Three-Dimensional Composite Nanostructures for Lean NO_x Emission Control

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Project ID #
ACE030

Project Overview

Project Objective

–To develop a unique class of 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.

Timeline

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

Budget

- Total project funding
  - DOE share: $1,248,242
  - Contractor share: $314,504
- Funding received in FY10-11 from DOE: $809,446

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

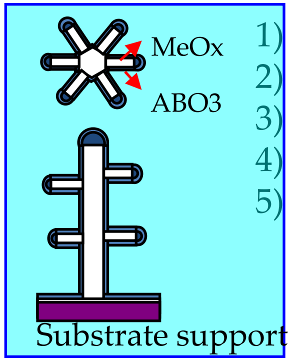
Partners

- Honda Research Institute (OH)

Objectives and Approaches

- Objectives (quarters 3-6, 04/1/2010-3/31/2011)
  - Synthesis and characterization of 3D nanoarray catalysts.
  - Metal loading and thermal stability testing
  - Modeling of surface NO_x catalytic chemistry in 3D nanocomposite surface and interface.

- Approaches:
  - **Synthesis:**
    To synthesize 3D composite nano(wire/dendrite)arrays rooted on different substrates by solution and vapor phase approaches.
  - **Characterization:**
    To investigate the structure, morphology, chemical and electronic properties of composite nanorrays using a range of microscopy and spectroscopy techniques.
  - **Activity, Selectivity, Durability and Regenerability:**
    To explore the catalytic behavior and 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.



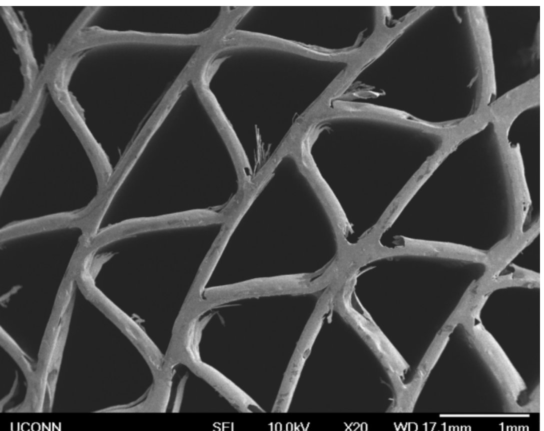
1) Ultrahigh surface;
2) High thermal stability;
3) Strong adherence;
4) Low cost;
5) High tailoring ability

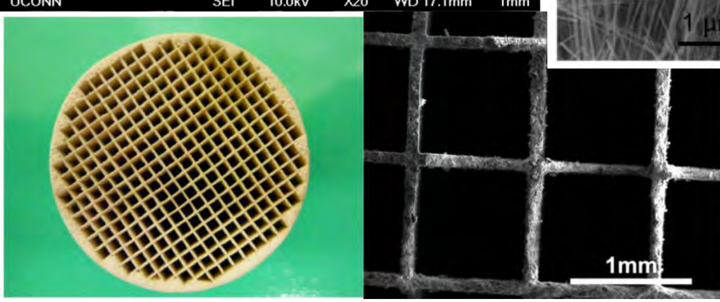
Accomplishments

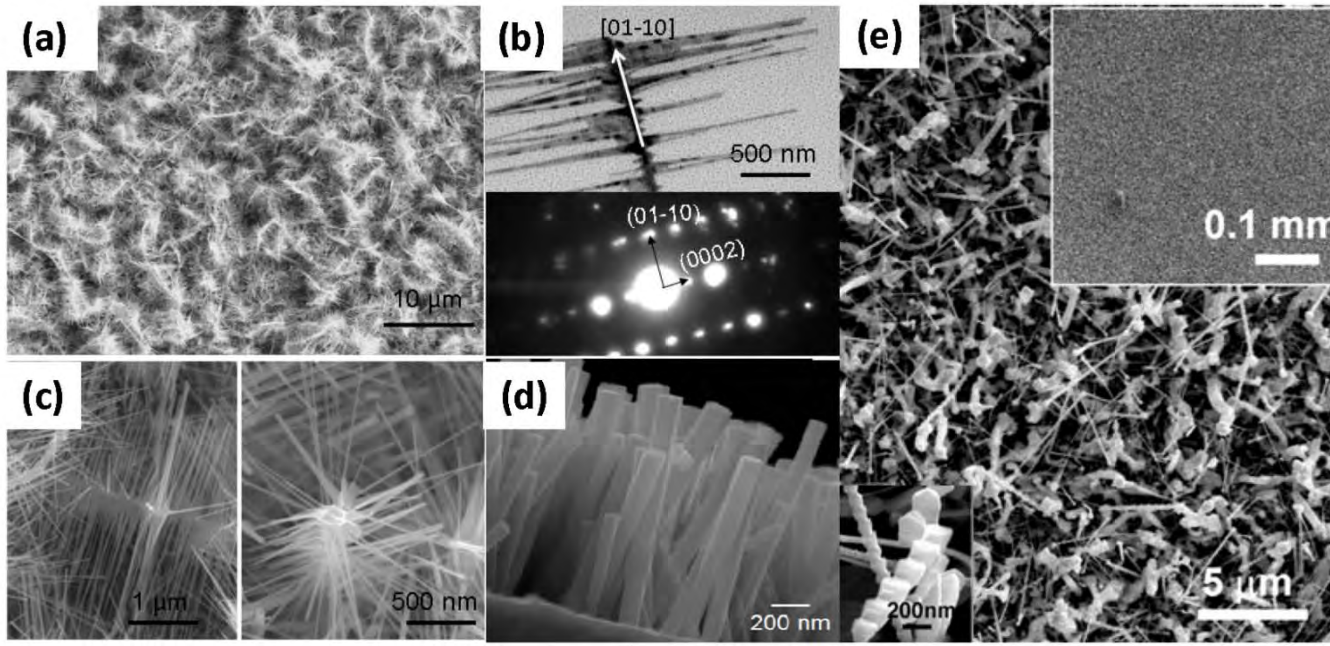
(Project period: 04/1/2010-03/1/2011)

1) Successful synthesized and characterized various metal oxide nanoarrays on various planar and monolith substrates.
2) Successful fabricated, characterized, and identified various 3D composite nanowires with very high specific surface area.
3) Successfully characterized and initially validated the thermal stability of various composite nanowires on monolith substrates under oxidative and reductive atmospheres.
4) Successfully initiated the emission testing over NO_x storage and reduction.
5) Successfully modeled and found the high activity of several perovskite crystal surfaces for O involved reactions.

