Three-Dimensional Composite Nanostructures for Lean NO$_x$ Emission Control

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Project Overview

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

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

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

Partners
• Honda Research Institute (OH)
Project Objectives

• Overall Objective:
  – To develop a unique class of three-dimensional (3D) metal oxide (MeOₓ)/perovskite (ABO₃) composite nanostructure catalysts to reduce and control lean NOₓ 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 NOₓ catalytic chemistry in 3D nanocomposite surface and interface.
## Milestones

<table>
<thead>
<tr>
<th>Task description</th>
<th>Month 1-6</th>
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<td>1. 3D semiconductor nanostructure arrays synthesis</td>
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<td>1.1 Planar substrates</td>
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<td>1.2 Monolith substrates</td>
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<td>2. Mesoporous perovskite nanoshell deposition</td>
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<tr>
<td>2.1 Planar substrates</td>
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<td>2.2 Monolith substrates</td>
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<td>3. Structure and morphology characterization</td>
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<td>4. Surface catalysis modeling and design</td>
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</table>
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 °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
ABO₃ Nanoshell Deposition
Sputtering + 800 °C annealing in air

LSMO20nm as deposited
On ZnO nanowire arrays

LSMO20nm annealed
On ZnO nanowire arrays
ABO$_3$ Nanoshell Deposition

As-deposited LSMO 20nm thick on ZnO nanowire arrays

Poorly crystallized LSMO on single crystalline ZnO
ABO$_3$ Nanoshell Deposition

30 nm deposition, RT Sputtering + Annealing at 800 °C for 1 hour
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°C on Si substrate

(a) LSCO target and (b) LSCO films deposited at 750°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/O₂

PbTiO₃ (001) PbO-terminated

LaMnO₃ (001) LaO-terminated

PbTiO₃ (001) TiO₂-terminated

LaMnO₃ (001) MnO₂-terminated

ln(P₂O₅/P₀) vs T (K)

100% O ad-atom

100% O vacancy

Dilute limit O ad-atom

Dilute limit O vacancy

Clean surface
Surface phase diagrams for surfaces/NO

**PbTiO$_3$ (001) PbO-terminated**
- Clean surface
- 100% O ad-atom
- 100% O vacancy
- Dilute limit O vacancy
- Dilute limit O ad-atom

**LaMnO$_3$ (001) LaO-terminated**
- Clean surface
- 100% O ad-atom
- 100% O vacancy
- Dilute limit O vacancy
- Dilute limit O ad-atom

**PbTiO$_3$ (001) TiO$_2$-terminated**
- Clean surface
- 100% O ad-atom
- 100% O vacancy
- Dilute limit O vacancy
- Dilute limit O ad-atom

**LaMnO$_3$ (001) MnO$_2$-terminated**
- Clean surface
- 100% O ad-atom
- 100% O vacancy
- Dilute limit O vacancy
- Dilute limit O ad-atom
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 $\text{MeO}_x/\text{ABO}_3$ 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
Acknowledgements

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