University of Connecticut
School of Engineering

Monolithic Metal Oxide based Composite Nanowire Lean NO_x Emission Control Catalysts

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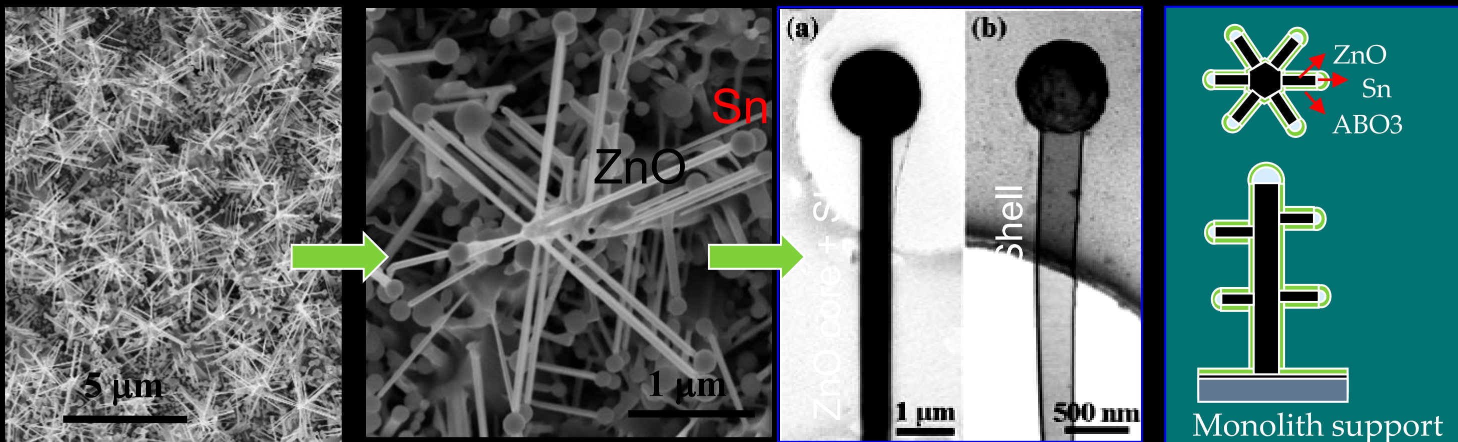
Outline

- ❖Monolithic nanowire catalyst concept
- ❖Goal and approaches
- ❖Monolithic nanowire catalysts
  - ❖ Specific surface area
  - ❖ Thermal and chemical stability
  - ❖ CO and NO oxidation behaviors

Monolithic Nanowire Catalyst Concept

What is New?

- First conceptual composite nanocatalysts made from MeO_x/ABO_3 semiconductor/perovskite nanowires.



- ➢ ZnO: Sulfur (S) absorbent > Poison resistance;
- ➢ ABO_3: Perovskite catalysts > Flexible tailoring capability
- ➢ ZnO/ABO_3: No Chemical Interaction!

Advantages: 1) Ultrahigh surface area; 2) High thermal stability; 3) Strong adherence; 4) Low cost; 5) High tailoring ability; 6) Reduce or Eliminate PGM usage by incorporating ABO_3 perovskite.

Potential Multifunctional Nanocatalysts

1) Selective adsorption/storage of excess oxygen (surface and lattice oxygen) and catalytic extraction of oxygen from NO_x, potentially allow direct reaction of CO, HC with NO_x in the lean-burn engine operation.

2) *Mesoporous perovskite shell* allows desulfurization via substitution reaction of metal oxide core into sulfide or sulfate, eliminating or reducing the surface poisoning tendency.

3) The strong adhesive forest-like composite nanocatalysts allow itself to survive in high flow-velocity exhaust conditions, and potentially function as an effective particular matter filter for the lean-burn diesel engines.

4) With dopants either Pt or Pd, or Sr, Ba, K, Ce, the 3D composite nanocatalysts could be tailored as an excellent candidate as either lean NO_x catalysts or LNT's absorbents.

Monolithic Nanowire Catalyst Concept

Compare to other Technologies?

Parameter \ Tech	1	2	3*
Surface area	High	Average	Ultra-high
Thermal stability	High	Average	High
Poison resistance	High	Poor	High
Tailoring capacity	Poor	Average	Excellent
Adhesion	Good	Poor	Good
Availability	Limited	Average	High

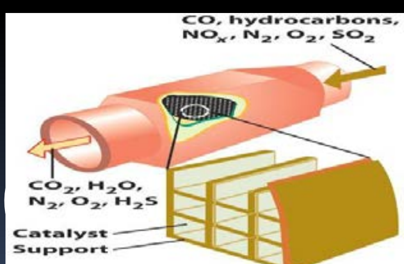
Technologies:

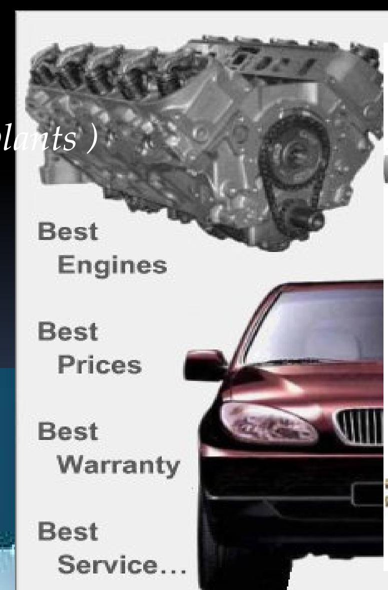
1. Noble metals (Pt, Pd, etc.)
2. Hybrid particle catalysts ABO_3 + noble metal

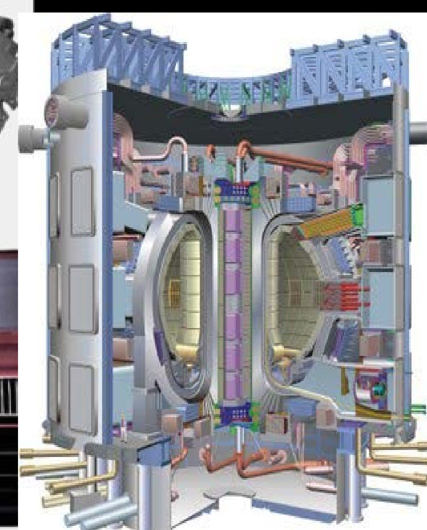
3*. 3D composite nanowire catalysts

Potential Applications

- Lean NO_x emission control in vehicle and aircrafts
- Industrial combustion emission control (*reactors, power plants*)