Large scale nanoarrays by solution and vapor phase depositions







Metal oxide nanowire arrays on solid substrates.

W. Cai, P. Shimpi, D. Jian, P.-X. Gao, J. Mater. Chem. ***2010****; G. Liu, Y. Guo, P.-X. Gao et al.,* ***2011****, submitted; Y. Guo, Z. Zhang, P.-X. Gao et al.,* ***2011****, submitted.*

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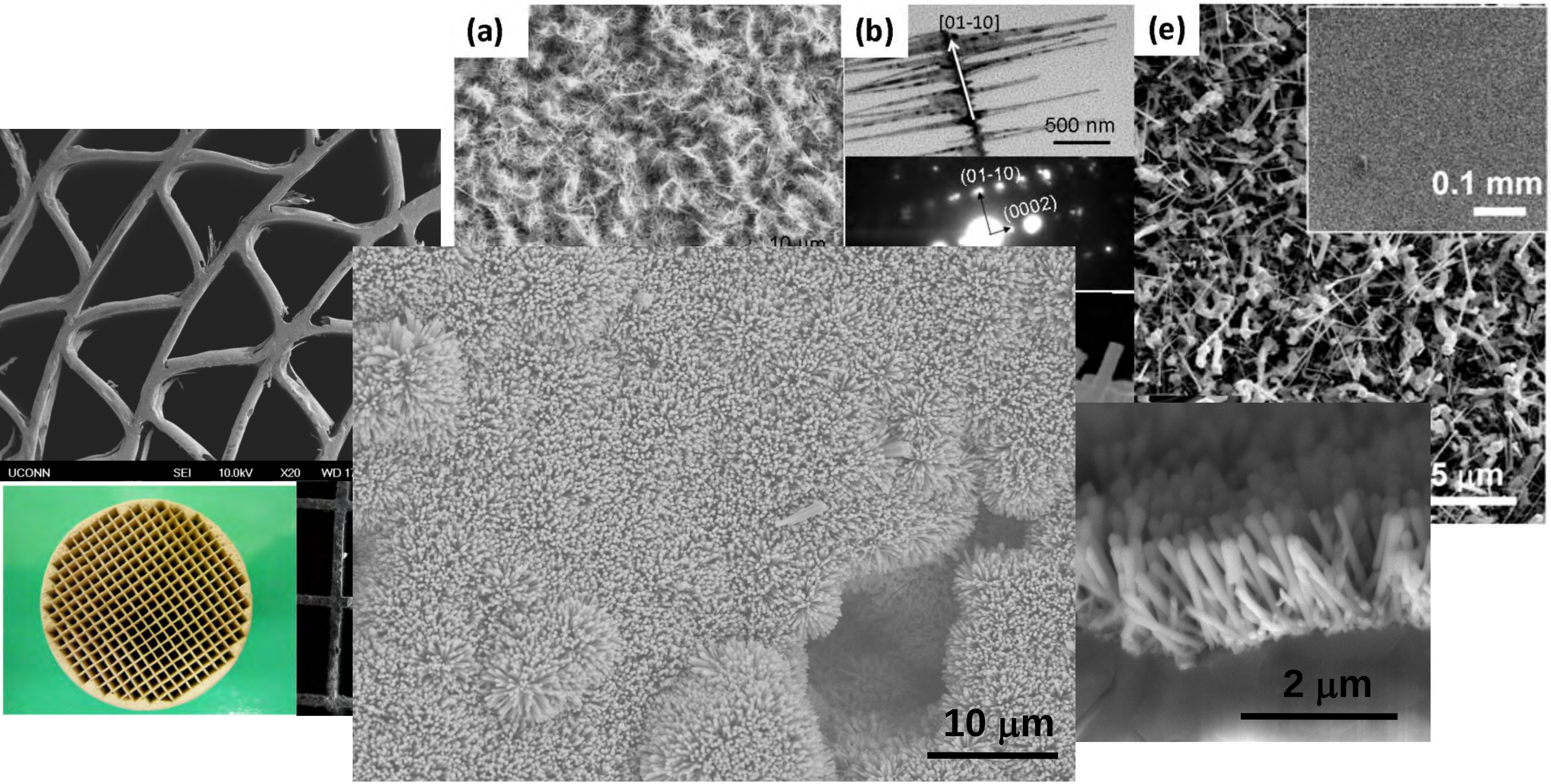

