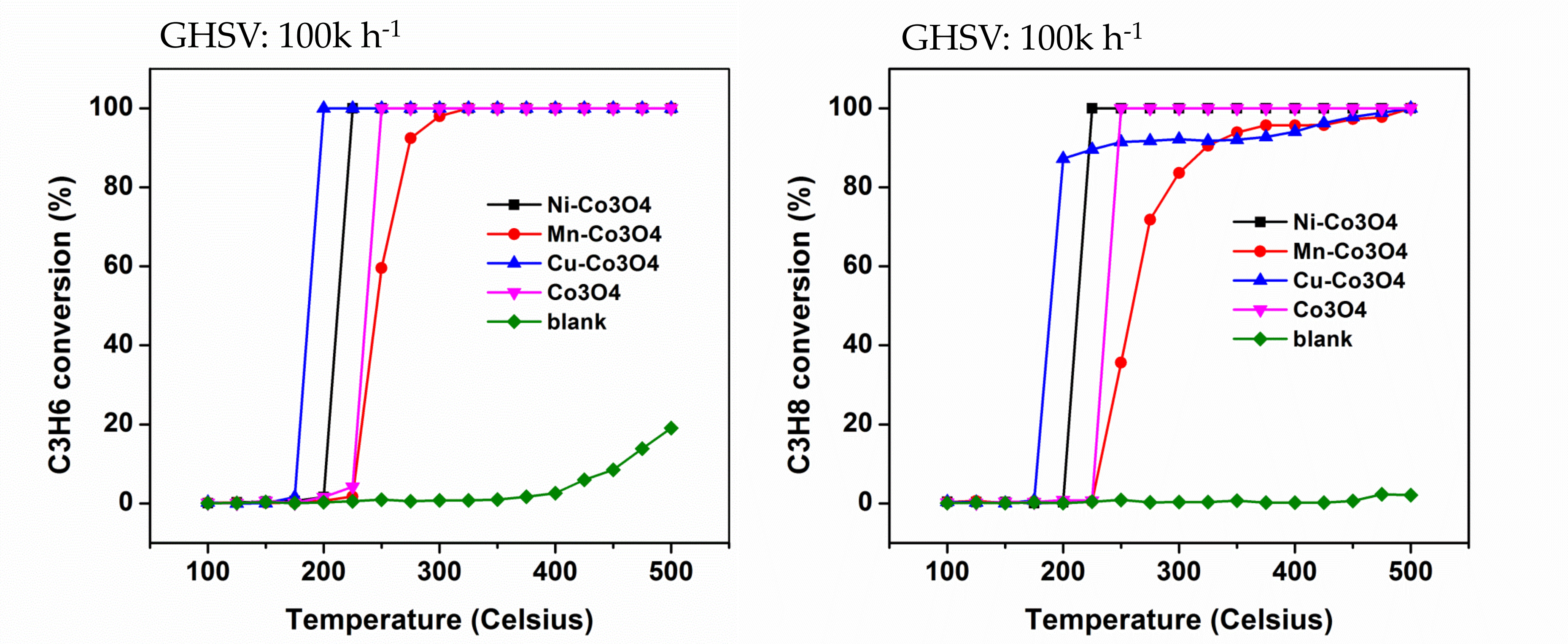
Shape Control and Transition Metal Doping



Ren, Gao, *unpublished*.

Transition Metal Doping Effect

- 0.3% C_3H_8, 0.5% C_3H_6, 10% O_2 balanced by N_2, 25mg catalyst, 100sccm

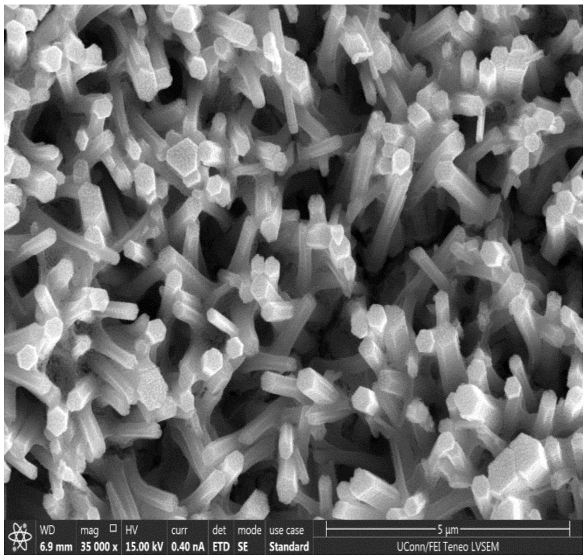


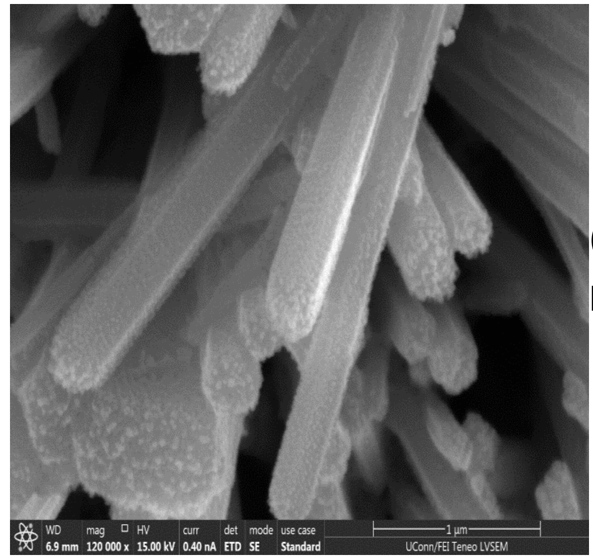
- Under mixed gases, both HC oxidation performance are very good at low temperature (T90 ~200^{o}C in Cu doping case)
- The dopant oxidation activity enhancement sequence: Cu>Ni>Mn, with Cu being the best to enhance by 60 ^{o}C in HC conversion, while Mn doping slowing down the conversion a bit.

Ren, Tang, Gao, *unpublished.*

Structure Characterization of ZnO/Pt-doped Perovskite Nano-arrays

Before acid treatment





(ZnO/Pt-perovskite nanorod array)