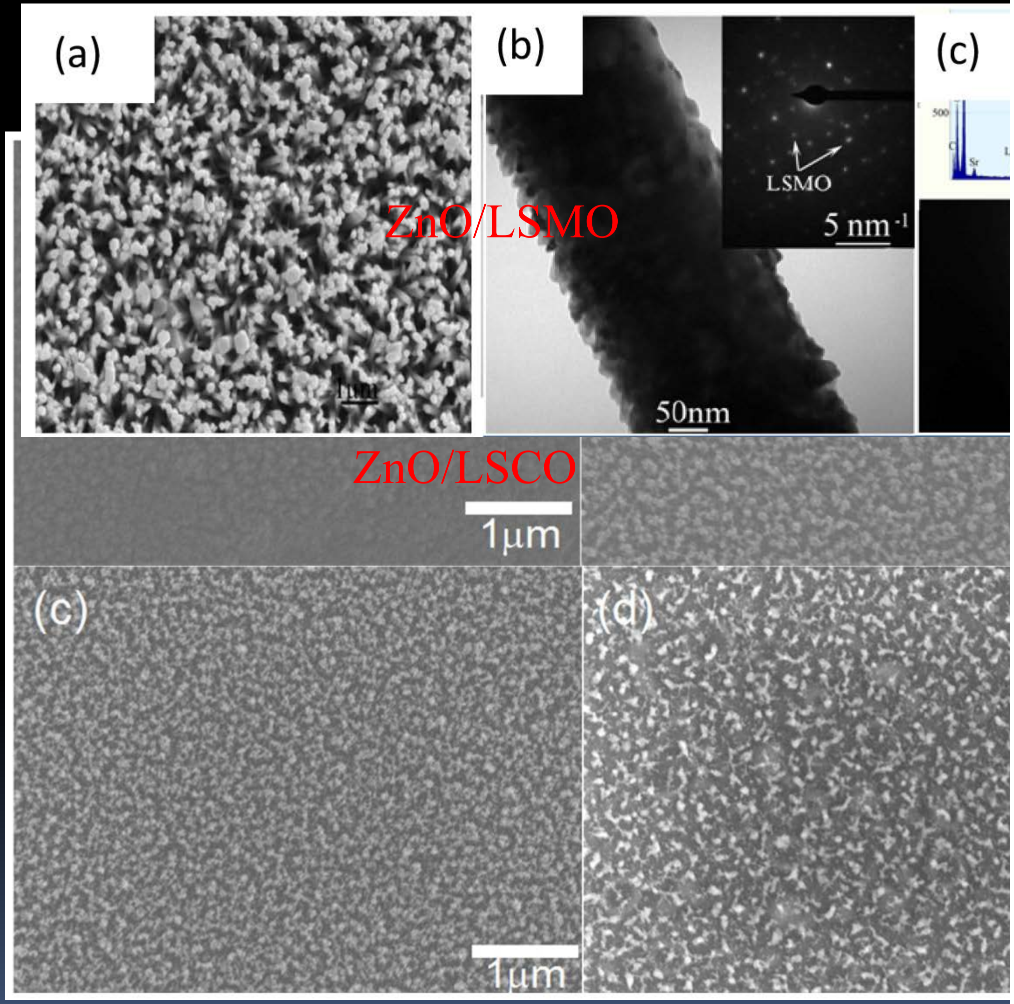
Goal and Approaches

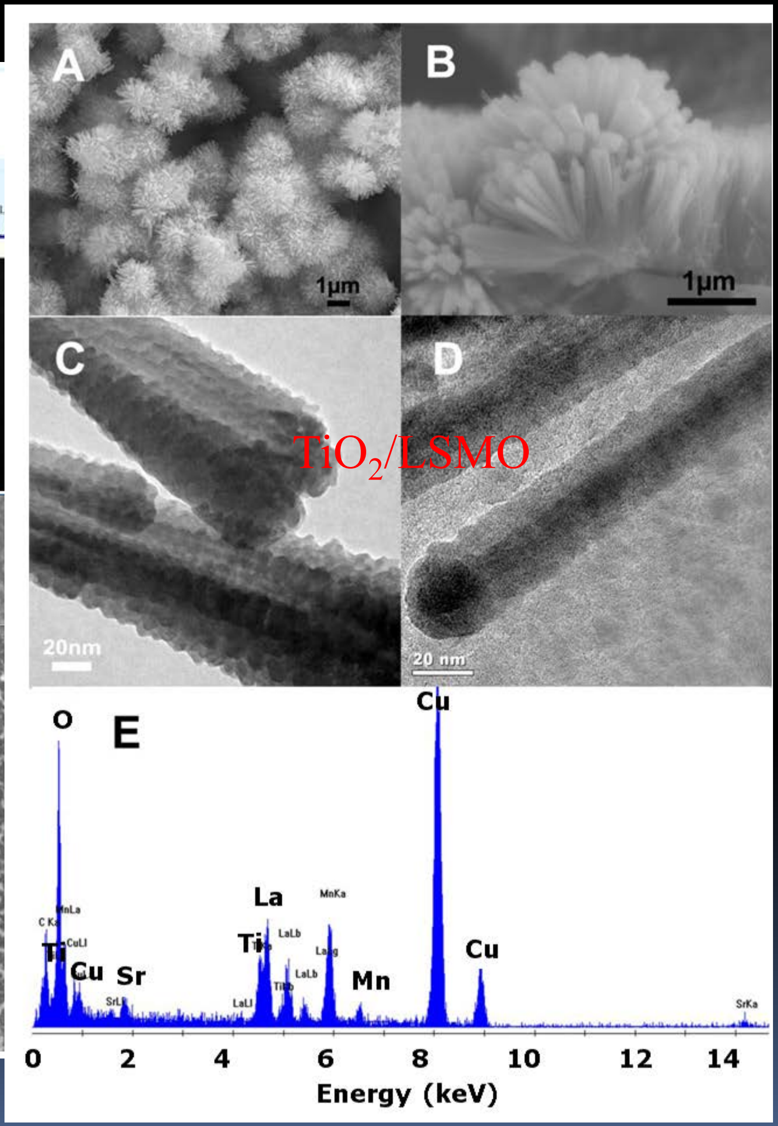
1) **Goal:** To reduce CO, NO_x, HC and PM emission by introducing a new concept composite nano-catalysts, eventually to replace or reduce the usage of the Pt-group metal (PGM) catalysts.