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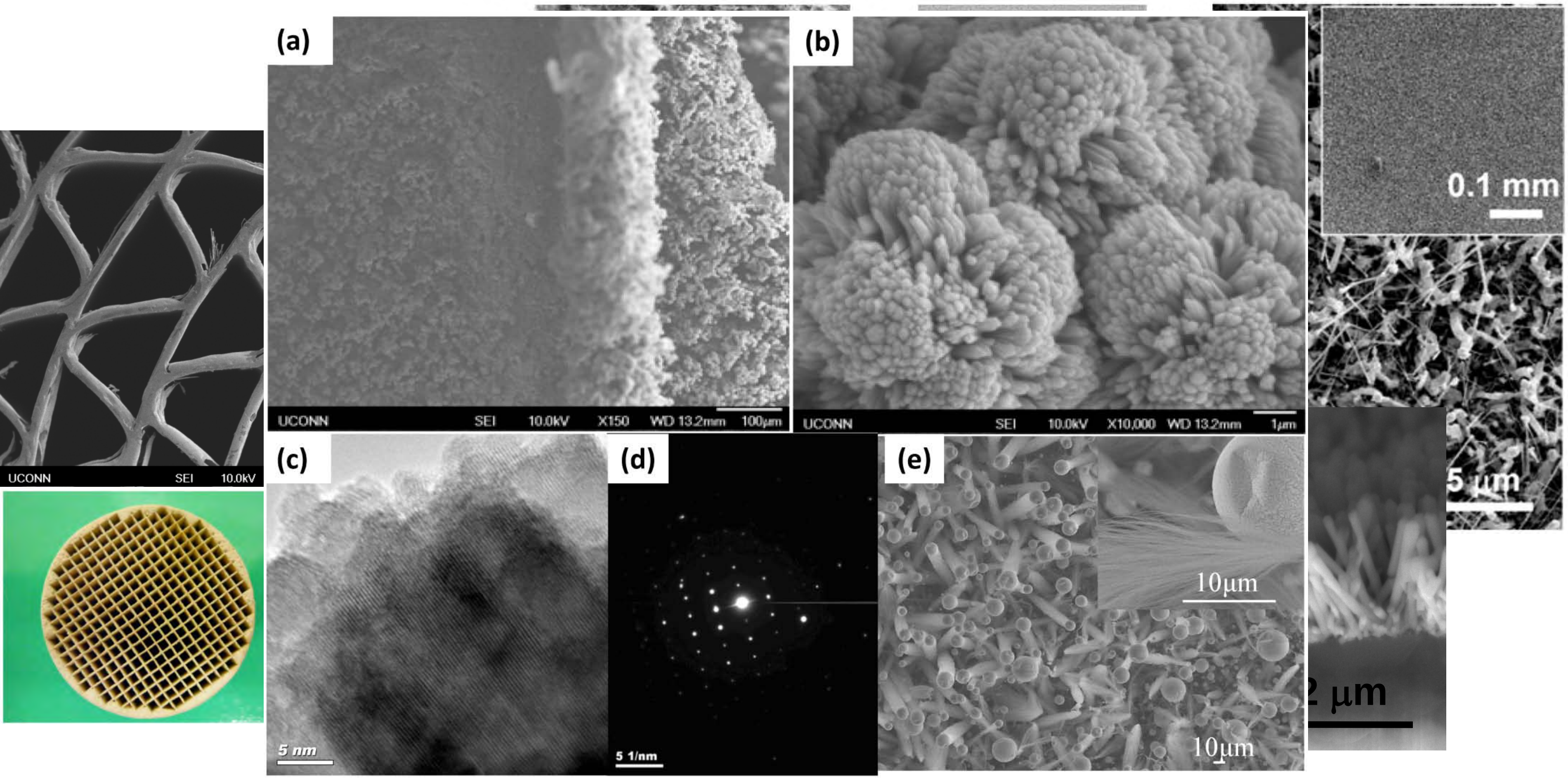

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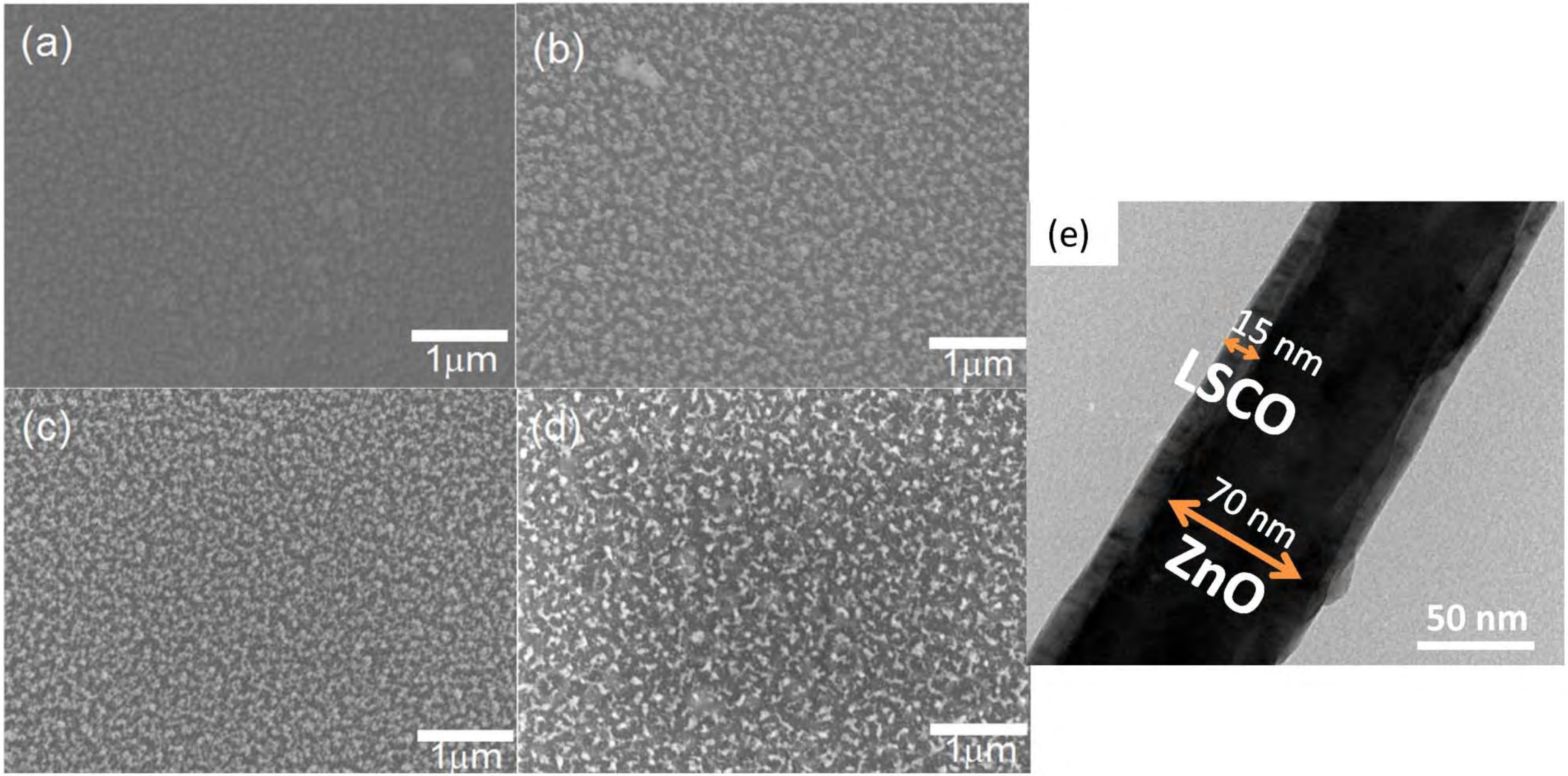
MeO_x/ABO_3 composite nanoarrays



Composite nanowire arrays on solid substrates.