Wang, Lu, Gao, *unpublished.*

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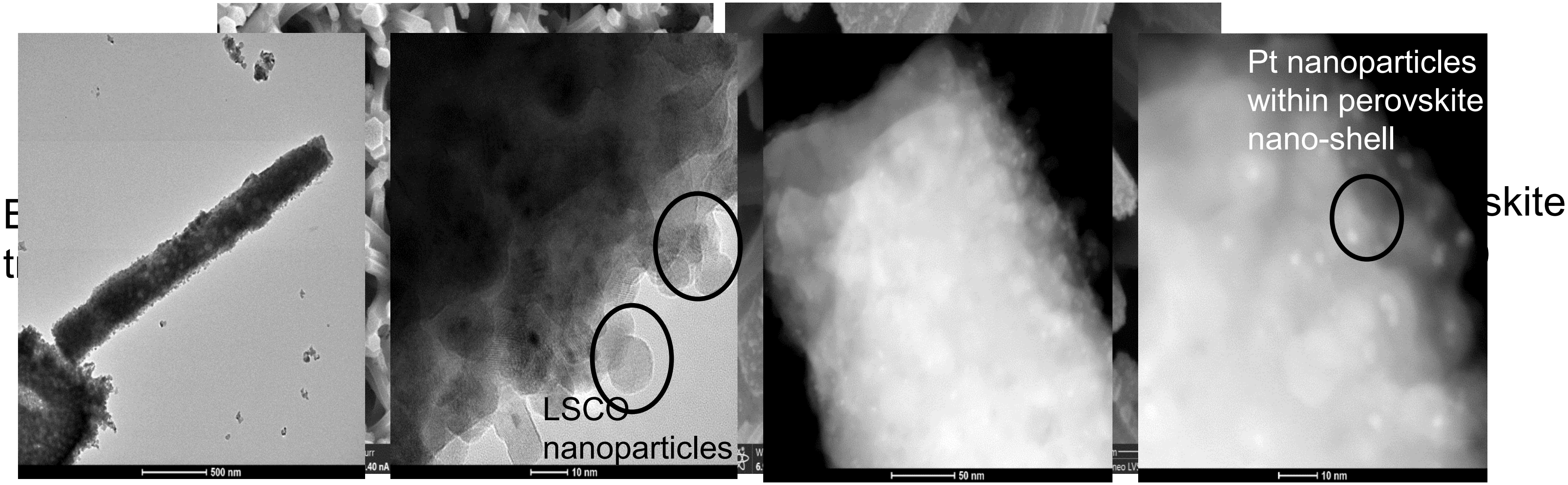
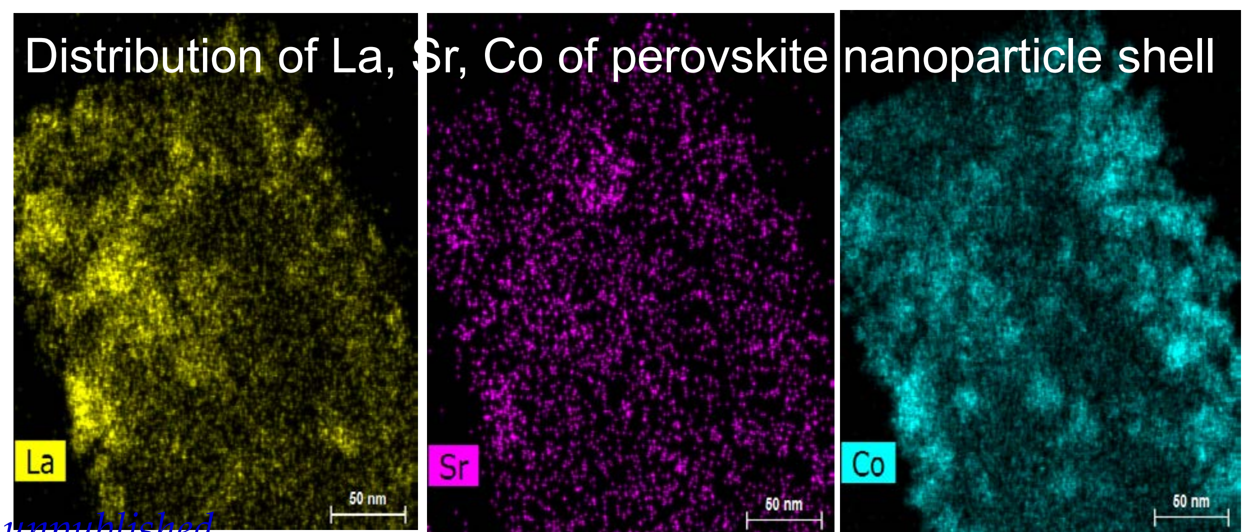


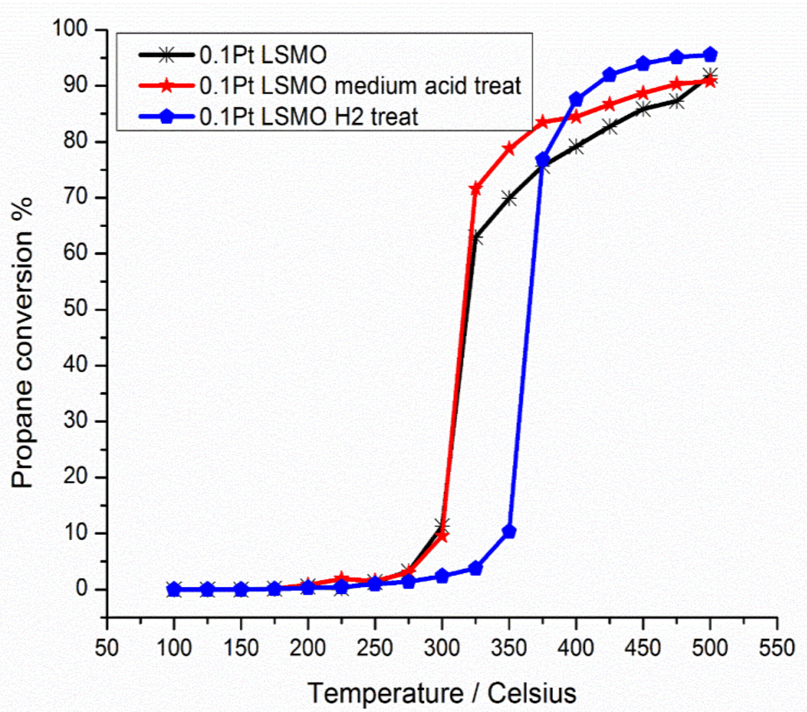


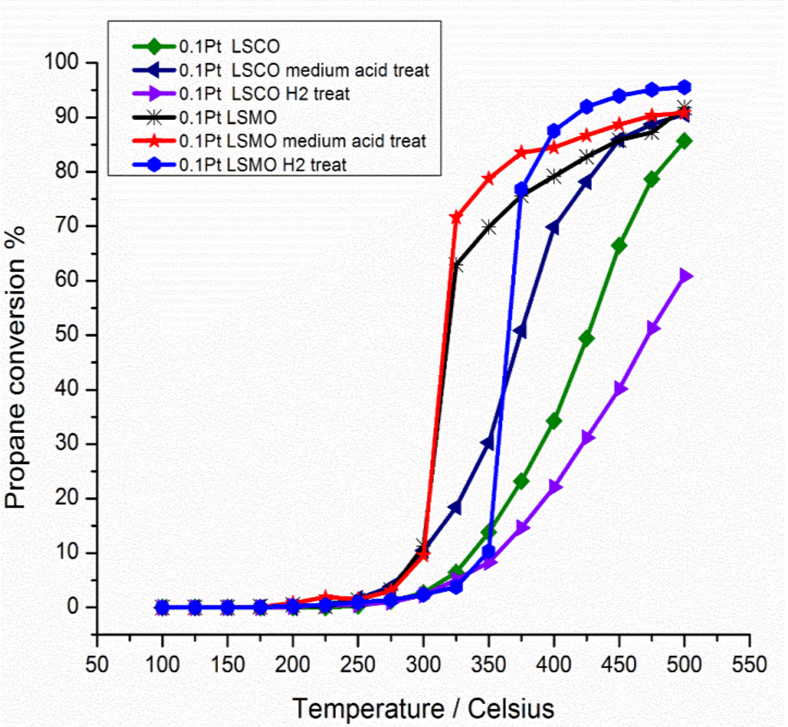
Wang, Lu, Gao, *unpublished*.