2) **Approaches**

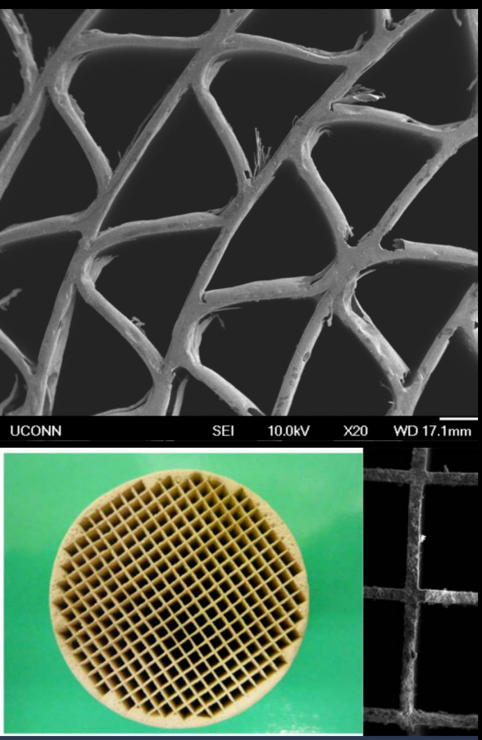
- **Synthesis:**
  $(ZnO, TiO_2)/(La, Sr)(Co \text{ or } Mn)O_3$ (LSCO or LSMO) composite nanowire arrays rooted on monolithic cordierite or stainless steel.
- **Characterization:**
  Structure, morphology, and chemical properties of composite nanowire arrays using a range of microscopy and spectroscopy techniques.
- **Durability:**
  Thermal stability by using a variety of microscopy, spectroscopy and thermal analysis tools.
- **Activity:**
  Catalytic behavior: CO oxidation and NO oxidation, storage and reduction, etc..