*W. Cai, P. Shimpi, et al., **2011**, submitted;*
*P. Shimpi, C. Chung, et al., **2011**, to be submitted; H. Gao, et al., APL, **2011**.*

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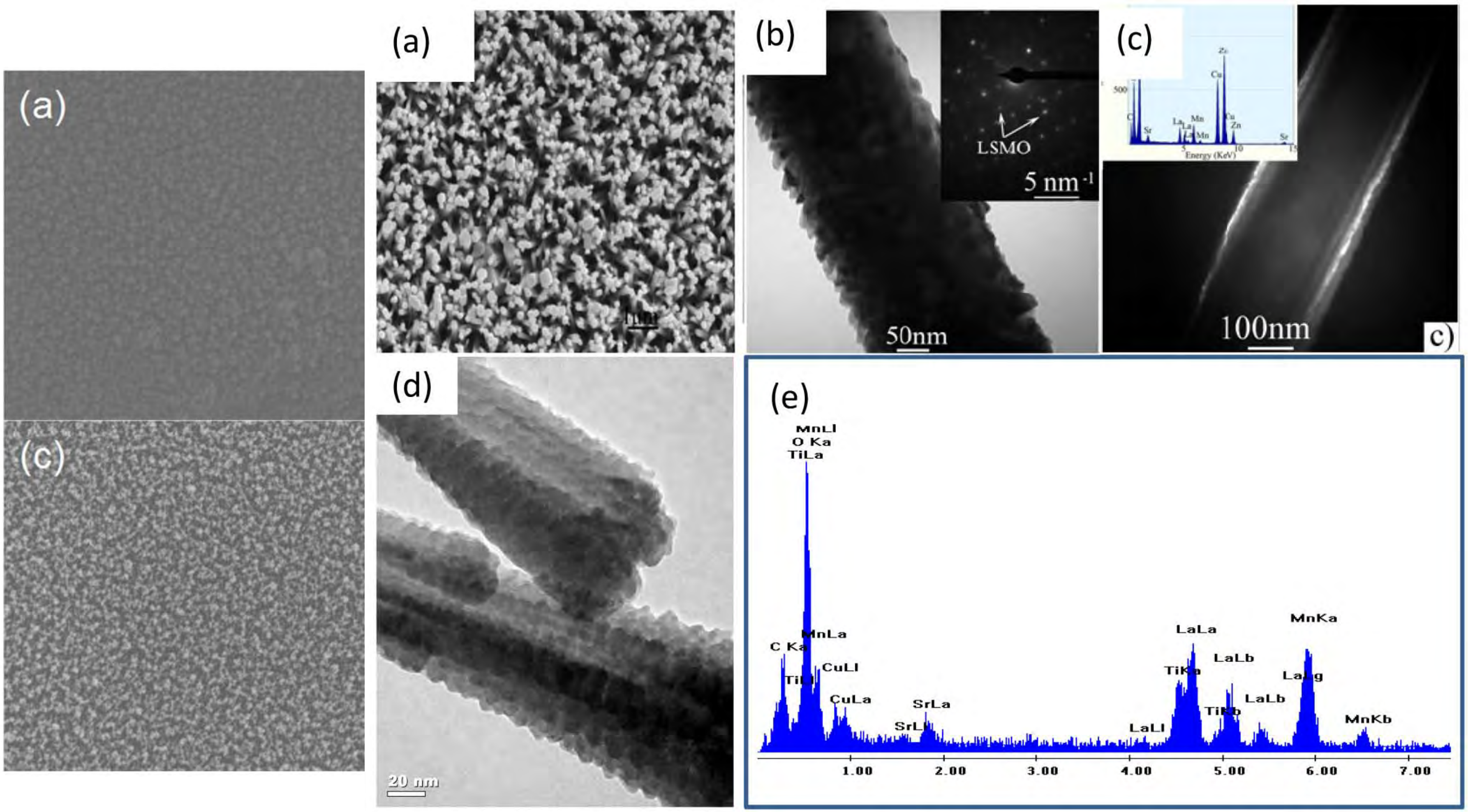

