Three-Dimensional Composite Nanostructures for Lean NO_x Emission Control

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ACE030

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Project Overview

Timeline

- Project start date: 10/01/2009
- Project end date: 09/31/2012
- Percent complete: 16.67%

Budget

- Total project funding
  - DOE share: $1,248,242
  - Contractor share: $314,504
- Funding received in FY09 from DOE: $392,282

Barriers

- Barriers addressed
  - Lean NOx emission reduction
  - Particulate filtering using new catalysts
  - New catalysts for reducing/eliminating usage of noble metals
  - Simplification of emission control devices to reduce the cost

Partners

- Honda Research Institute (OH)

Project Objectives

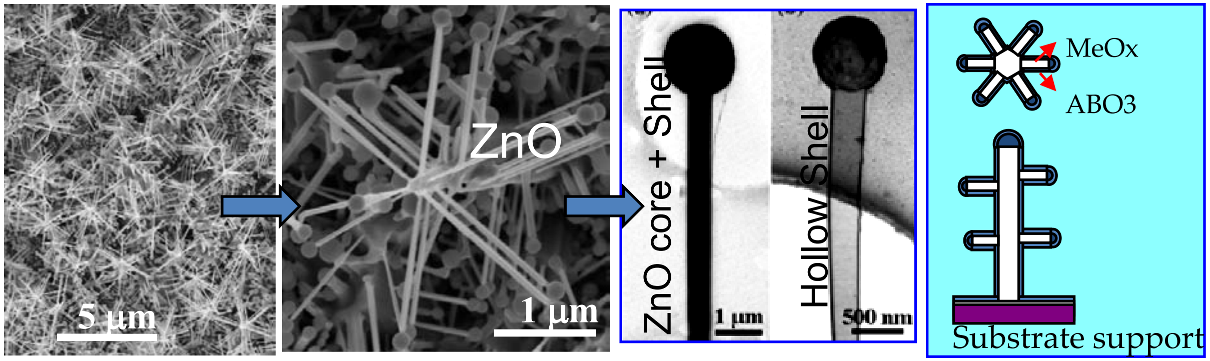
- Overall Objective:
  - To develop a unique class of three-dimensional (3D) metal oxide (MeO_x)/perovskite (ABO_3) composite nanostructure catalysts to reduce and control lean NO_x emission in vehicles, eventually to replace or reduce the usage of the Pt-group metal catalysts.

- Quarters 1-2 (10/1/2009-3/31/2010) objective:
  - Initiate the synthesis and characterization of 3D nanocomposite catalysts.
  - Initiate the modeling of surface NO_x catalytic chemistry in 3D nanocomposite surface and interface.

Milestones

	Task description	Month 1-6
1.	3D semiconductor nanostructure arrays synthesis	
	1.1 Planar substrates	
	1.2 Monolith substrates	
2.	Mesoporous perovskite nanoshell deposition	
	2.1 Planar substrates	
	2.2 Monolith substrates	
3.	Structure and morphology characterization	
4.	Surface catalysis modeling and design	

Approach



1) Ultrahigh surface; 2) High thermal stability; 3) Strong adherence; 4) Low cost; 5) High tailoring ability

- **Synthesis:**

To synthesize 3D composite nanowire/dendrite arrays rooted on different substrates by solution phase approaches and vapor phase approaches.

- **Characterization:**

To investigate the structure, morphology, chemical and electronic properties of composite nanodendrite arrays using a range of microscopy and spectroscopy techniques.

- **Activity, Selectivity, Durability and Regenerability:**

To explore the catalytic behavior and thermal stability using microscopy, spectroscopy, thermal analysis and temperature programmed surface analysis tools.

- **Surface Catalysis Modeling :**

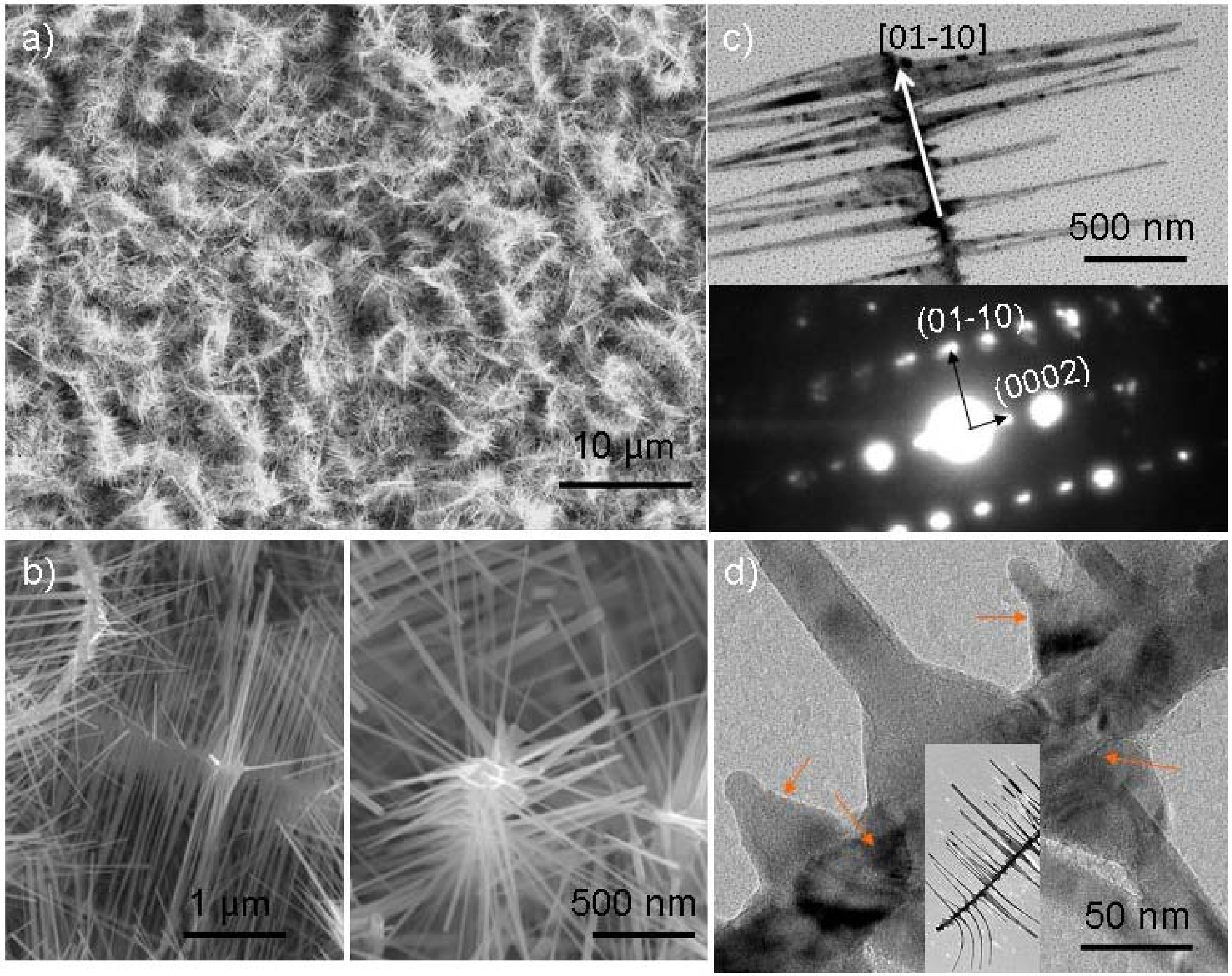
To simulate and model the surface catalysis behavior on composite nanocatalyst surfaces and interfaces using DFT atomistic calculation.