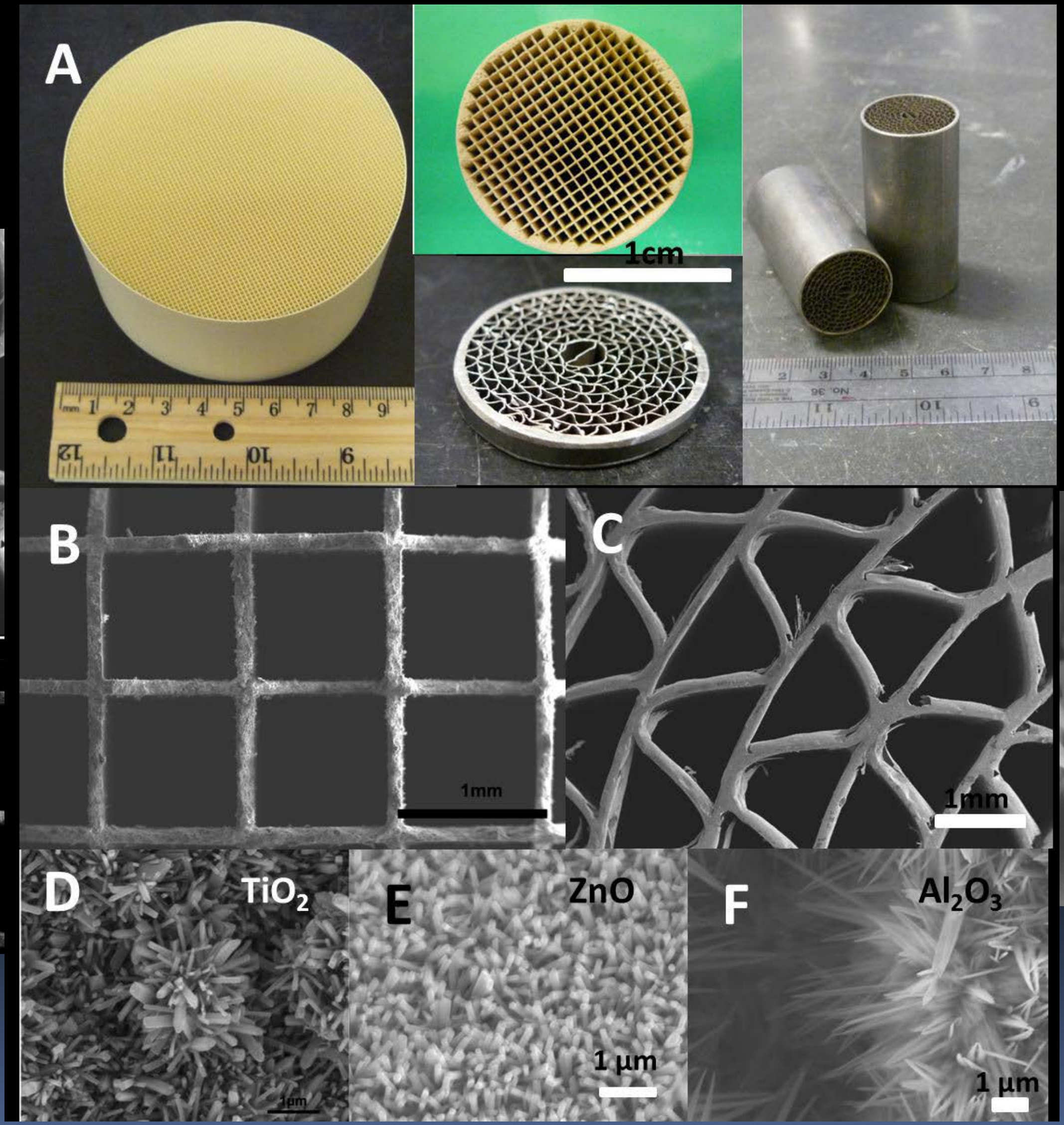
Composite nanowire arrays

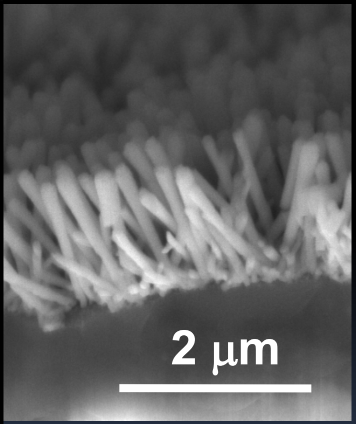




Large scale ZnO and TiO_2 nanowire arrays grown in monolithic substrates

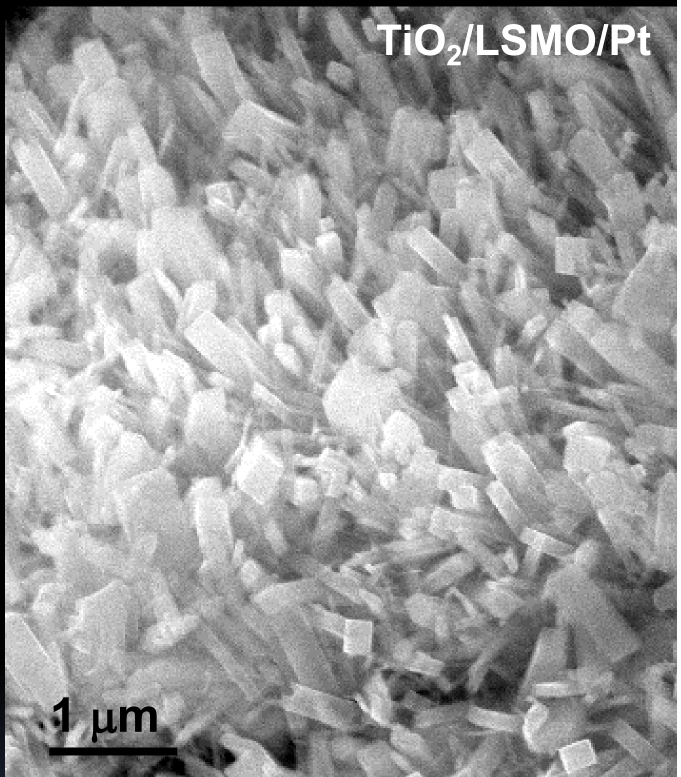


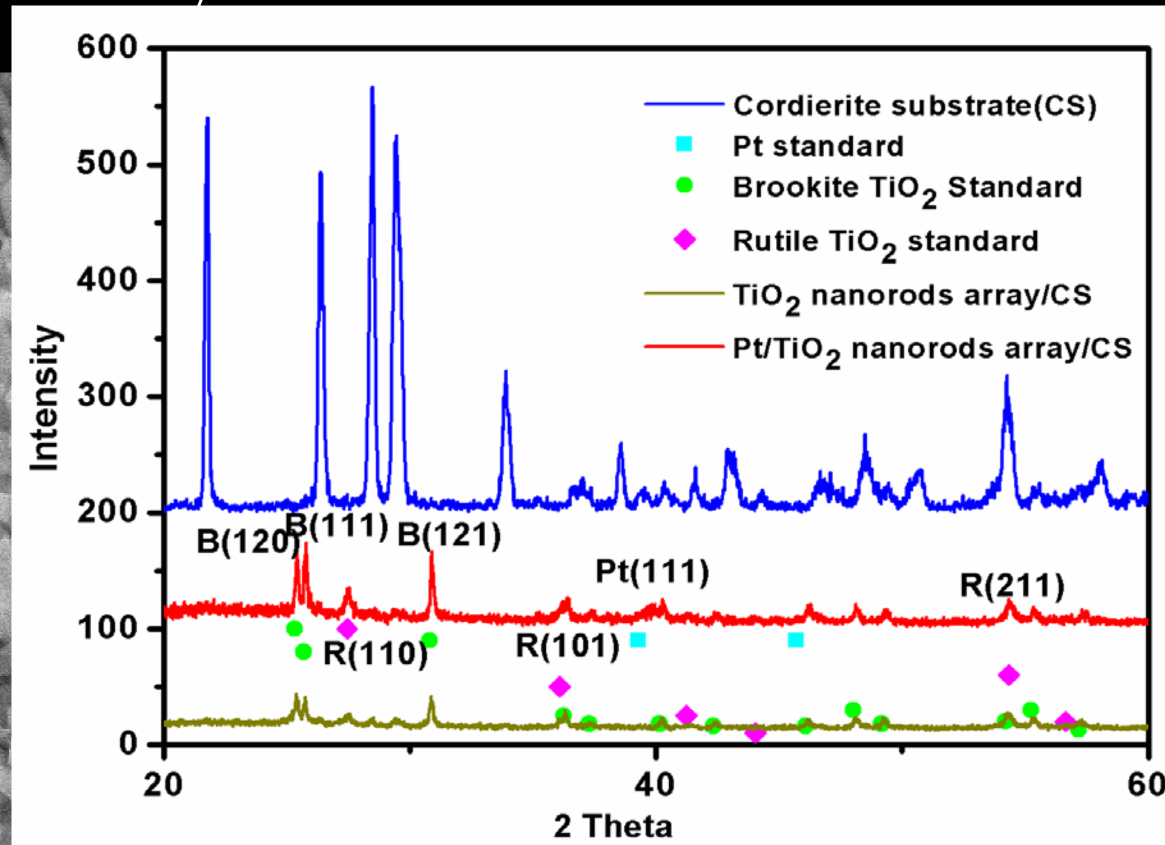




Metal oxide nanowire arrays on monolithic substrates.

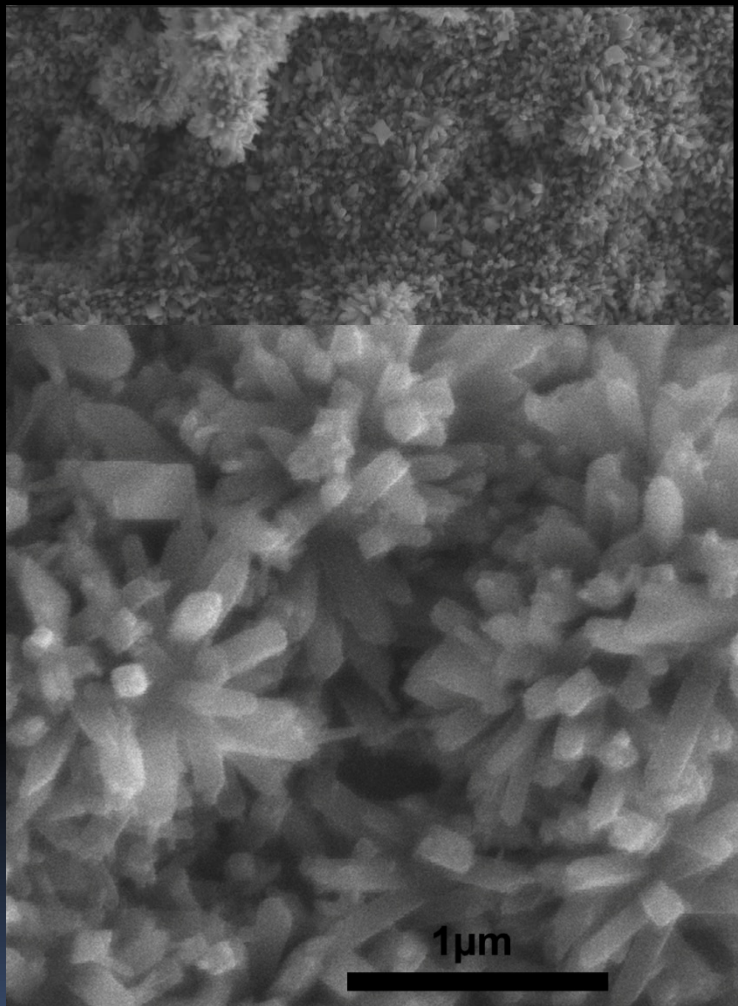
Structure and surface areas of TiO_2 nanoarrays on substrate