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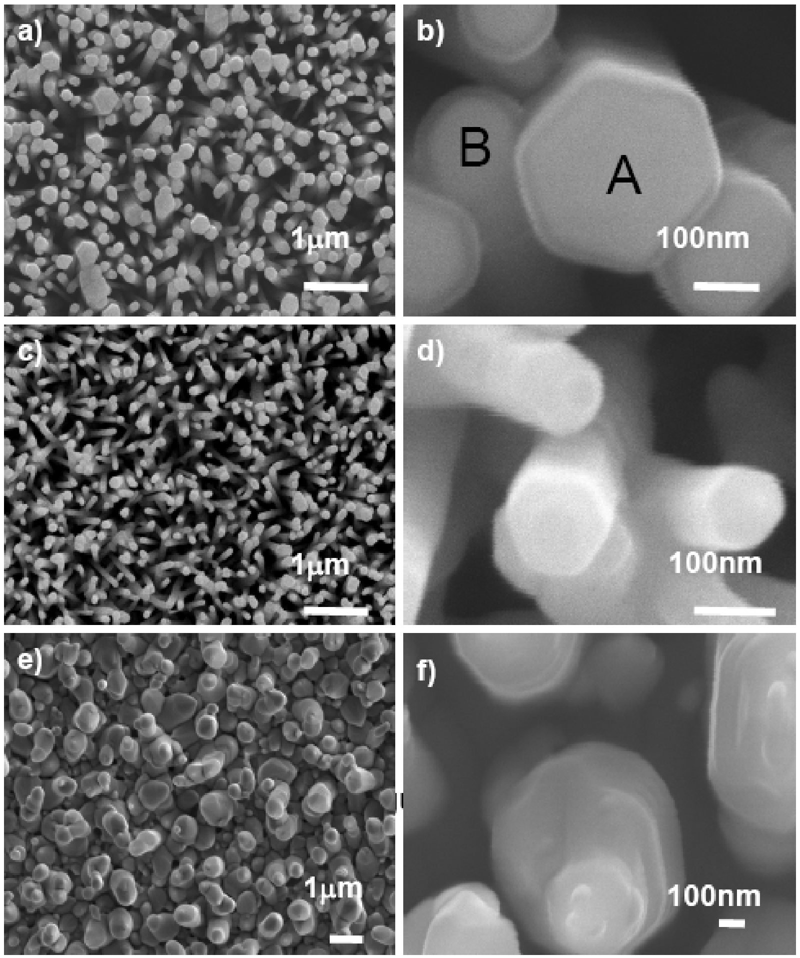
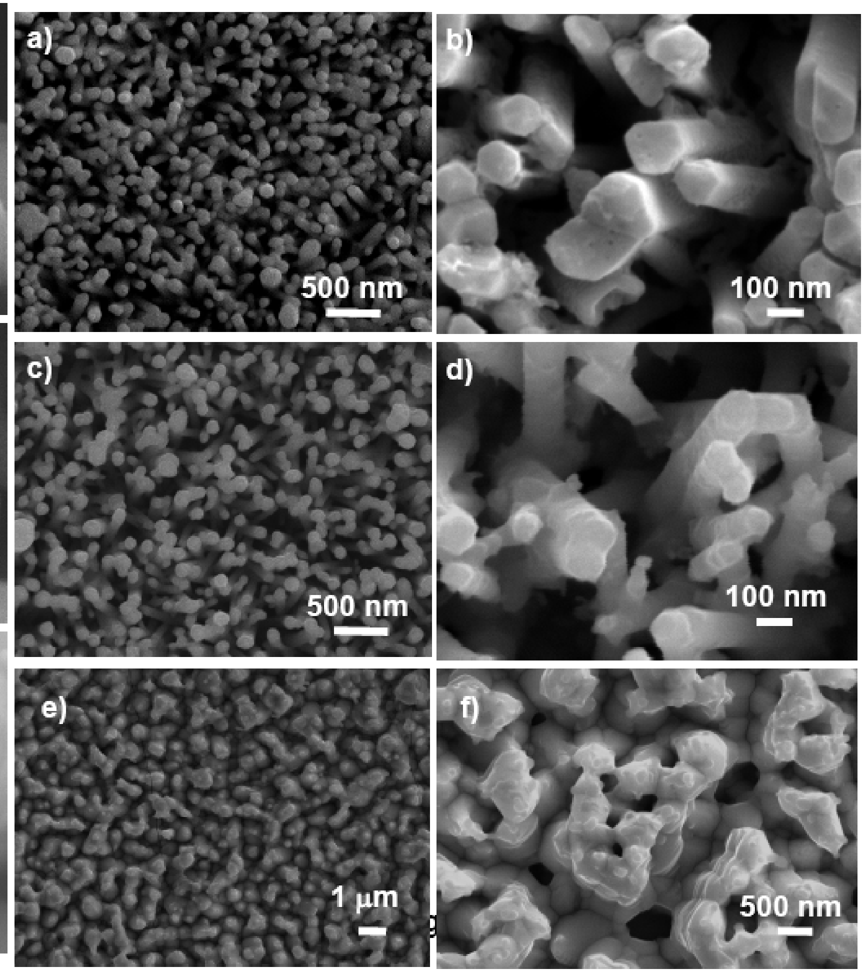
Thermal stability of ZnO/LSCO nanoarrays





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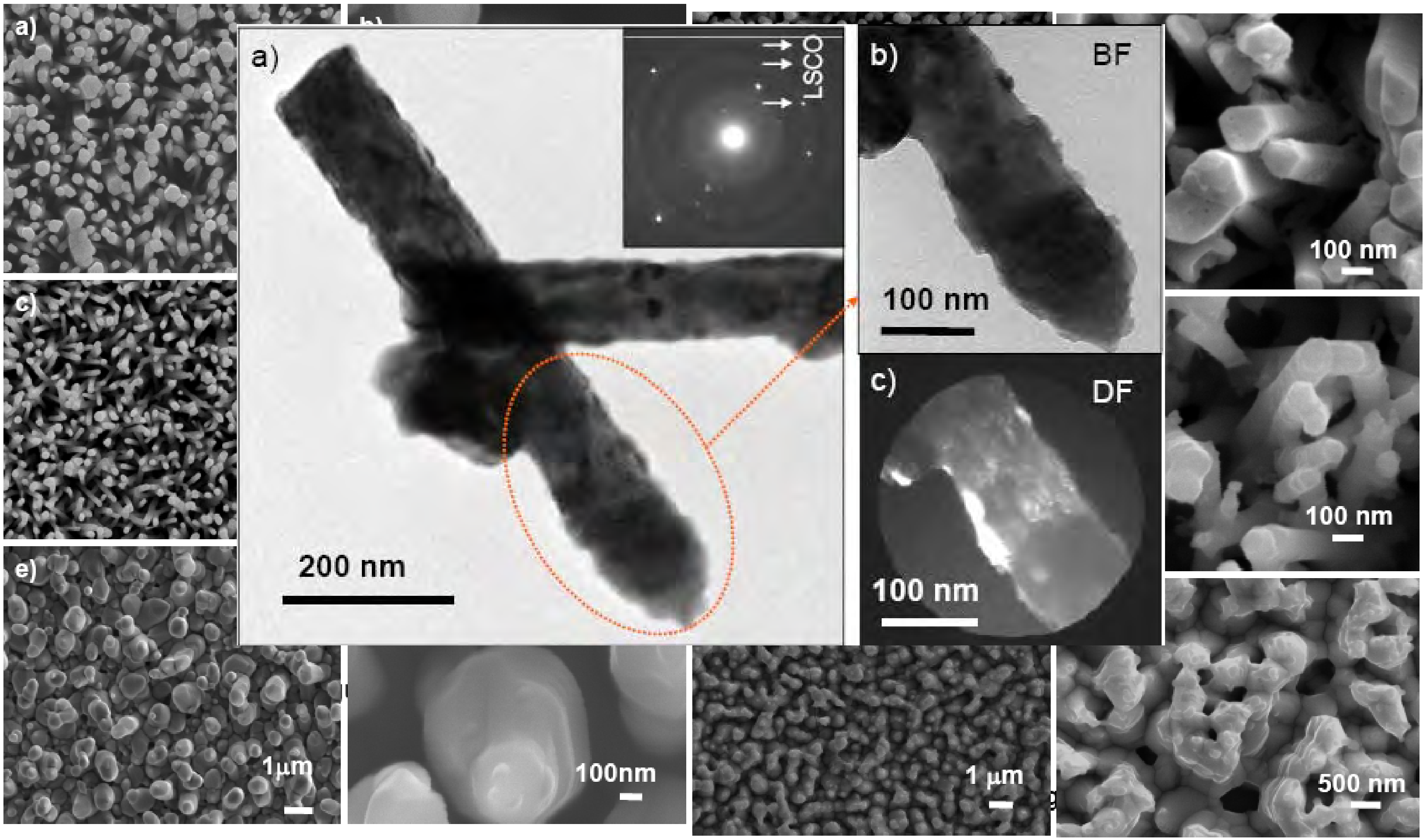