Accomplishments

(Project period: 10/1/2009-03/31/2010)

1) The research personnel team smoothly assembled;
2) Project successfully initiated for synthesis of 3D nanostructures of various metal oxides; and fabrication, initial structure and chemical characterization;
3) Some initial results achieved, particularly synthesis in ZnO, TiO_2, $ZnO/(La,Sr)CoO_3$ (LSCO), and $ZnO/(La,Sr)MnO_3$ (LSMO) systems, and surface catalysis modeling of $LaMnO_3$ (LMO) system.

Large scale nanodendrite array by carbothermal CVD

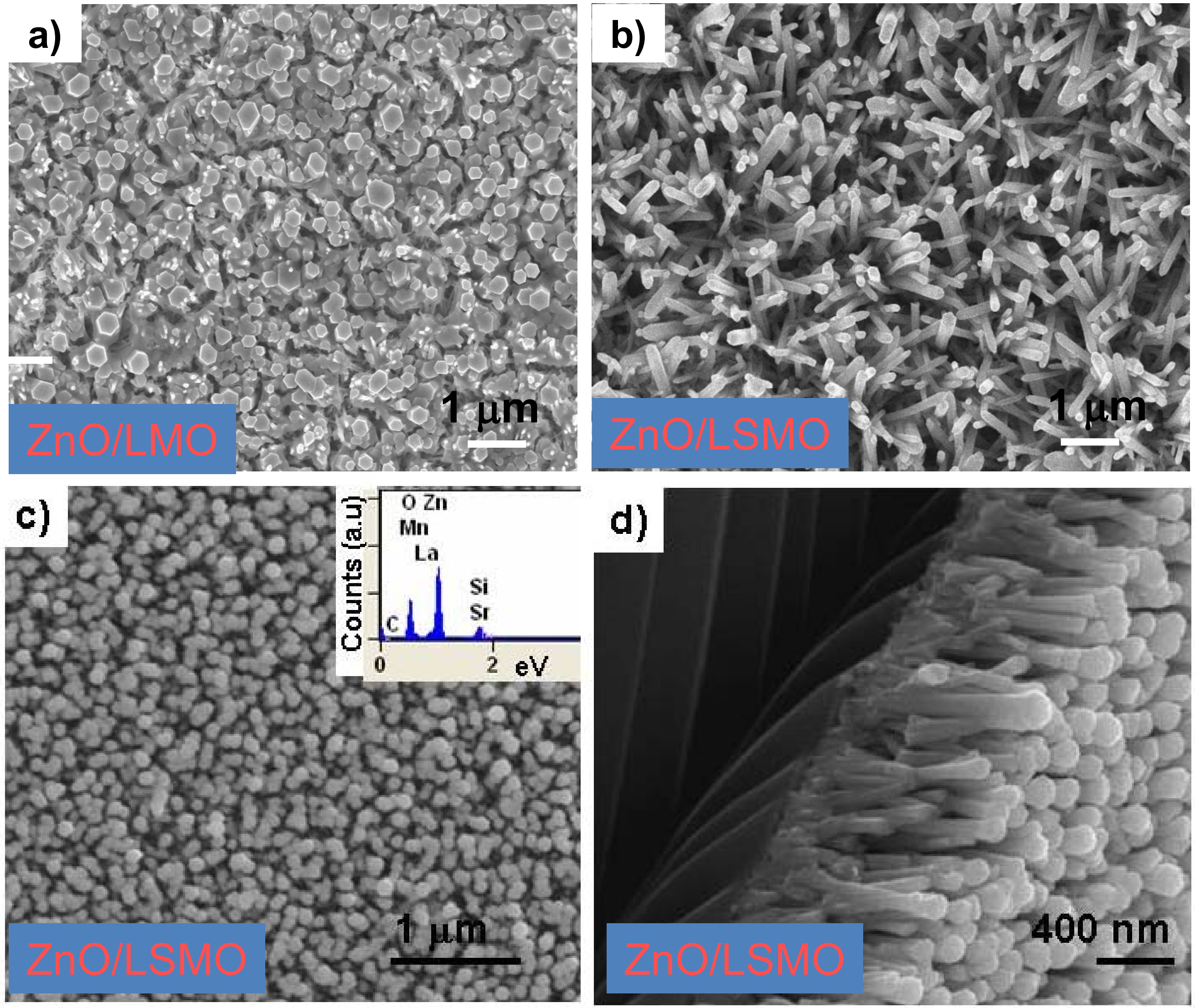


Advantage: in-situ, large scale, low temperature , <700 ^{o}C.