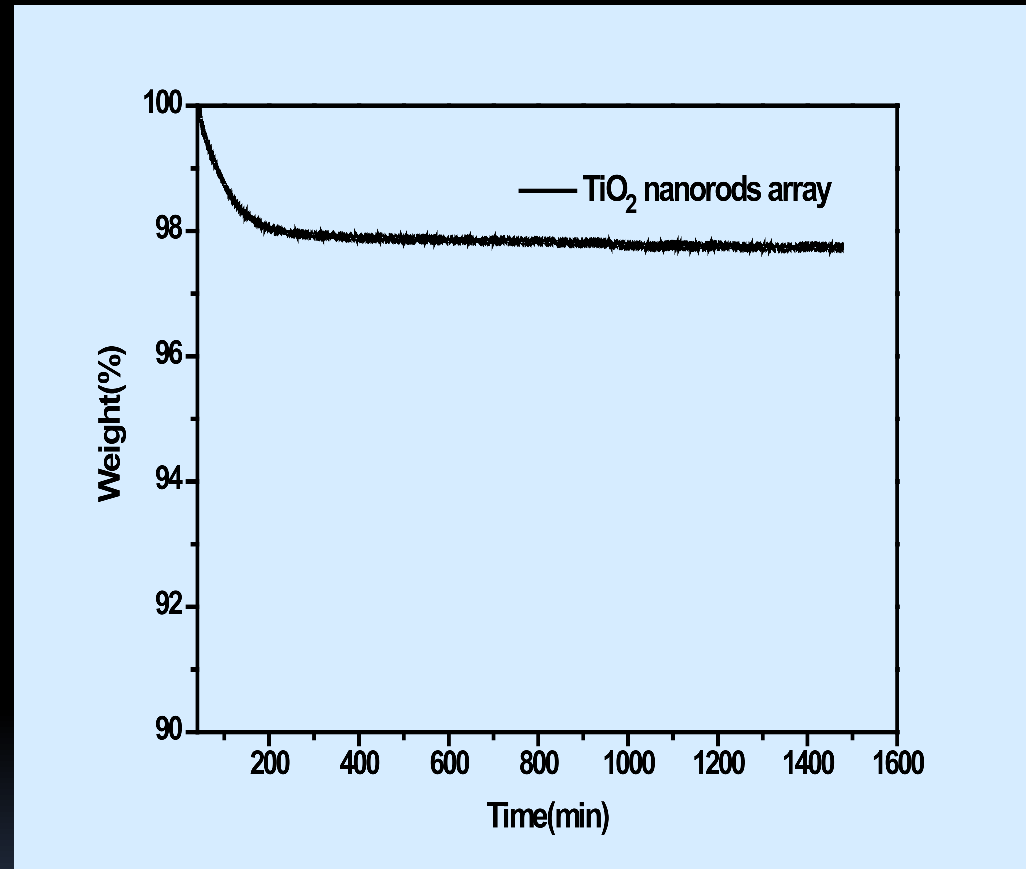




Samples	TiO_2-Cordierite	TiO_2	800°C 24 hrs TiO_2-Cordierite	800°C 24 hrs TiO_2
Specific Surface Area (m^2/g)	37.96	704.47	24.51	454.86