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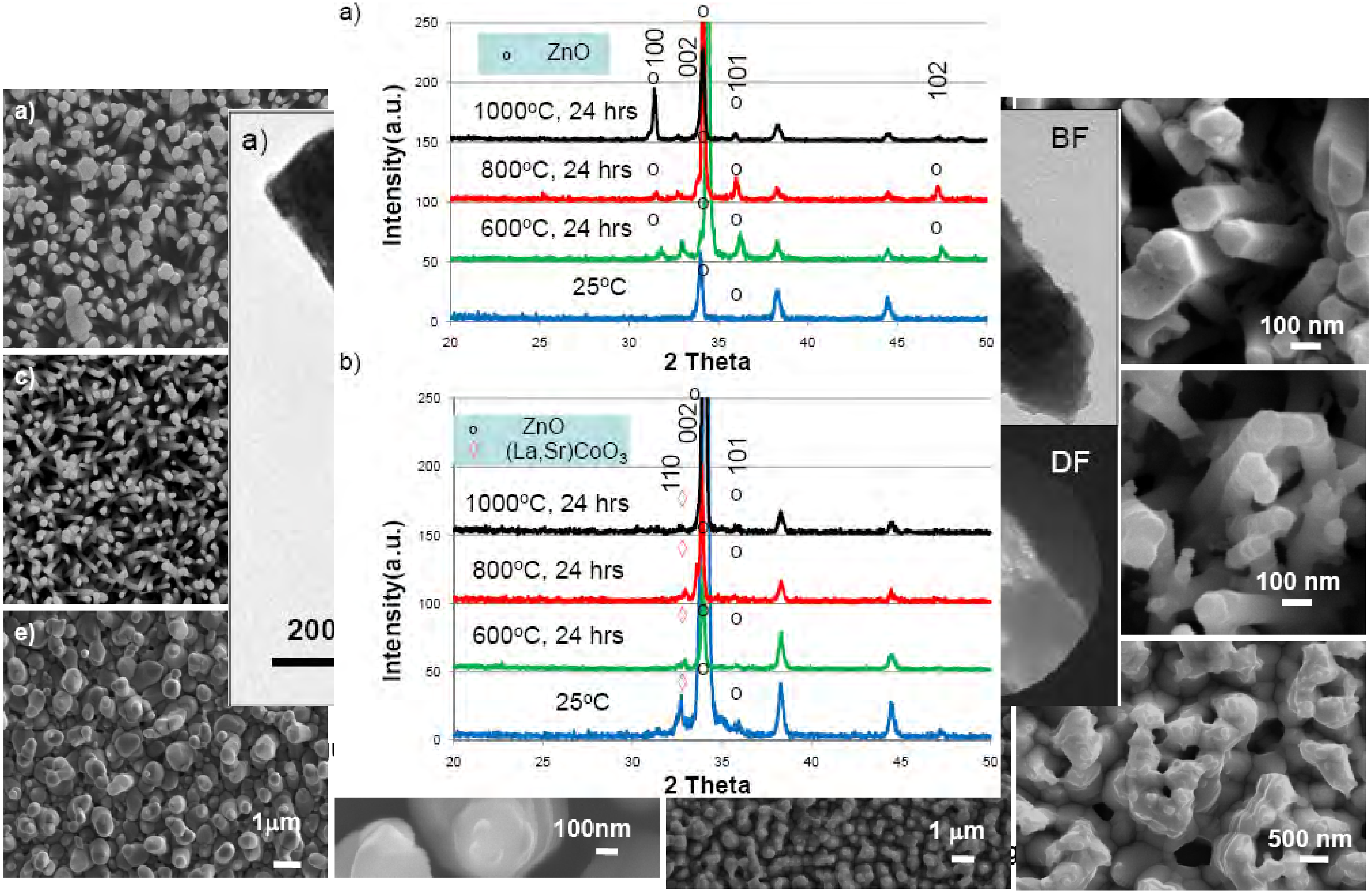