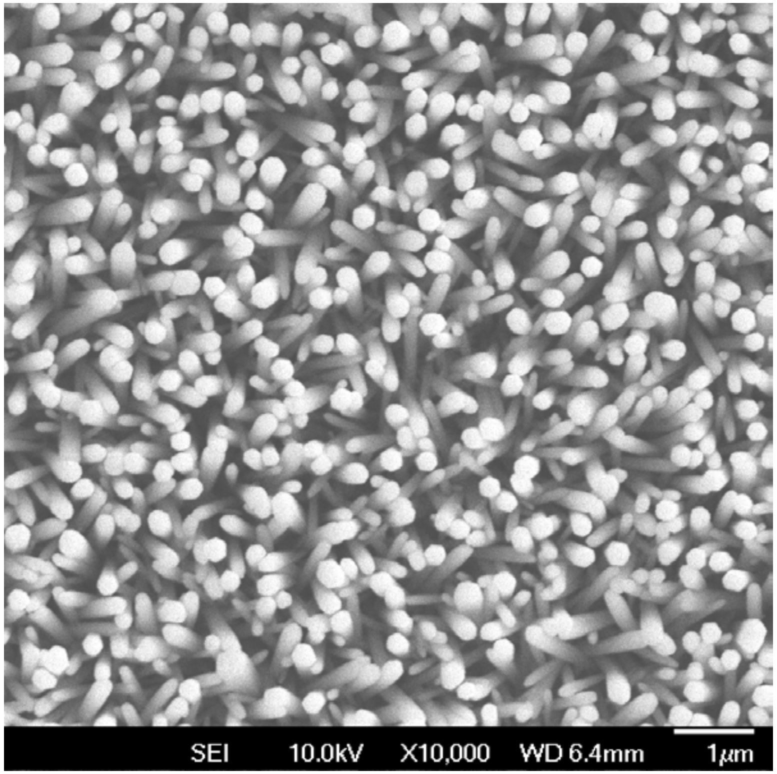
ABO_3 Nanoshell Deposition

Sol-gel as-deposited LMO and LSMO shells on ZnO NWs

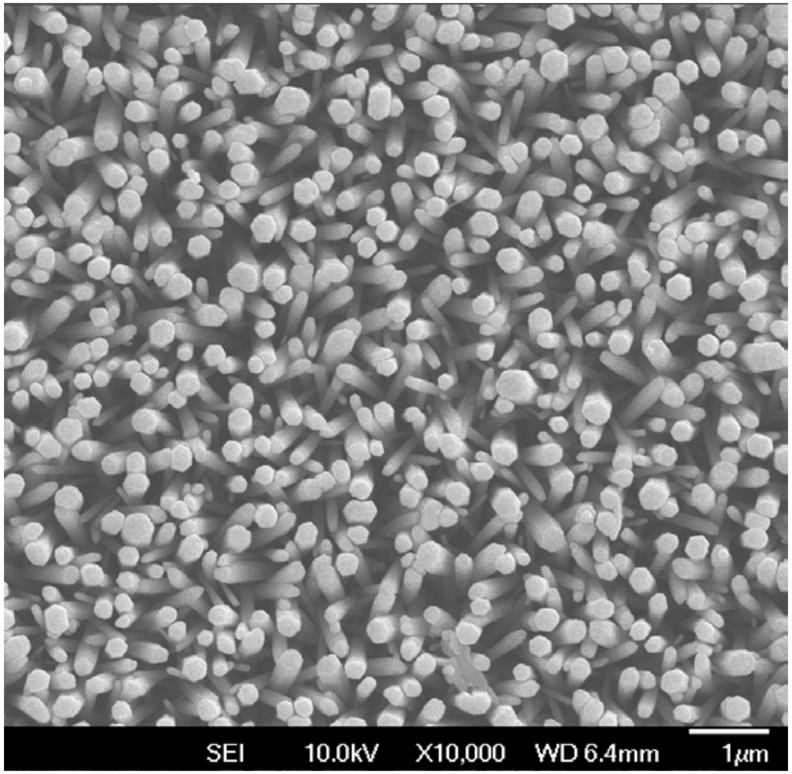
Sputtering: as-deposited LSMO shells on ZnO NWs