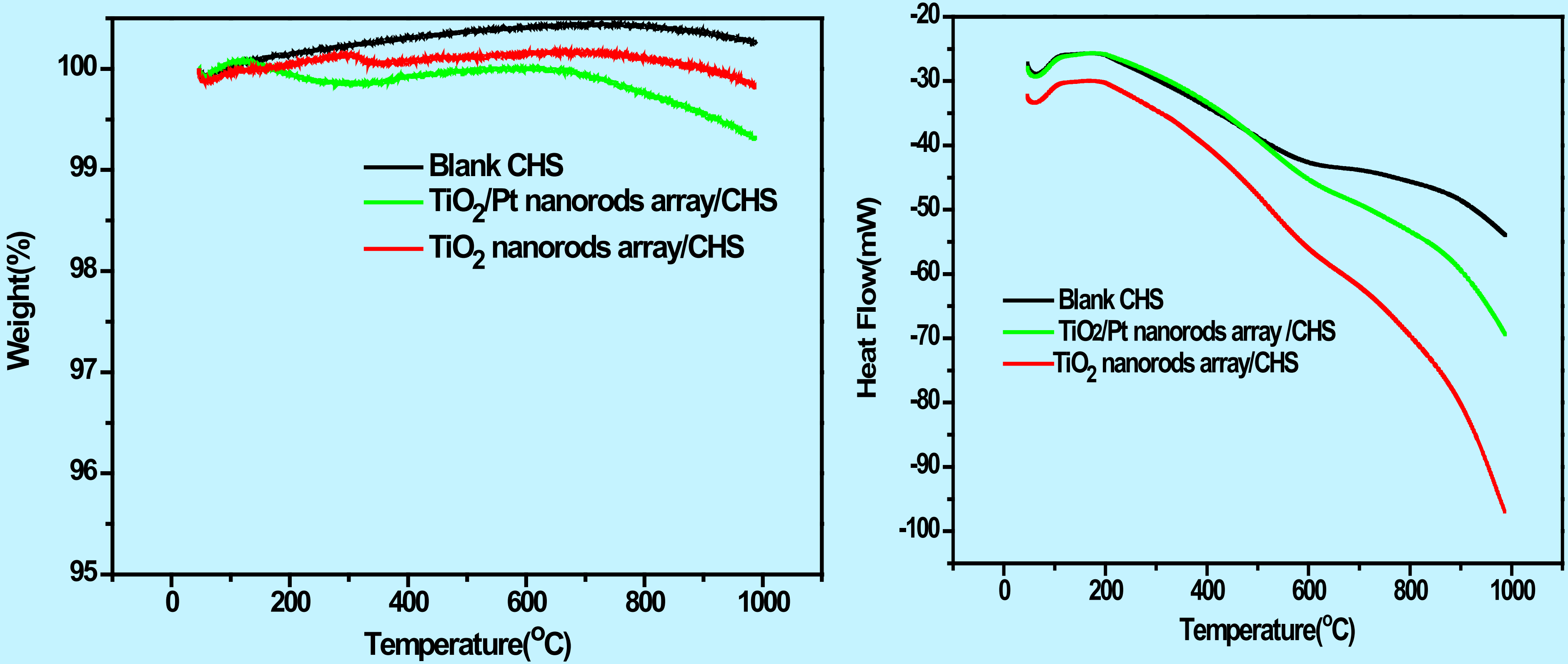
Thermal stability of TiO_2 nanoarrays





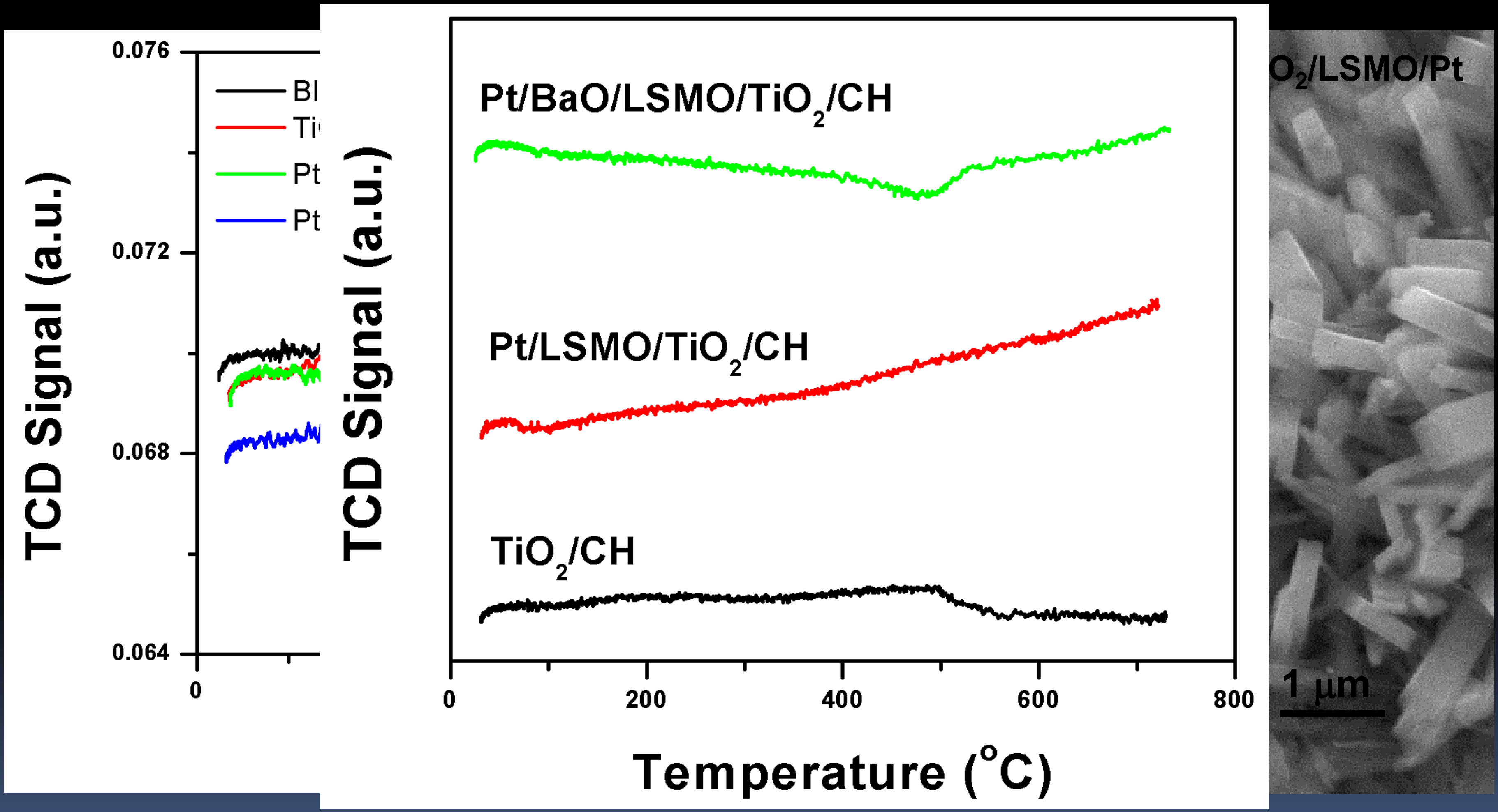
Thermal stability of TiO_2 nanorods array at 800°C for 24h

Thermal stability of TiO_2 nanoarrays under oxidative atmosphere



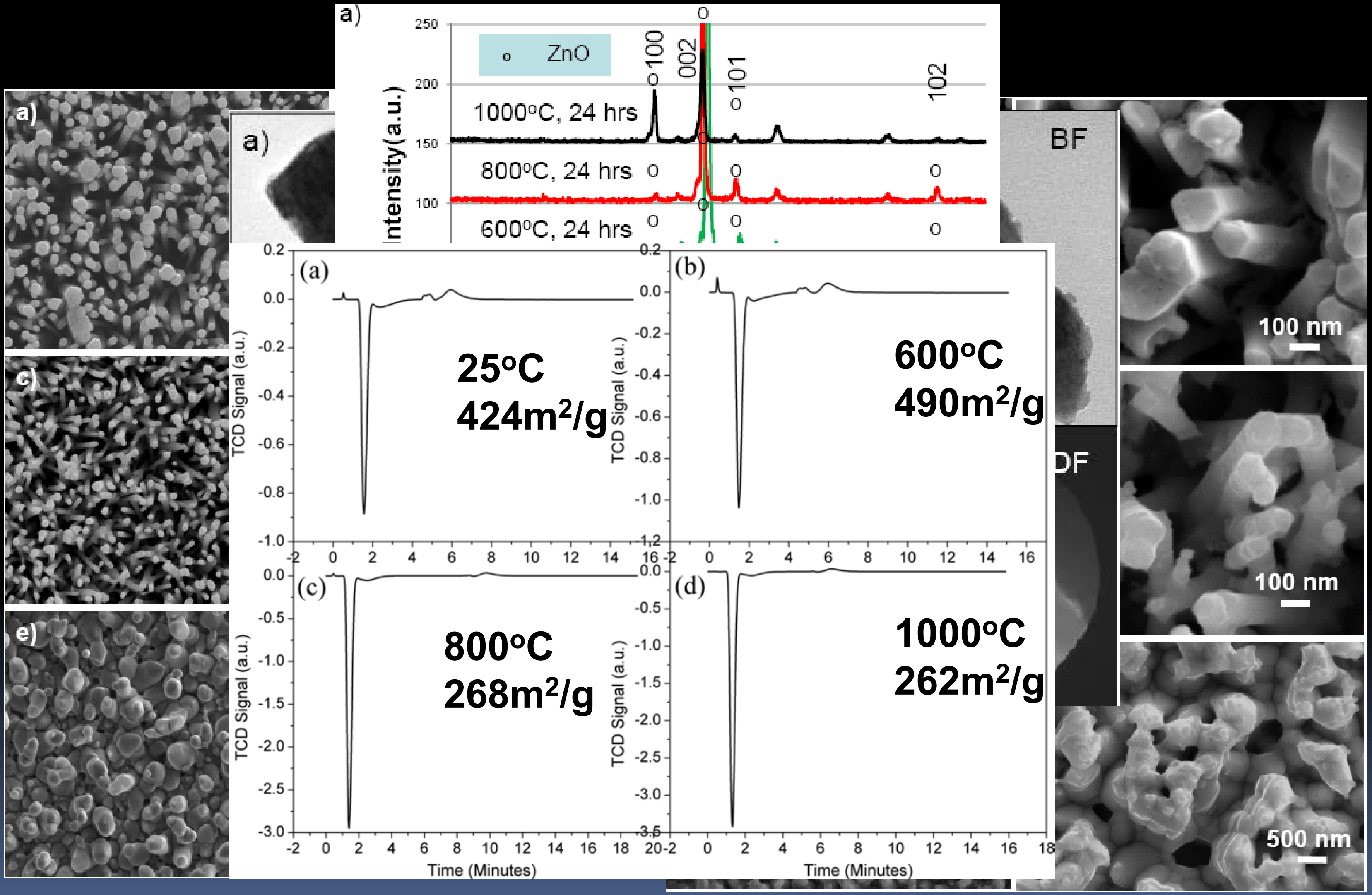
TGA and DSC of TiO_2 nanorods array on substrates