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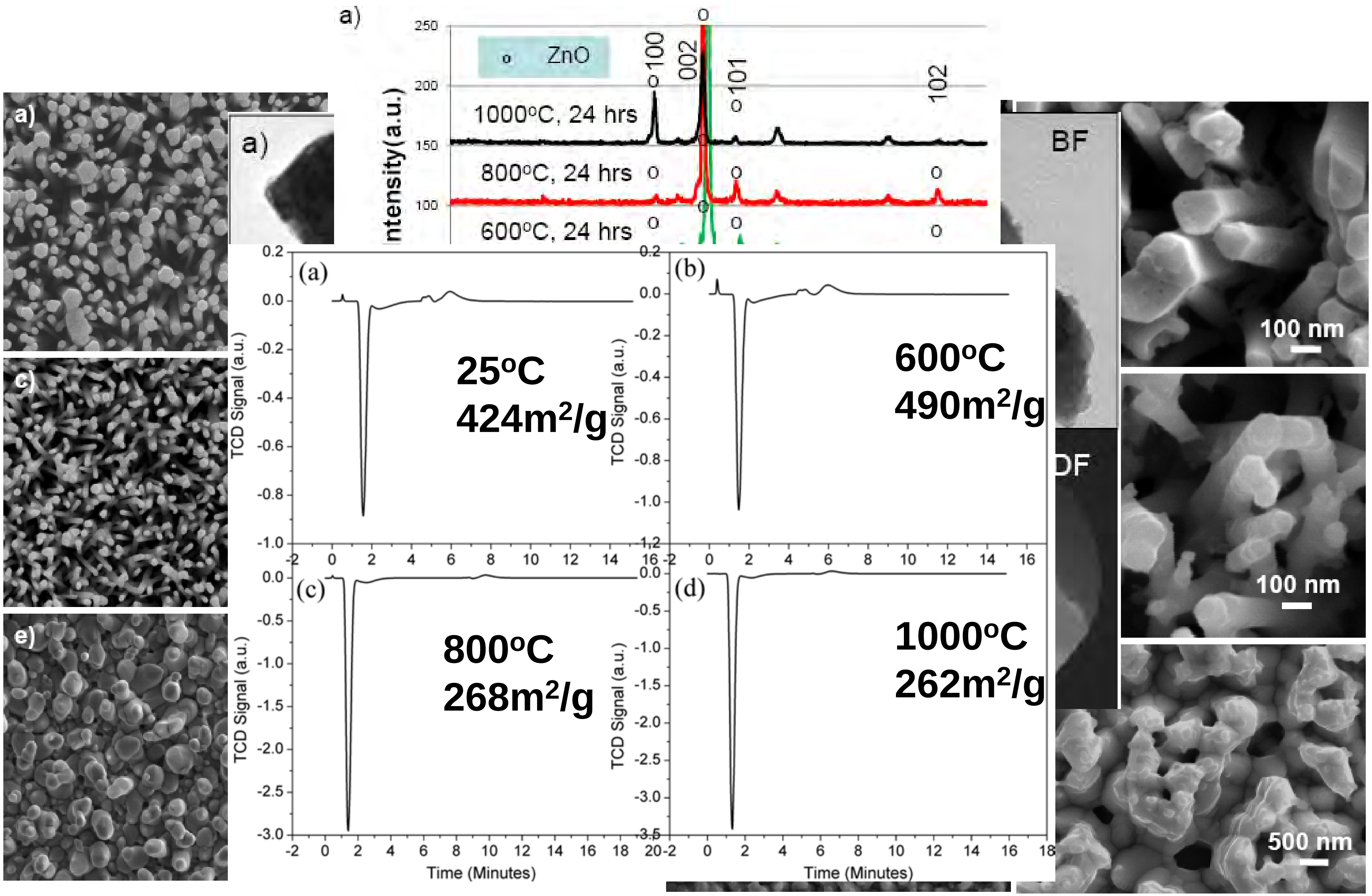

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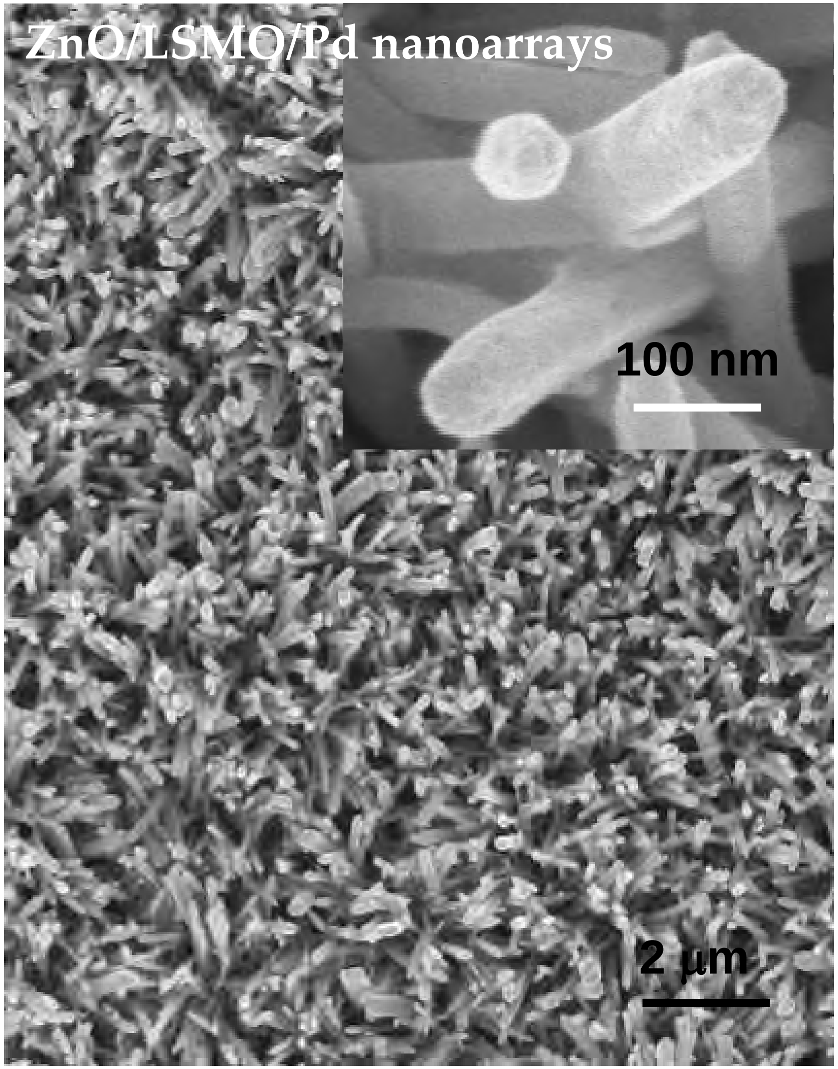
Metal loading on metal oxide nanoarrays