Acid or H_2 Treated ZnO/Pt-doped Perovskite Nano-arrays: Improved Propane Oxidation

- Pt-incorporated perovskite nano-array

Pretreated in 50 ml/min O_2 for 1 h.
0.75% C_3H_8 + 8% O_2, GHSV: 48000 h^{-1}





< 1.5g/L Pt for 0.1Pt (La,Sr)CoO$_3$ (LSCO) and 0.1Pt (La,Sr)MnO$_3$ (LSMO)

- Higher conversion region tailed off with slow kinetics, possibly due to mass transport issue,
- Chemical treated nano-arrays formed tubular structures, elevated the curve to higher conversion, possibly due to improvement of the mass transport at high conversion region.

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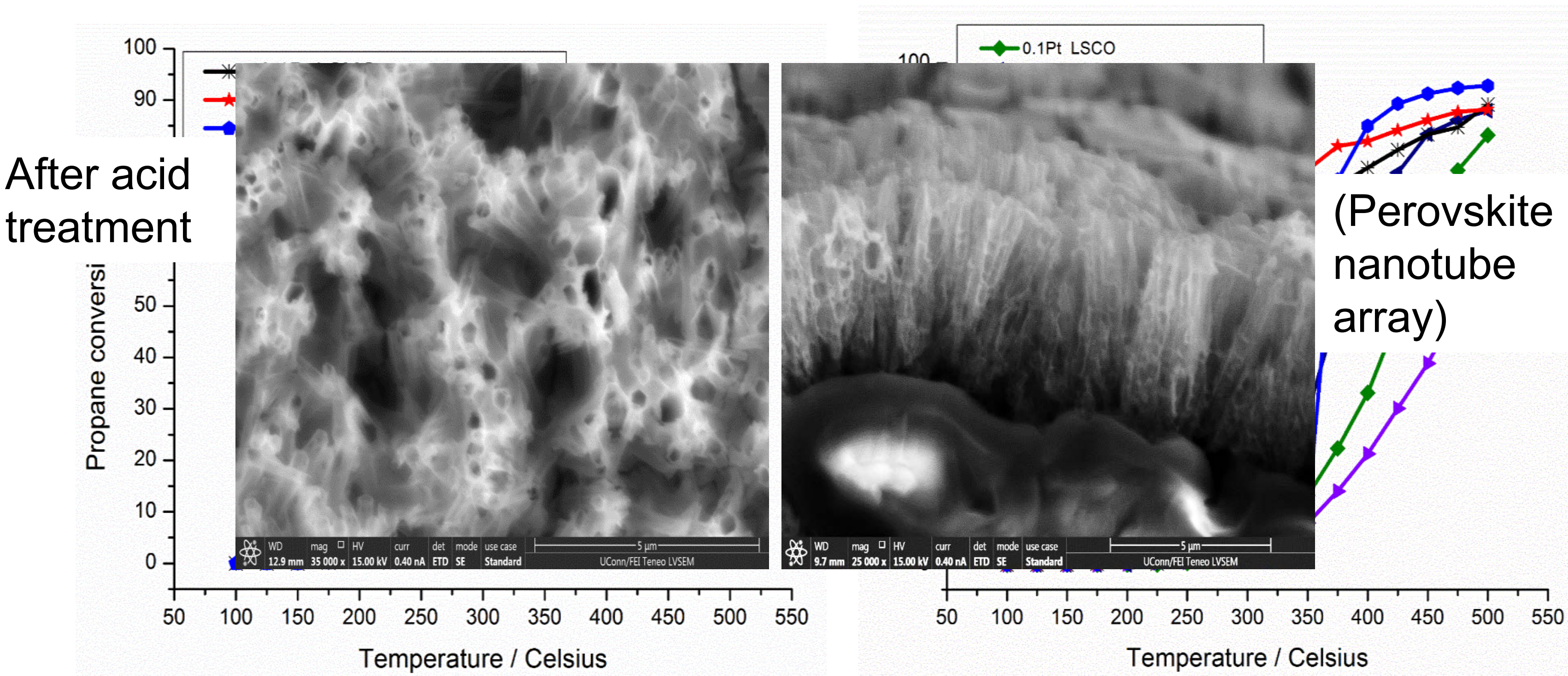

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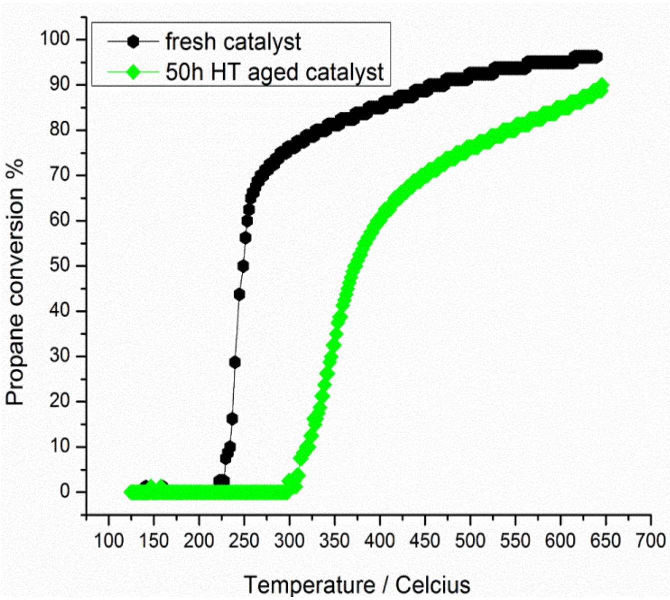
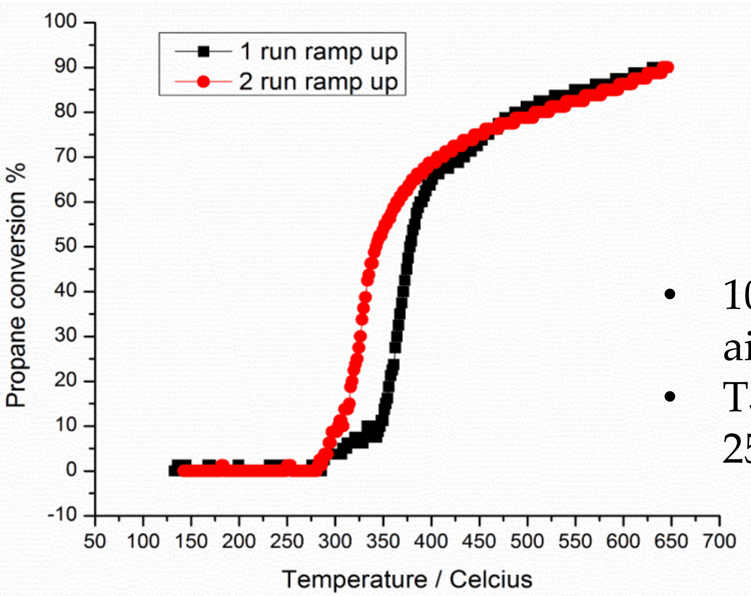
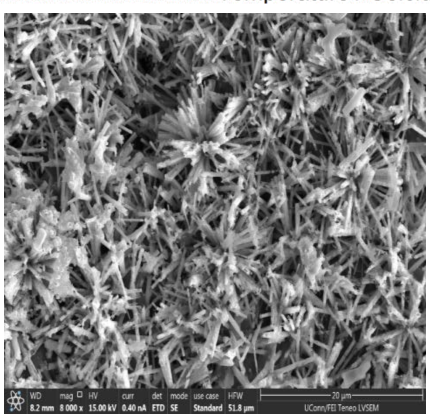
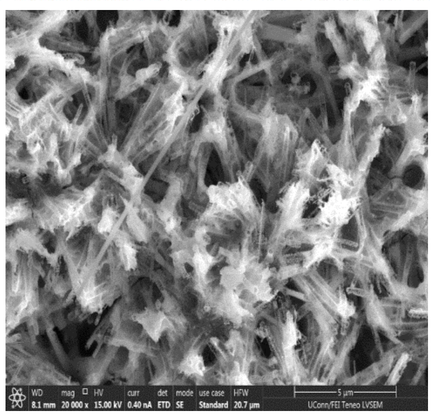
Hydrothermal Stability of ZnO/Perovskite/Pt Nano-array Catalysts