Thermal stability of TiO_2 nanowire based catalysts under reductive atmosphere

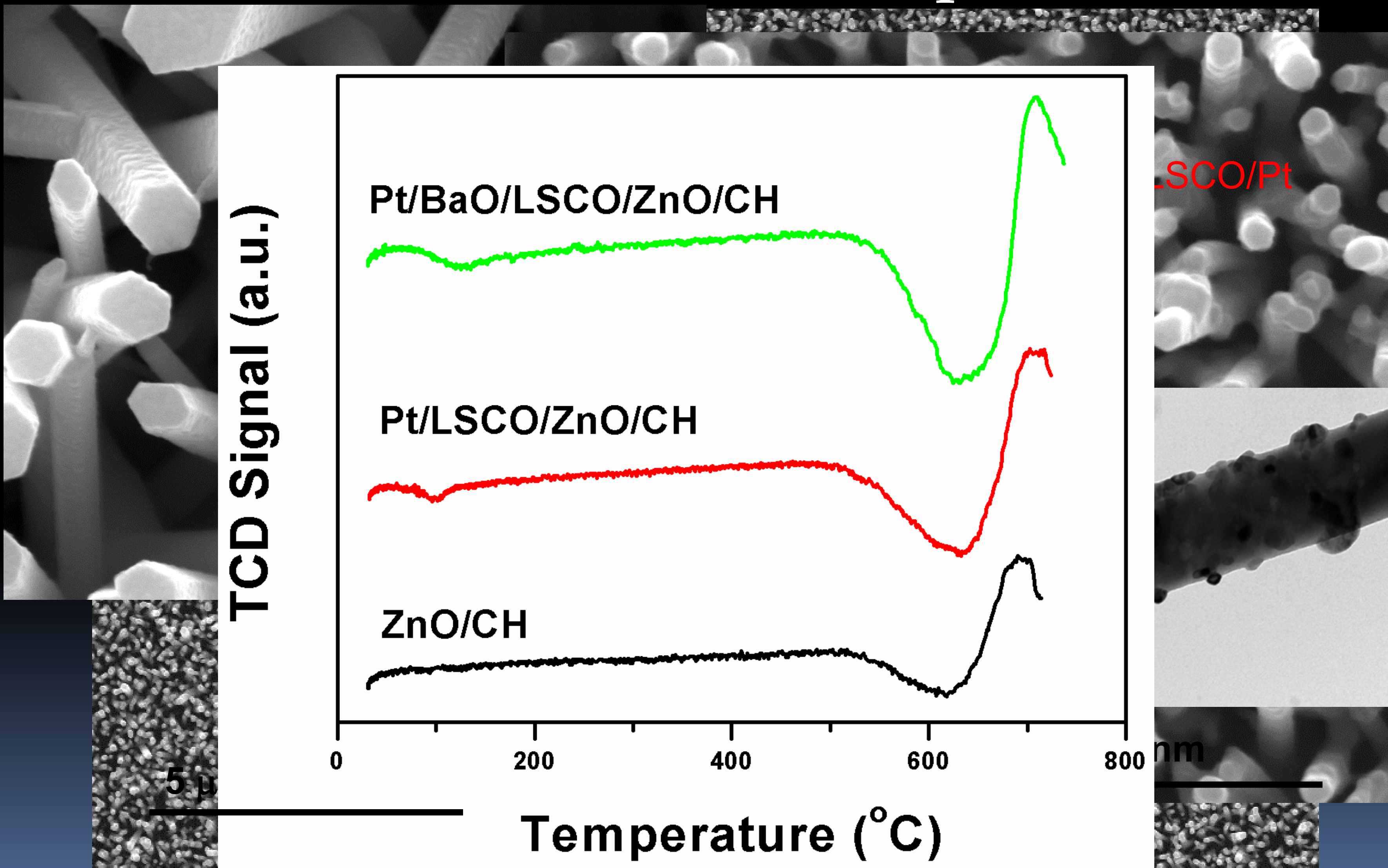


TPR-H_2 of Pt coated TiO_2 or TiO_2/LSMO nanowire arrays on substrates.