ABO_3 Nanoshell Deposition
Sputtering + 800 °C annealing in air

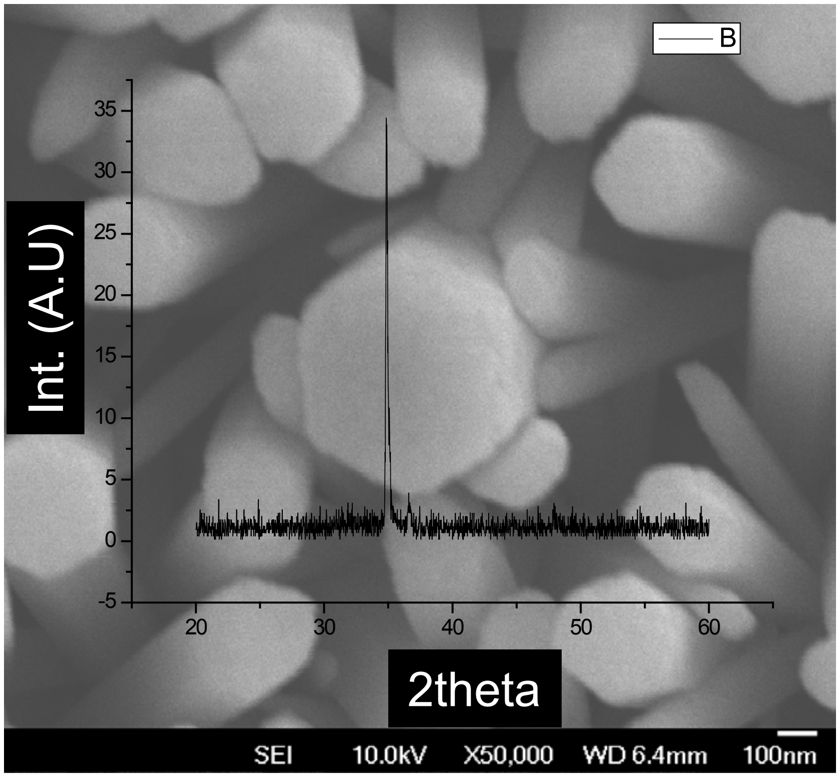


LSMO30nm as deposited
On ZnO nanowire arrays

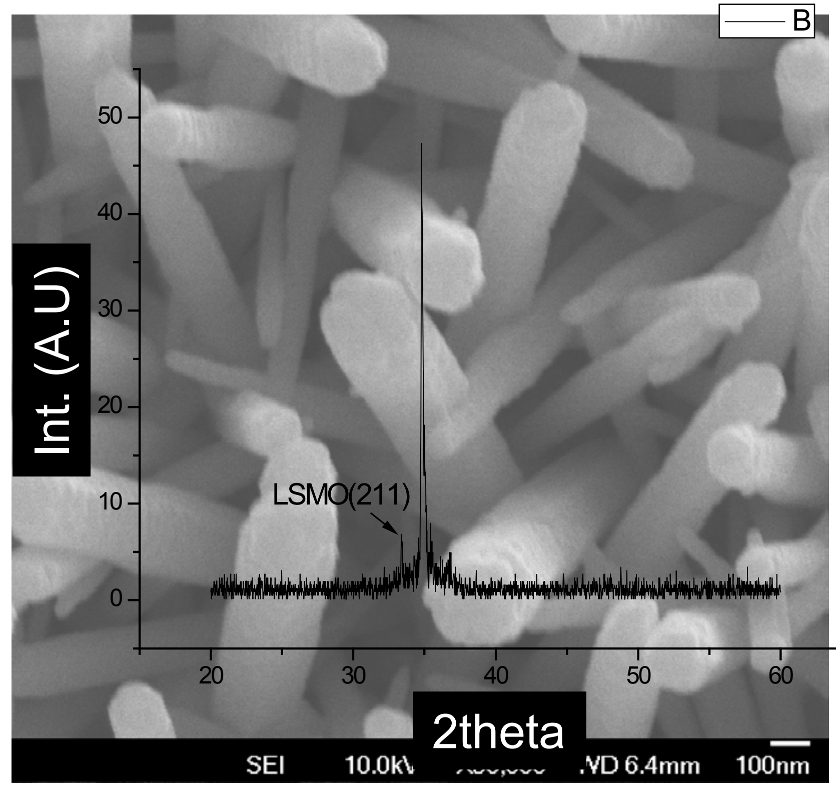


LSMO30nm annealed
On ZnO nanowire arrays

ABO_3 Nanoshell Deposition
Sputtering + 800 ^oC annealing in air



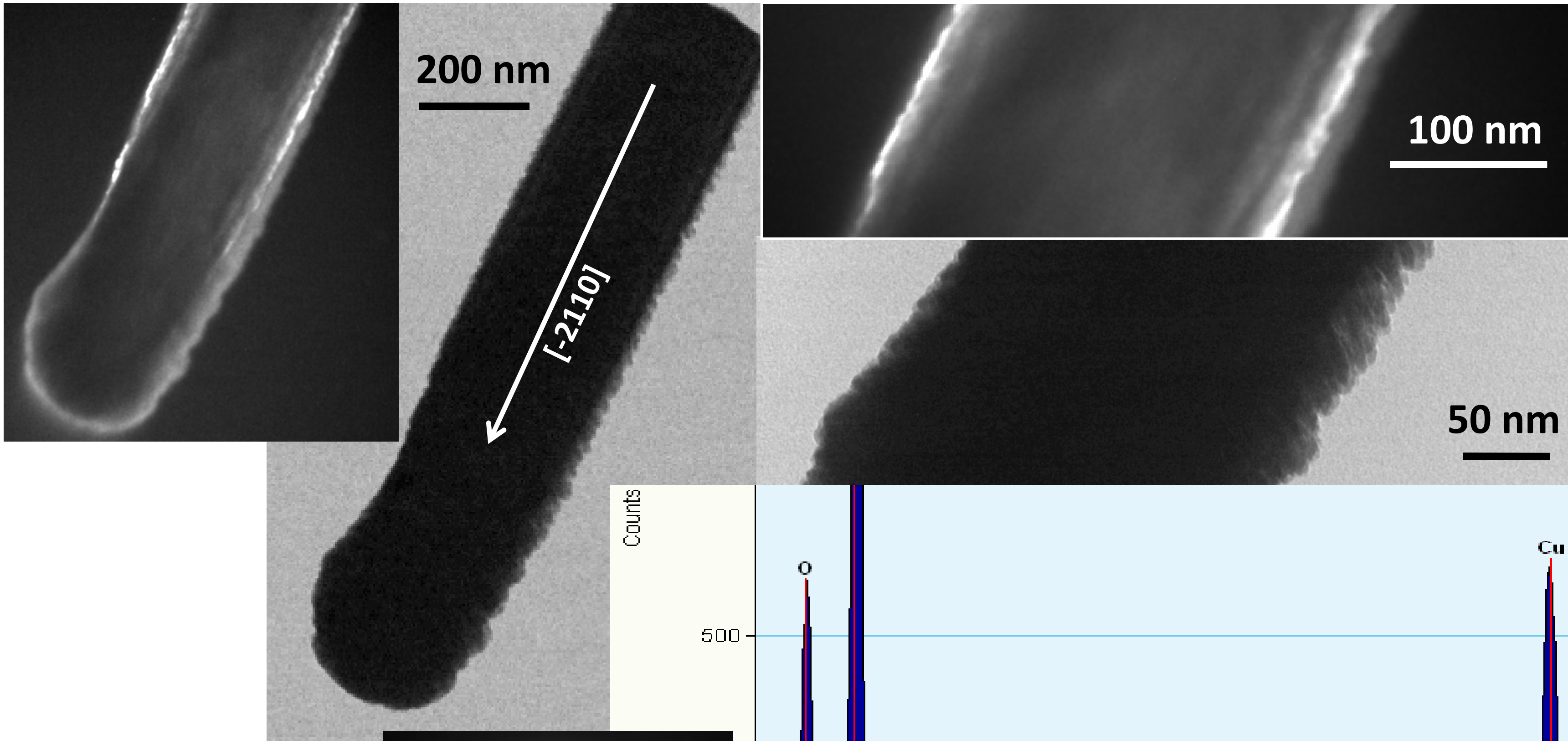
LSMO20nm as deposited
On ZnO nanowire arrays