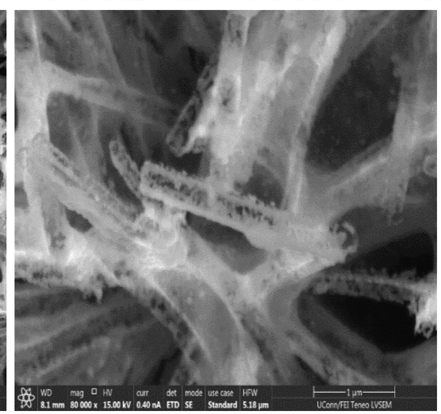




- 10% water vapor + 90% air. 800°C x 50 hr.
- T50 postponed from 250°C to 360°C.



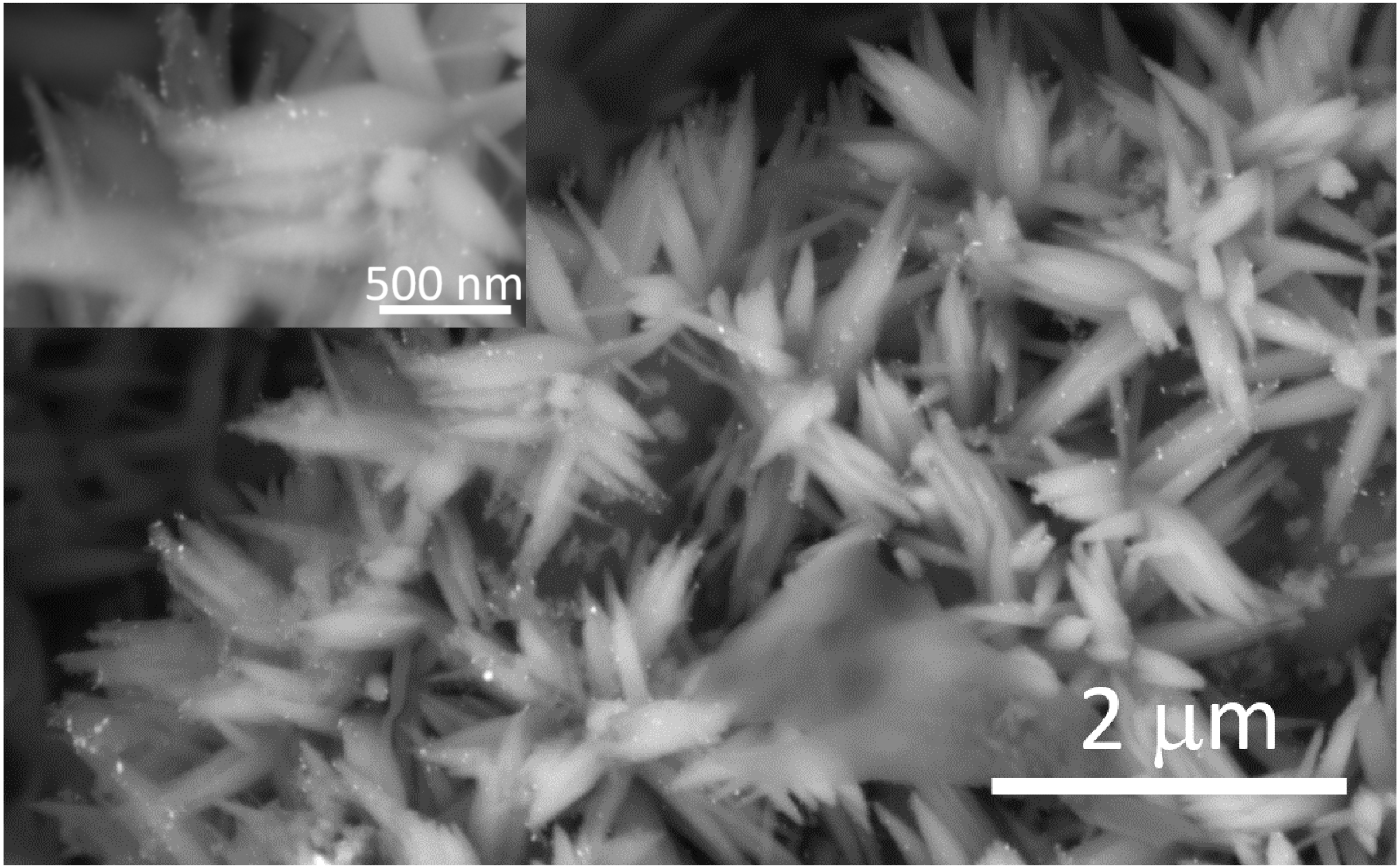




- Array-structure retained despite loss of ZnO
- BET surface area reduced from 11.9 m^2/g to 5.7 m^2/g.
- T50 after aging is ~380°C, about 120°C delay than fresh one