Thermal stability of ZnO/LSCO nanoarrays

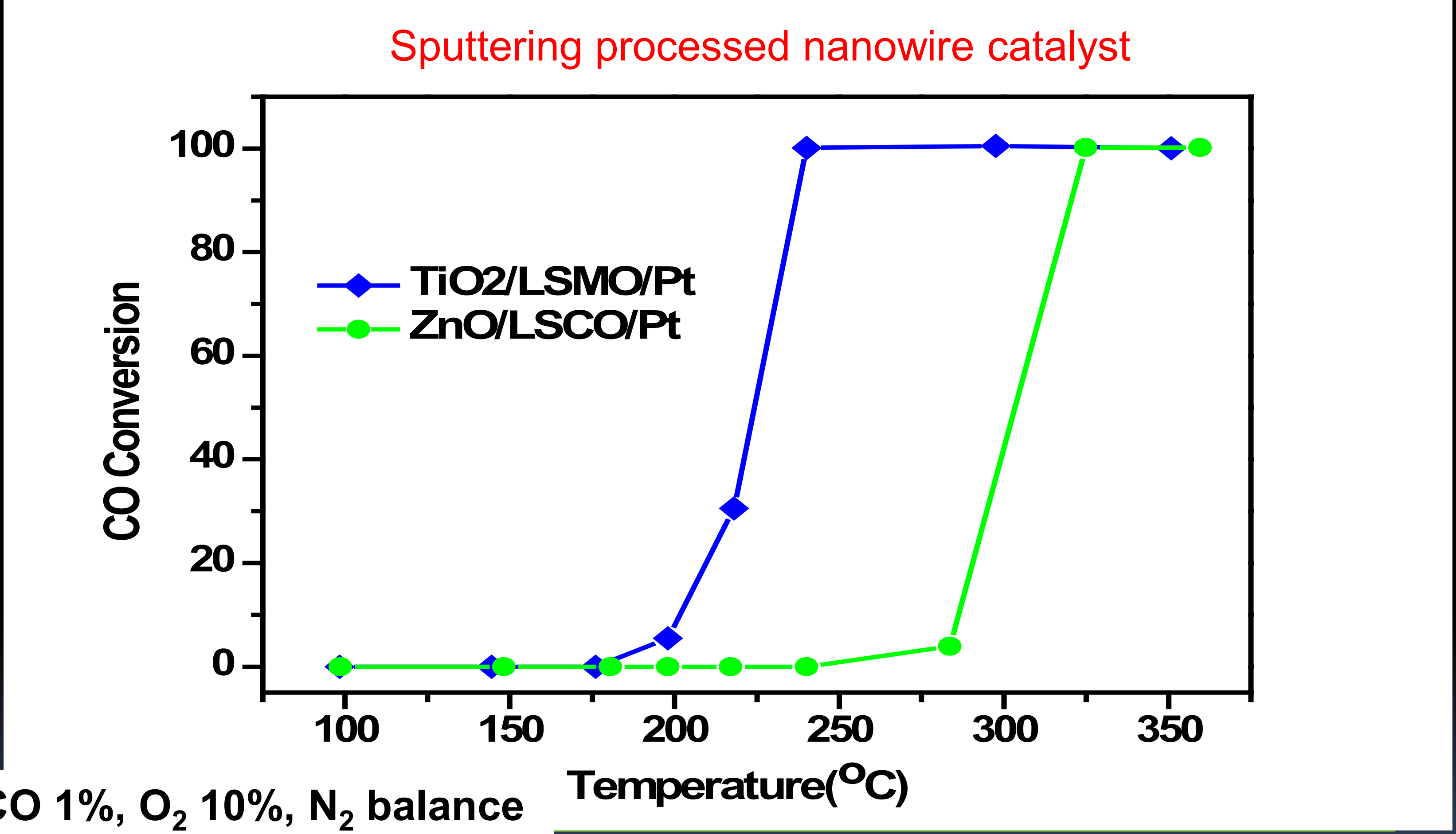


Thermal stability of ZnO nanowire catalysts under reductive atmosphere



TPR-H_2 of Pt coated ZnO/LSCO nanowire arrays on substrates.

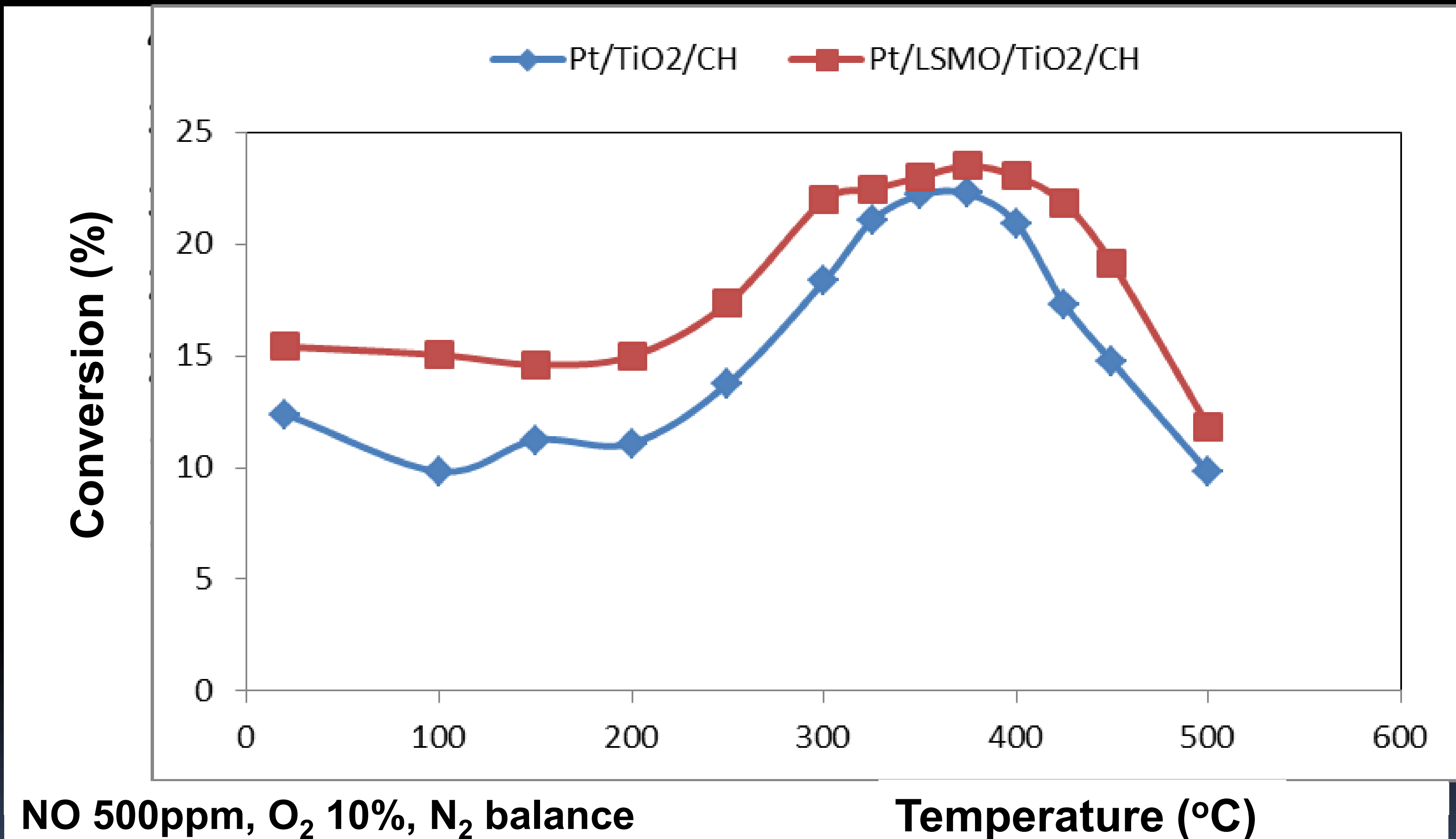
CO oxidation behaviors of monolithic composite nanowire catalysts



CO 1%, O_2 10%, N_2 balance
Pt: <1%; SV:45,454 h^{-1}

- ✓ Better performance in sol-gel processed nanowire catalysts;
- ✓ LSCO reduces the light-off temp in CO oxidation;
- ✓ TiO2/LSMO/Pt is better than ZnO/LSCO/Pt for CO oxidation.

NO oxidation behaviors of monolithic composite nanowire catalysts



NO 500ppm, O_2 10%, N_2 balance
Pt: <1%; SV:166,667 h^{-1}

- ✓ LSCO loading in ZnO/Pt catalyst seems to reduce the NO oxidation performar
- ✓ LSMO loading improved the NO oxidation;
- ✓ High space velocity induced low conversion efficiency

Conclusions

1) Monolithic metal oxide composite nanowire emission control catalysts demonstrated with achievable high specific surface area.
2) ZnO/LSCO have very good thermal stability under ambient condition, while tend to decompose at ~600^{o}C due to reduction of ZnO, still with good structure integrity.
3) TiO_2/LSMO have good thermal stability under both ambient and reductive atmospheres with good structure integrity.
4) Monolithic composite nanowire catalysts are catalytically active to both CO and NO oxidation under high space velocity and low Pt loading;
5) LSCO and LSMO improve the CO oxidation conversion efficiency of ZnO/Pt nanowire catalysts; sol-gel processed nanowire catalysts have better catalytic performance than sputtering process.
6) LSMO improves the NO oxidation behavior in TiO_2/Pt nanowire catalyst, while LSCO seemed to degrade the catalytic performance in ZnO/Pt systems.