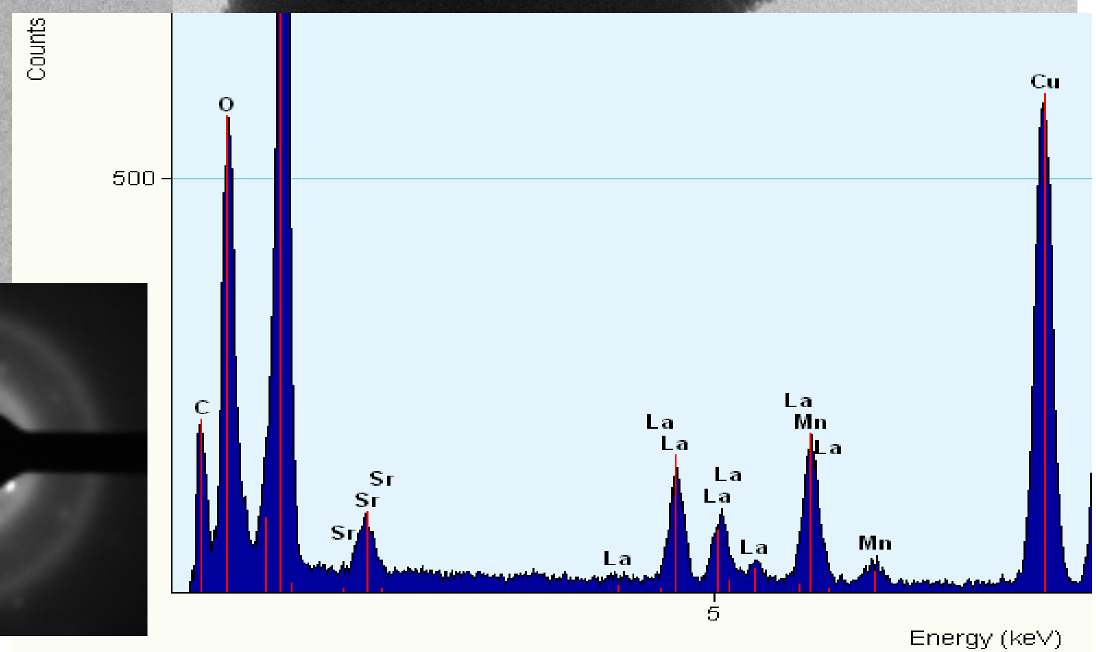


LSMO20nm annealed
On ZnO nanowire arrays

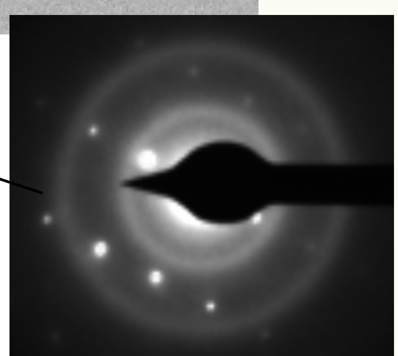
ABO_3 Nanoshell Deposition

As-deposited LSMO20nm thick on ZnO nanowire arrays



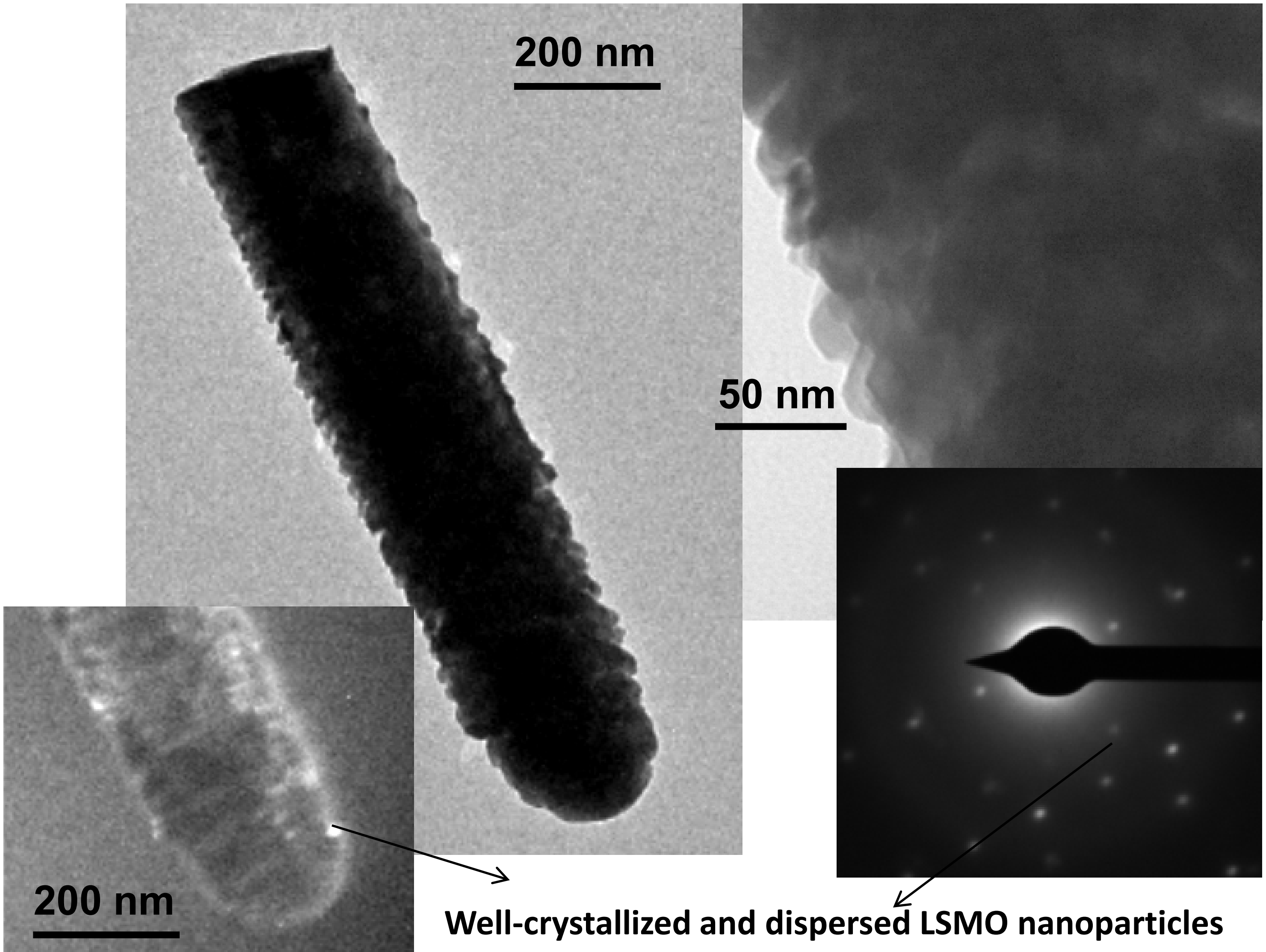


Poorly crystallized
LSMO on single
crystalline ZnO



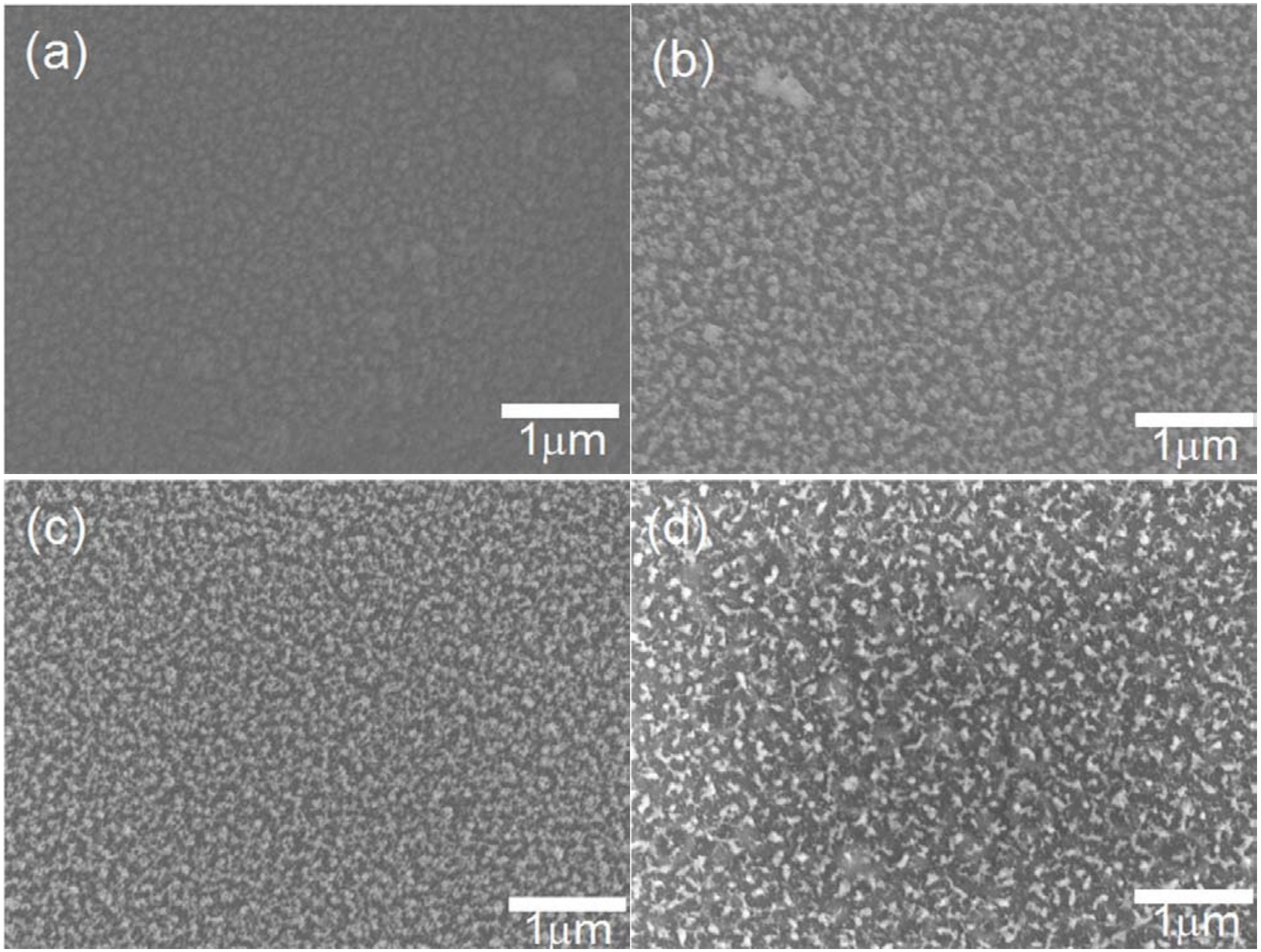
ABO_3 Nanoshell Deposition

30 nm deposition, RT Sputtering + Annealing at 800 ^oC for 1 hour