Wang, Gao, *unpublished.*

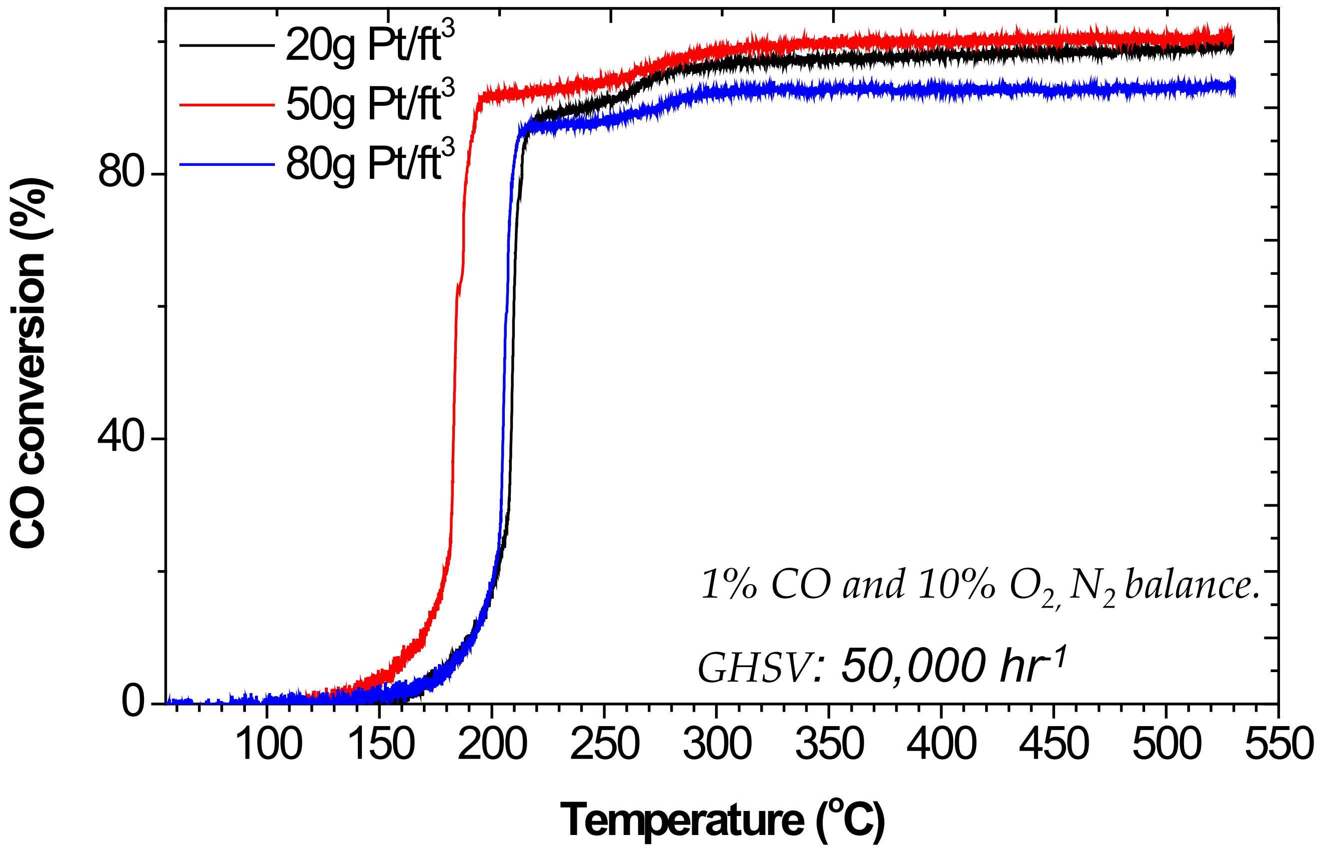
Pt/TiO_2 Nano-array based Catalyst



Angular Back Scattering (ABS) SEM images of Pt/TiO_2 nano-array (~ 2.8g/L).
White spots: Pt nanoparticles on TiO_2 mesoporous nanorods; BET surface area: 10-150 m^2/g dependent on synthetic protocols

Hoang, Gao, *unpublished.*

Pt Loading Effect on TiO_2 Nano-arrays: *CO oxidation performance*



- ~ 50g Pt/ft^3, reach 180°C T90;
- Low activity of the 80g Pt/ft^3 sample probably due to big Pt particles;
- Need improve impregnation for better dispersion of Pt;
- 90% tailed off possibly due to mass transport issue, need verification.

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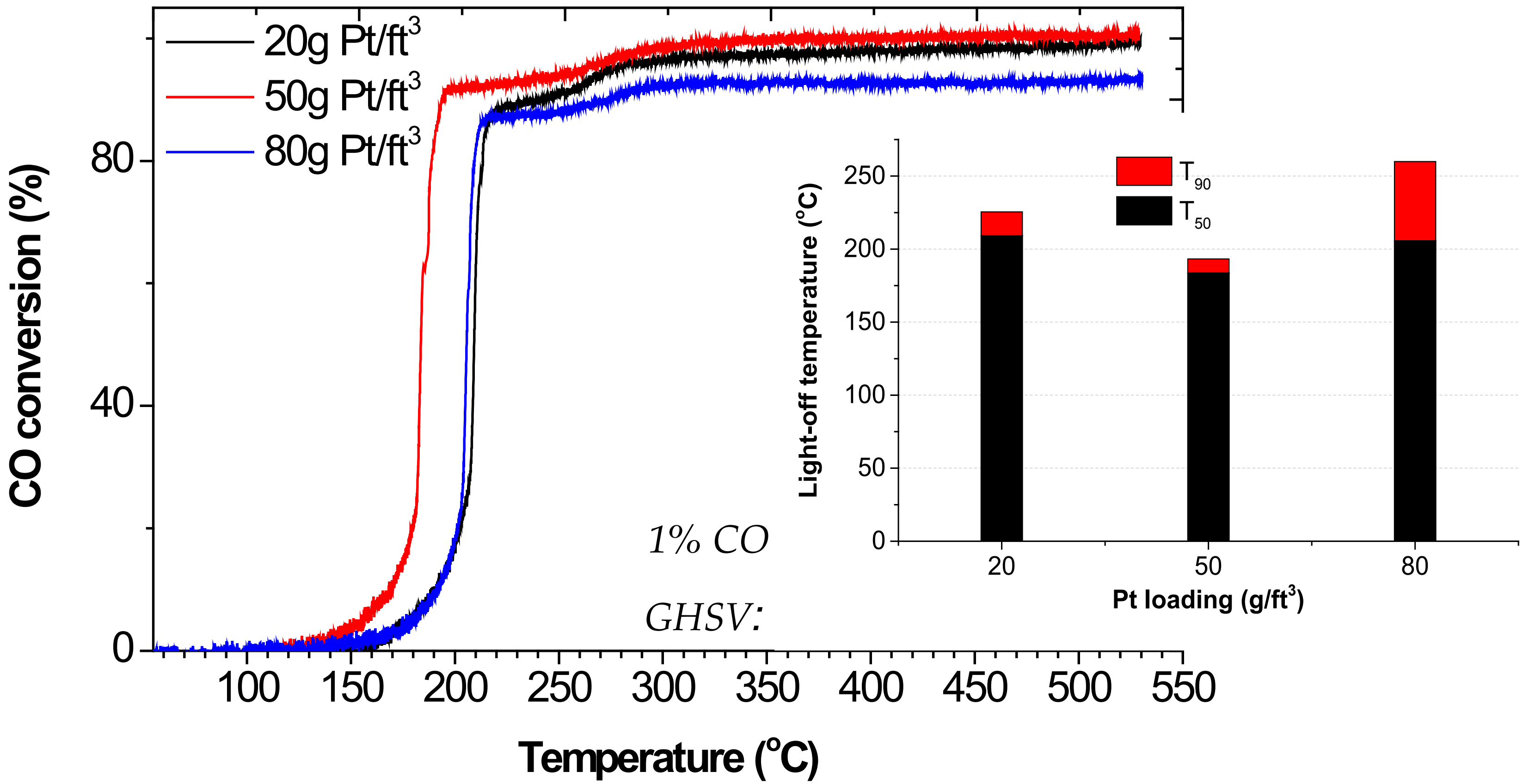

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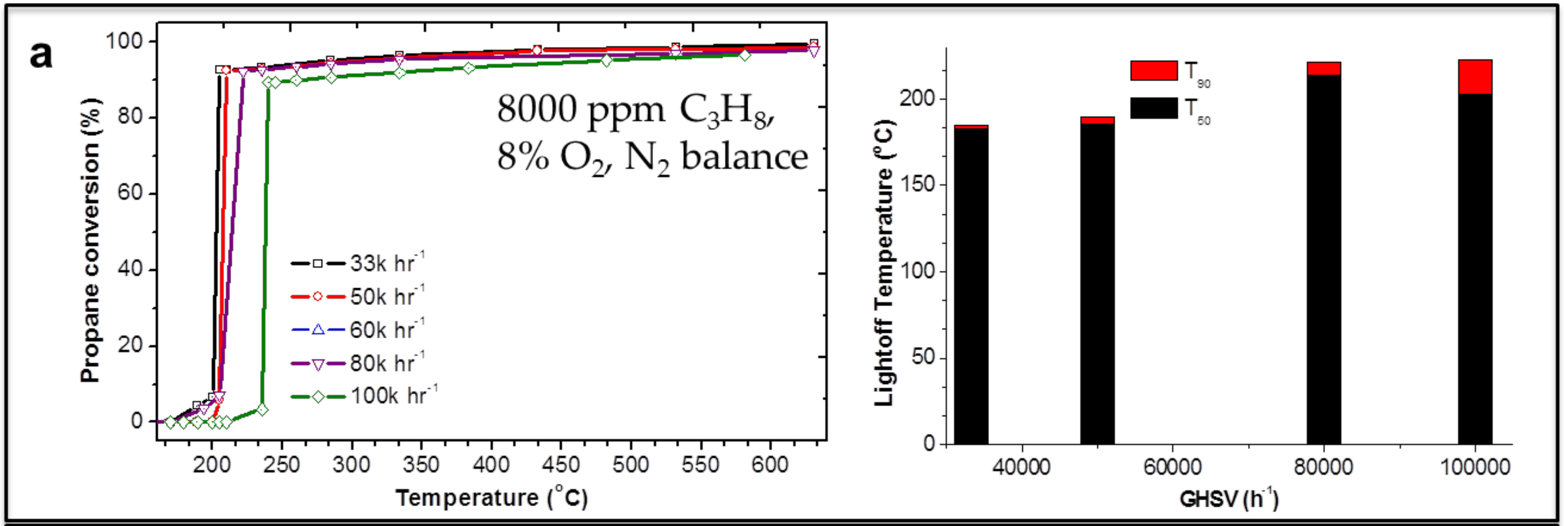
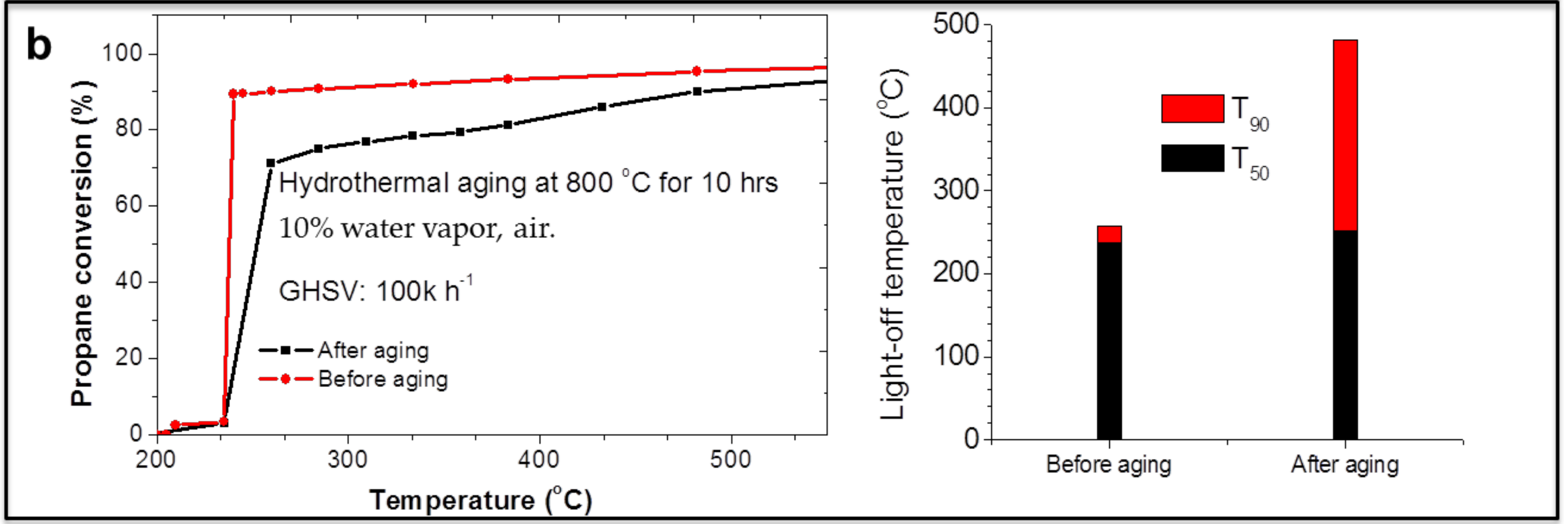
Pt/TiO_2 Nano-array based Catalyst
-Propane Oxidation Performance





- Pt size increased after aging, TiO_2 nano-arrays retained with little structure change → PGM dispersion/stability needed

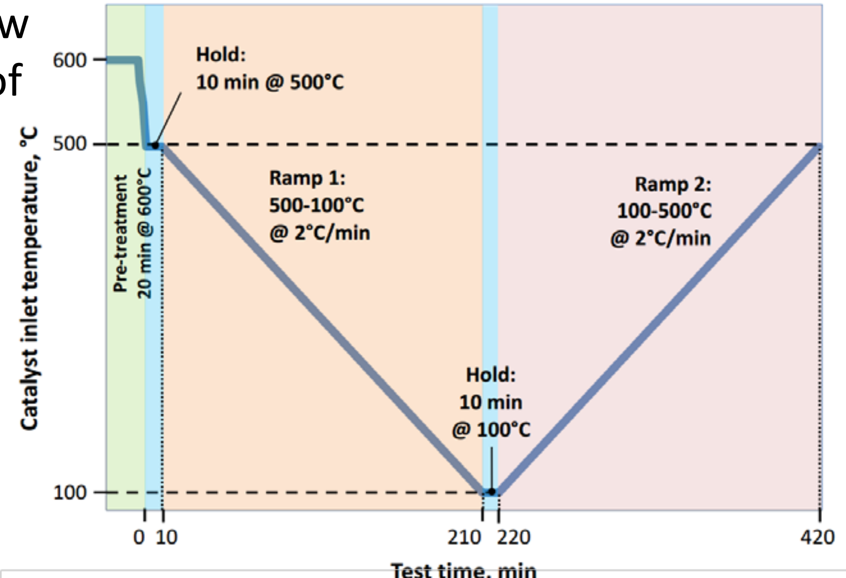
Hoang, Gao, *unpublished.*

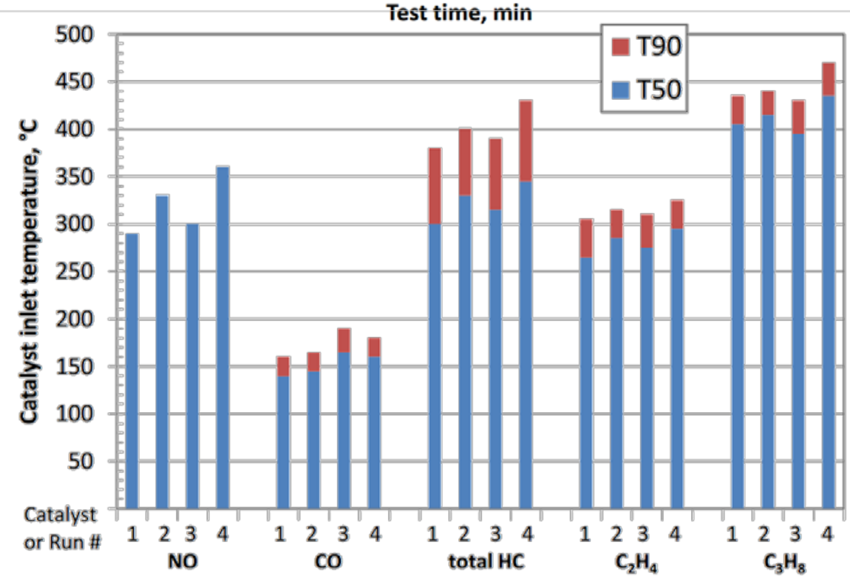
Low Temperature Protocols recently established by automotive manufacturers