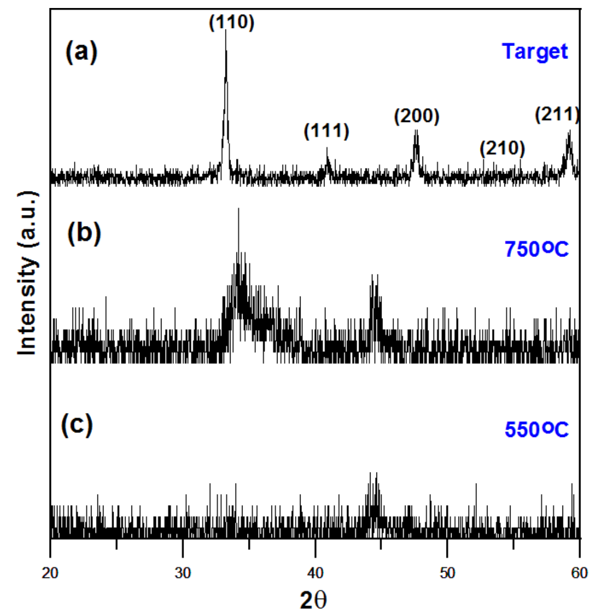


Well-crystallized and dispersed LSMO nanoparticles on single crystalline ZnO

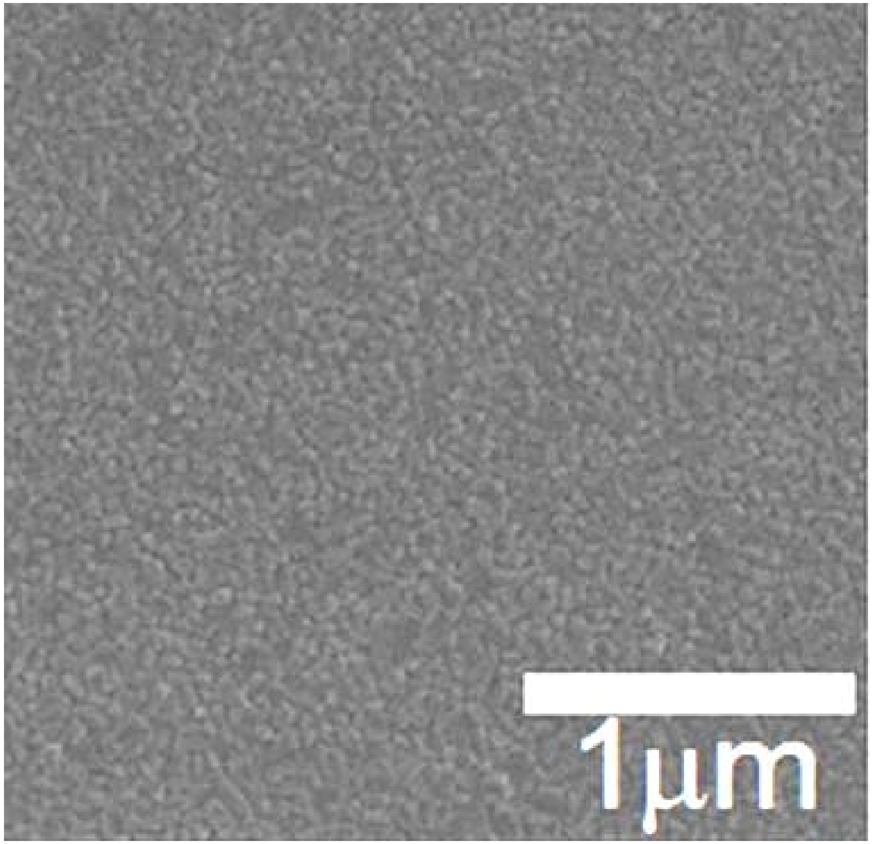
ABO_3 Nanoshell Deposition
Pulsed laser deposition



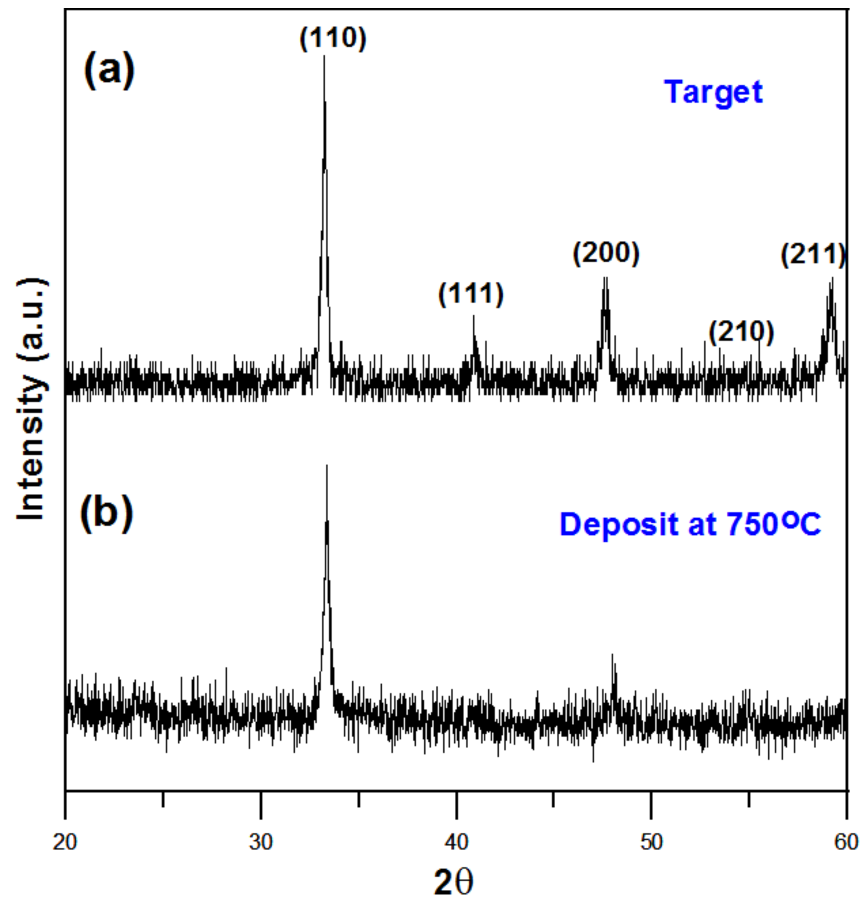
200 nm LSCO films deposited at RT
(a) as made;
(b) 350°C annealing,
(c) 550°C annealing,
(d) 750°C annealing
for 2 hours in air.



ABO$_3$ Nanoshell Deposition
Pulsed laser deposition

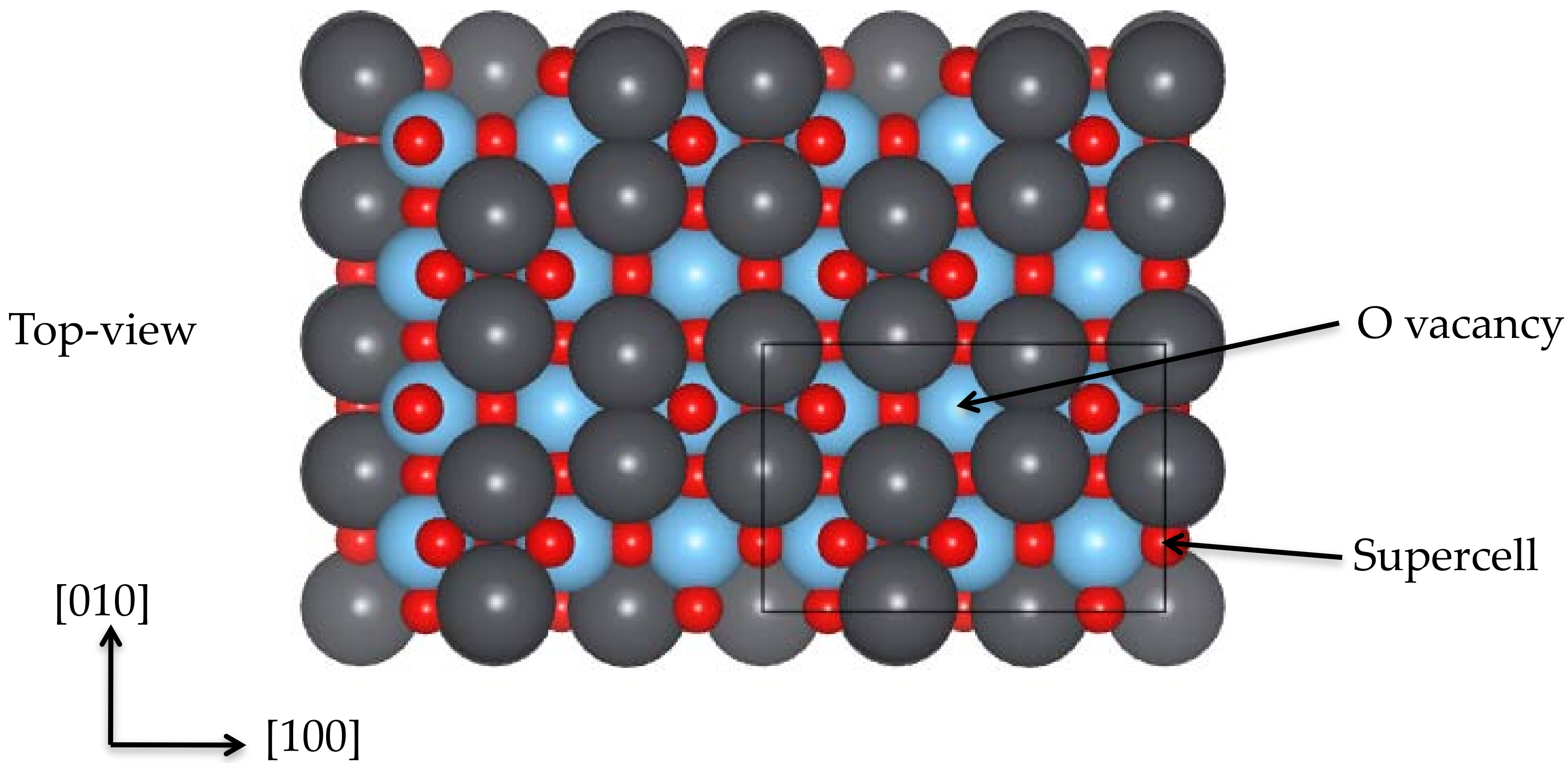


LSCO films deposited at 750^{o}C on Si substrate



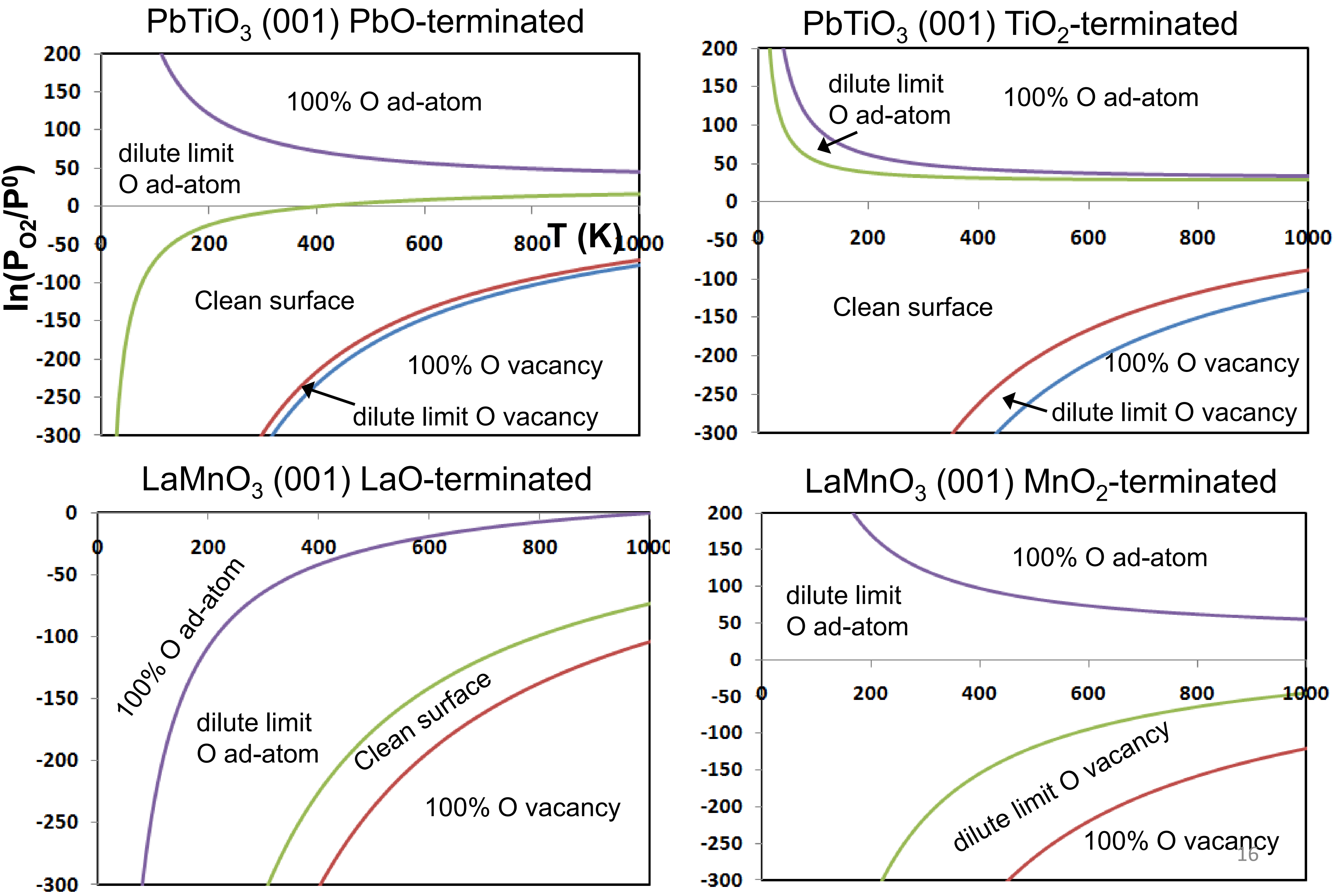
(a) LSCO target and (b) LSCO films deposited at 750^{o}C