- Protocol finalized in June 2015 by the Low Temperature Aftertreatment Sub-Team of the US DRIVE Advanced Combustion and Emission Control Team
- Full file at: www.CLEERS.org

<u>CDC Conventional Diesel Combustion</u>

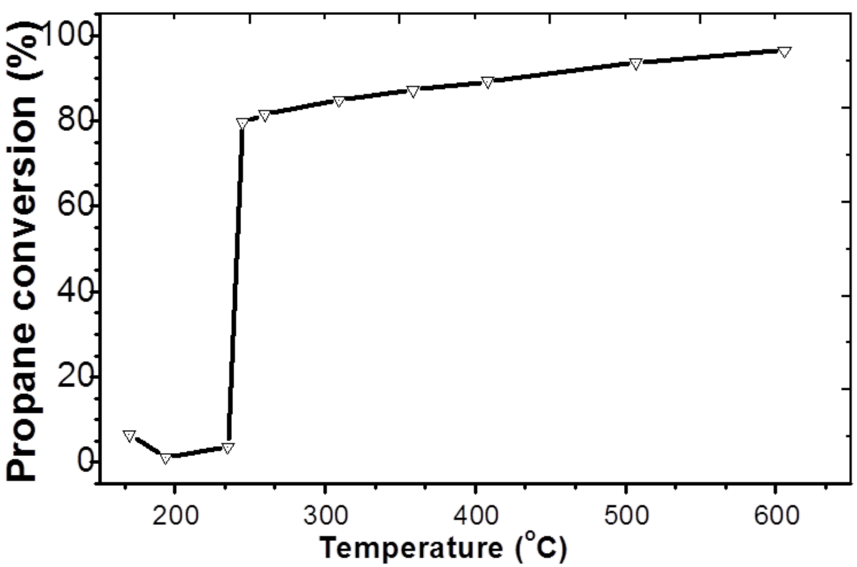
Total HC_1: 1400 ppm
C_2H_4: 778 ppm (C_1)
C_3H_6: 467 ppm (C_1)
C_3H_8: 155 ppm (C_1)
CO: 500 ppm
NO: 200 ppm
H_2: 100 ppm
H_2O: 6 %
CO_2: 6 %
O_2: 12 %
Balance N_2
GHSV: 30-60k h^{-1}





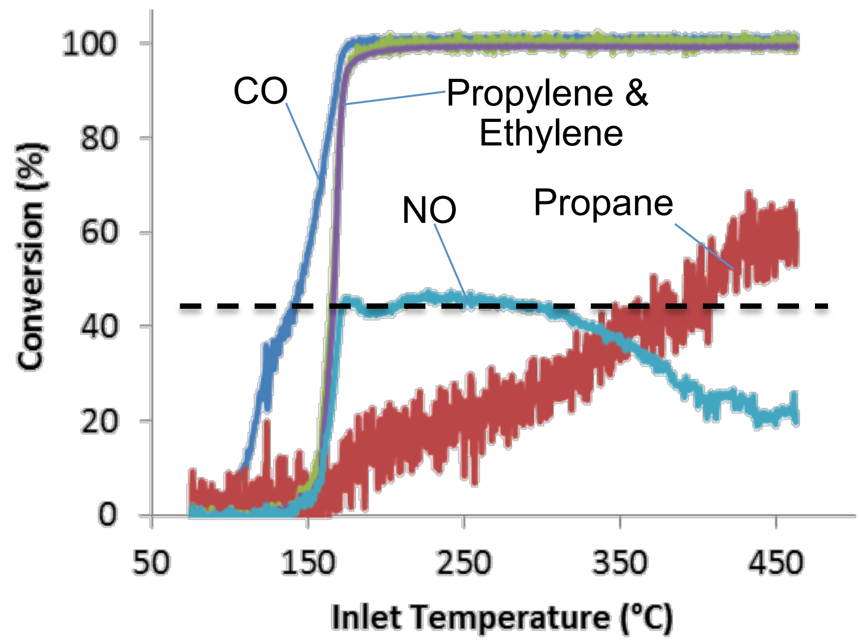
ACEC Protocol illustrates the challenges in automotive emissions control

- Initial data shows very good <u>propane</u> activity with Pt/TiO_2
  - simple conditions, not full protocol
  - Low PGM loading: < 0.3%Pt



GHSV: 50k h^{-1}

- When Pt/TiO_2 catalyst evaluated under CDC protocol, a more realistic evaluation is seen
  - <u>propane</u> conversion not as promising
  - HOWEVER, illustrates excellent <u>propylene/ ethylene</u> activity



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Hoang, Binder, Toops, Gao, et al., *unpublished*.

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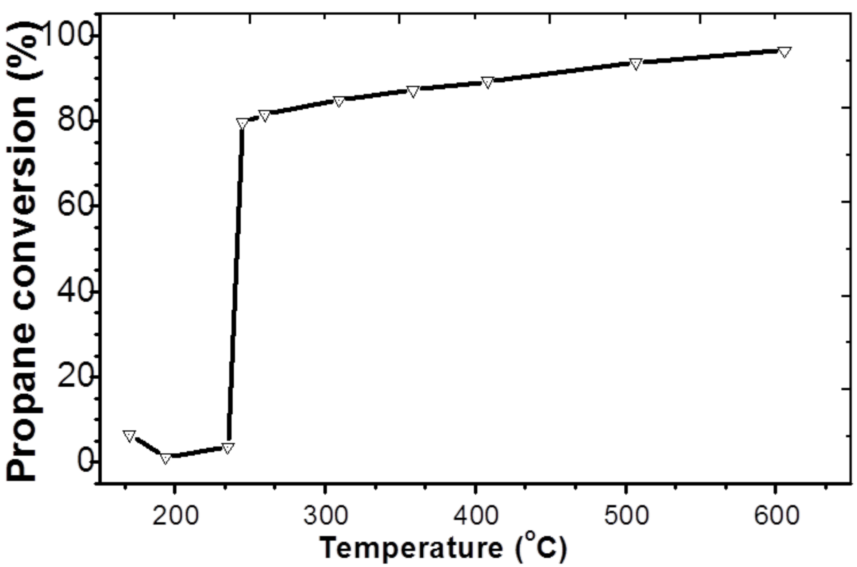

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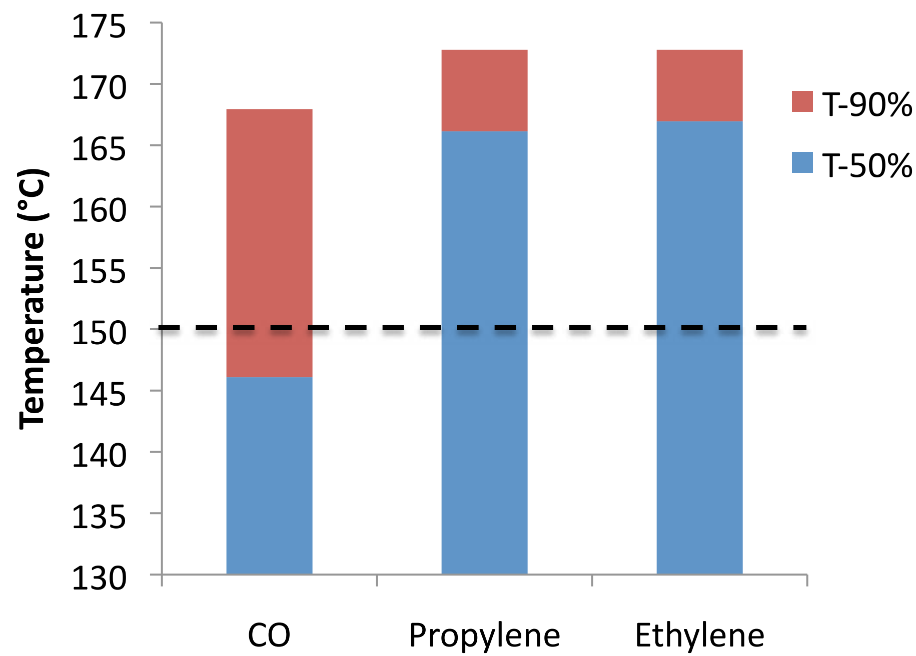

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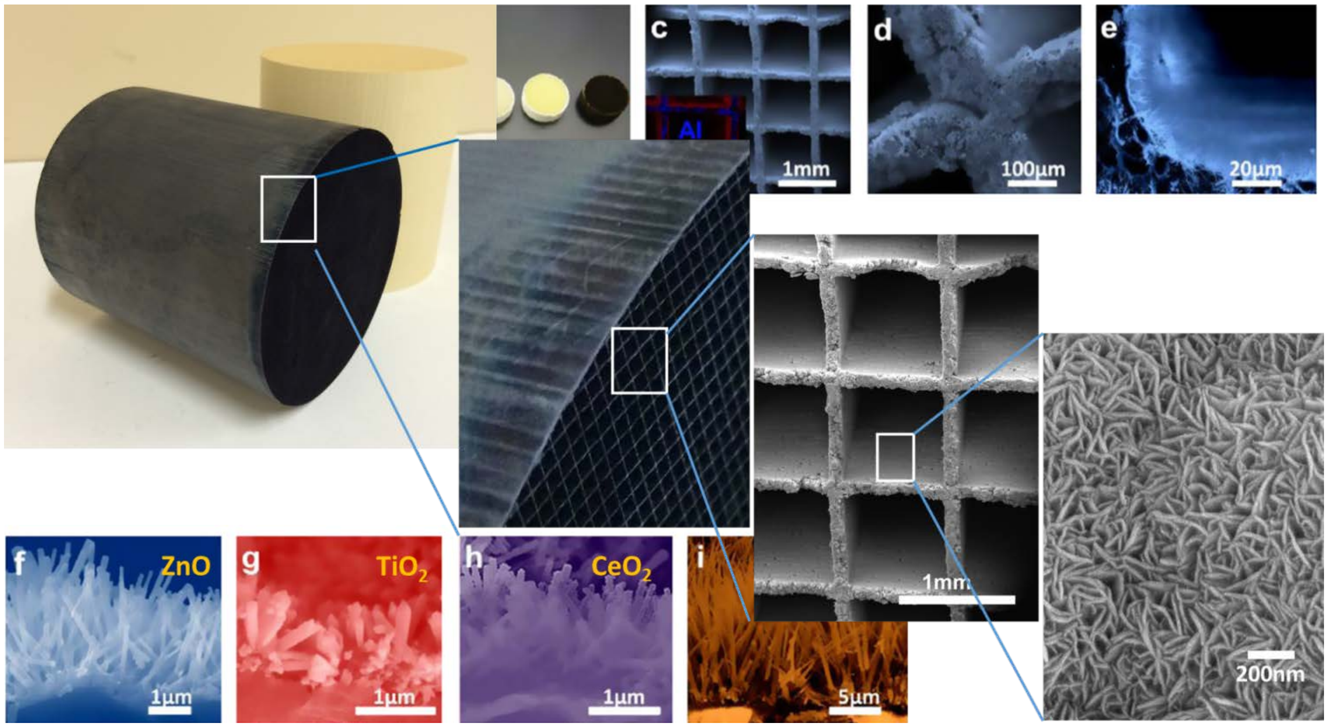
Large Scale Nano-array Catalytic Device



Nano-array integrated DOC devices of Ø 2″~7.5″× *L* 3″~6″, to be tested at Umicore for transient syn-gas reactor and engine dyno performance.

Tang, Guo, Gao, et al., *unpublished*.

Remaining Challenges and Future work

	Remaining Challenges	Future Work
PGM-free nano-array	(1) Dopant evaluation (2) Hydrothermal aging	(1) More doping and loading study (2) S poisoning effect (3) Hydrothermal aging studies
Perovskite/Pt nano-array	(1) Pt-dopant/loading mixture evaluation (2) Hydrothermal aging (more) (3) Other metal oxide arrays	(1) More doping and loading study (2) More hydrothermal aging studies (3) Other metal oxide array studies
Metal Oxide/Pt nano-array	(1) Pt-loading evaluation (2) Hydrothermal aging (more) (3) Other metal oxide array	(1) Pt-loading evaluation (2) Hydrothermal aging (3) Other metal oxide array
Simulated gas testing	(1) More ACEC simulated gas testing (2) Propane activity studies (3) S-exposure (4) Other metal oxide arrays	(1) More focused simulated gas testing (2) Hydrothermal aging (3) Other metal oxide arrays
Large size nano-array	(1) Processing (more) (2) Hydrothermal aging protocols (3) Benchmark catalysts	(1) Processing (more) (2) Engine evaluation (3) Hydrothermal aging

Conclusions and Future Work

1. **Approach:** in-situ growth of well-defined nano-array based catalysts onto various honeycomb substrates. Both mixture and simulated exhaust gas conditions applied in catalytic oxidation testing.
2. **Relevance:** nano-array catalysts with low PGM and other materials usage, low temperature performance, and excellent robustness, meeting the needs of fuel economy, regulation, low temperature combustion, and environmental protection.
3. **Tech accomplishment:**

a) PGM free and Pt loaded nano-arrays grown in-situ onto the honeycomb substrates;

b) Doped Co-oxide with 200^oC T90 HC oxidation activities under C_3H_6 and C_3H_8 mixture gases, and TiO_2/Pt with CO, C_2H_4, C_3H_6 conversion T90 at 175^oC or below under CDC simulated exhaust test conditions;

c) After hydrothermal aging, TiO_2/Pt and ZnO/perovskite/Pt retained array structures despite Pt size increase and ZnO loss.

d) Chemical treated Pt-doped perovskite nano-arrays with improved HC conversion, possibly due to the enhanced mass transport with tubular structure formation.

e) Large scale nano-array devices prepared for transient reactor and engine tests.

4. **Collaboration:** ORNL, Umicore, and 3D Array Tech., and other labs (BNL, NETL) and universities (Georgia Tech and UT Dallas).
5. **Future work:**

a) More doping and loading studies on PGM free Co-oxide and TiO_2/Pt systems for the 90% 150^oC HC conversion under CDC simulated and mixed gases conditions;

b) Mitigation of water/S effects by co-loading/growth/doping of Pd, CeO_2 and Al_2O_3 onto nano-arrays;

c) Large scale nano-array catalysts for transient testing and engine dynometer evaluation.

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