Interaction of ABO_3 Surfaces with NO, O_2 and N_2

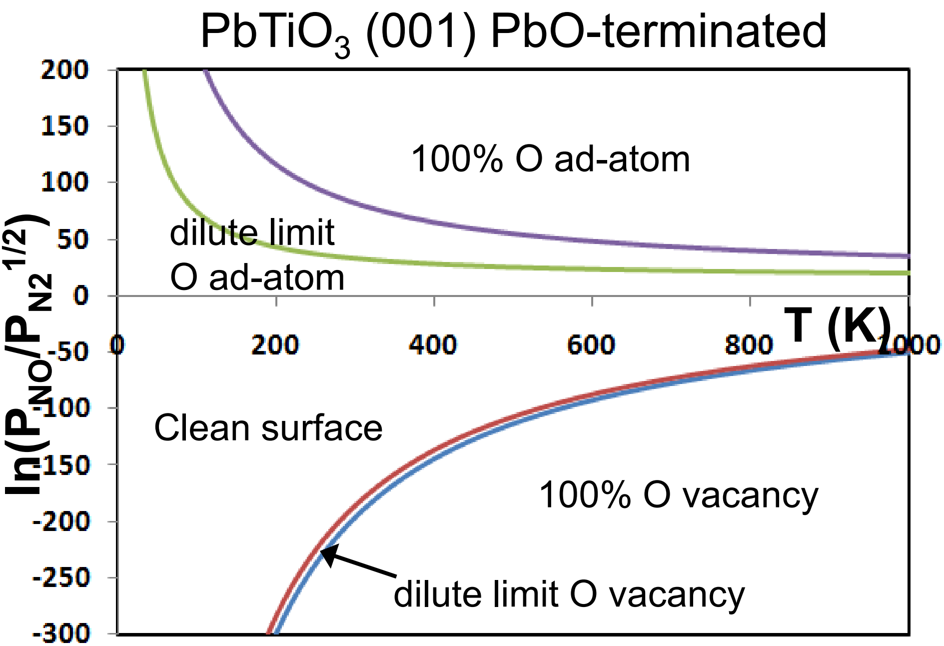


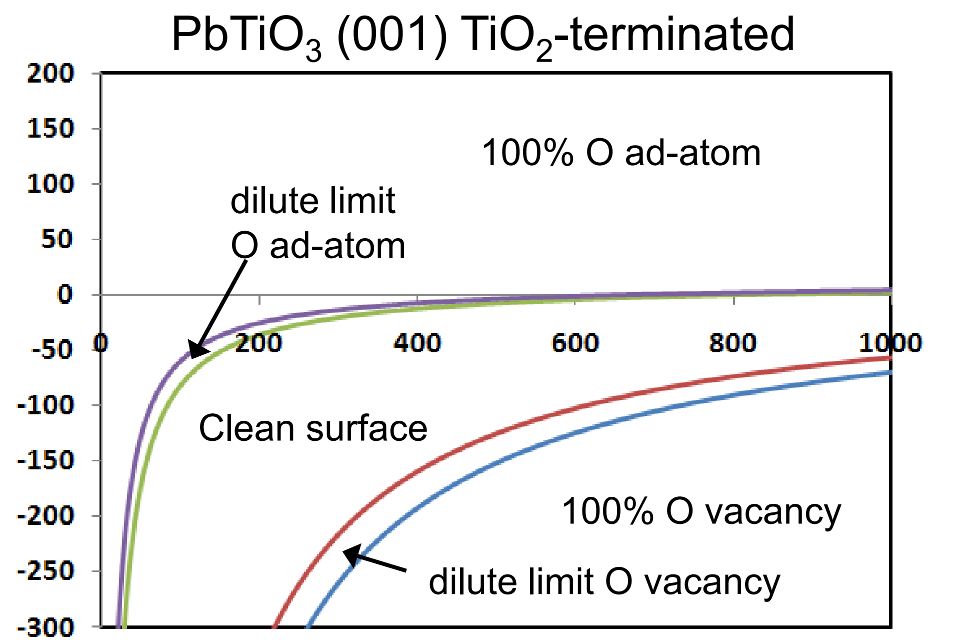
First step: equilibrium between ABO_3 surfaces and gases at various T and P

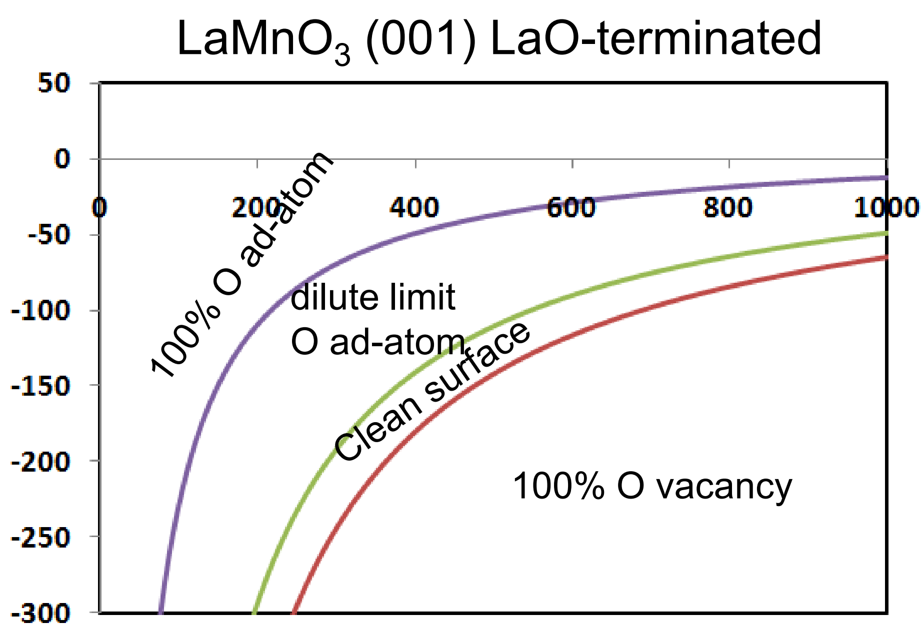
Surface phase diagrams for surfaces/O_2

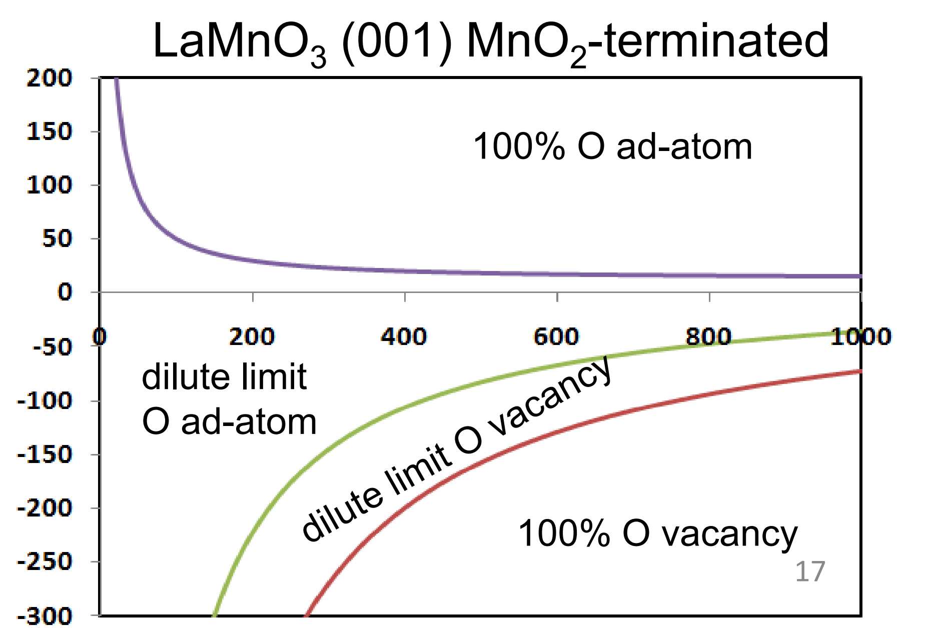


Surface phase diagrams for surfaces/NO









Collaborations

- Partners:
  - Honda Research Institute (industry): collaboration on catalyst design and synthesis, especially on the emission control catalytic behavior testing;
  - United Technologies (industry): collaboration on nanomaterials synthesis and surface analysis

Proposed Future work

- Process optimization of 3D composite nanocatalysts synthesis on planar substrates and initiation of the synthesis on monolith substrates
- Structure /morphology /chemical characterization
- Initiation of metal doping study of 3D composite nanocatalysts
- Initiation of thermal stability testing
- Initiation of emission control catalytic testing of 3D composite nanocatalysts.
- Continuation of surface catalysis modeling of MeO_x/ABO_3 surface

Summary

- **Project Briefs**

---- Project Overview

---- Objectives and Milestones

---- Approach

- **Accomplishments**

---- 3D MeO_x nanowire/dendrite array synthesis and characterization

---- Mesoporous ABO_3 nanofilm deposition

---- Surface catalysis modeling

- **Future work**

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