Y. Guo, Z. Zhang, et al., ***2011***, *submitted.*

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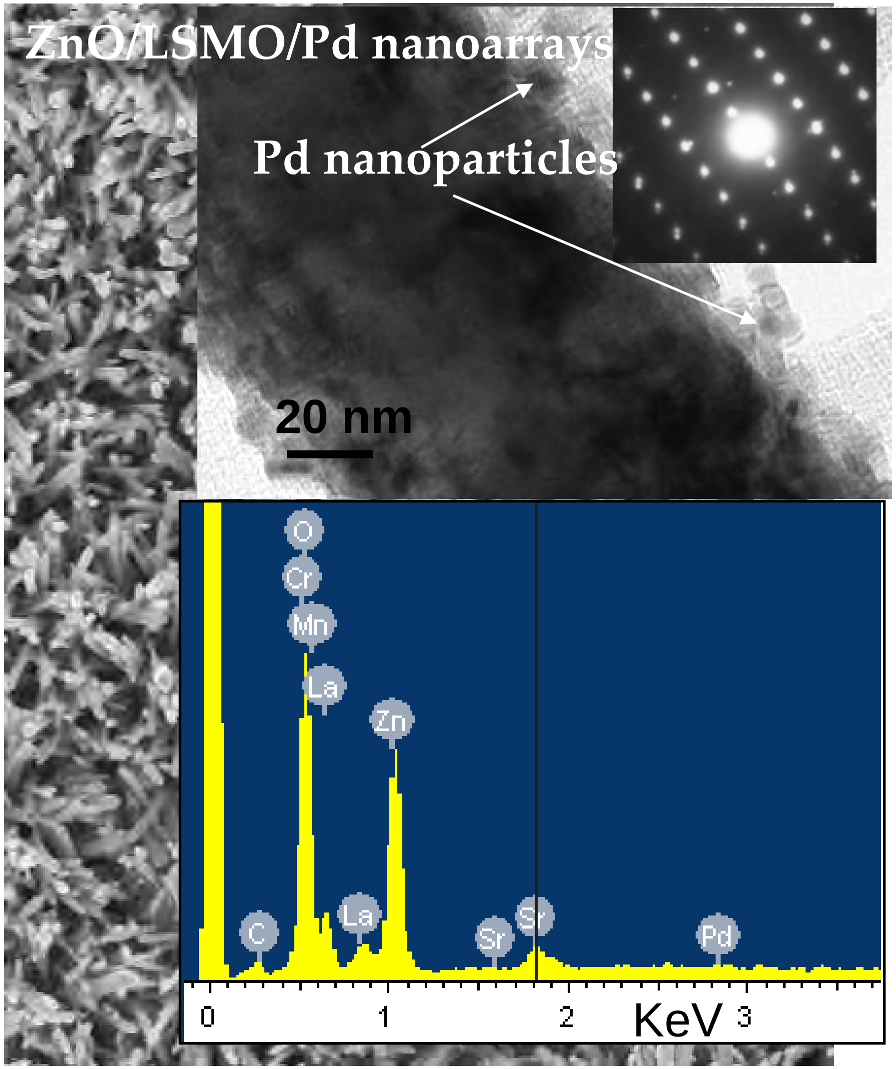

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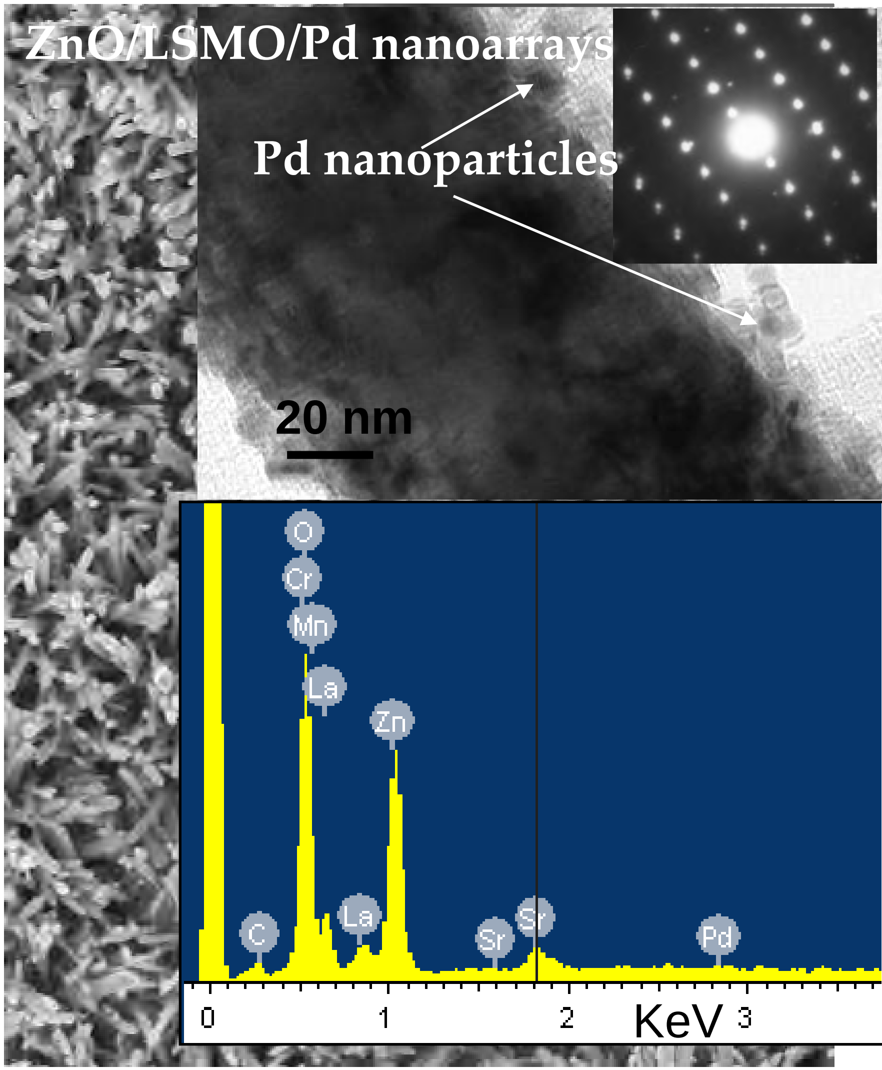

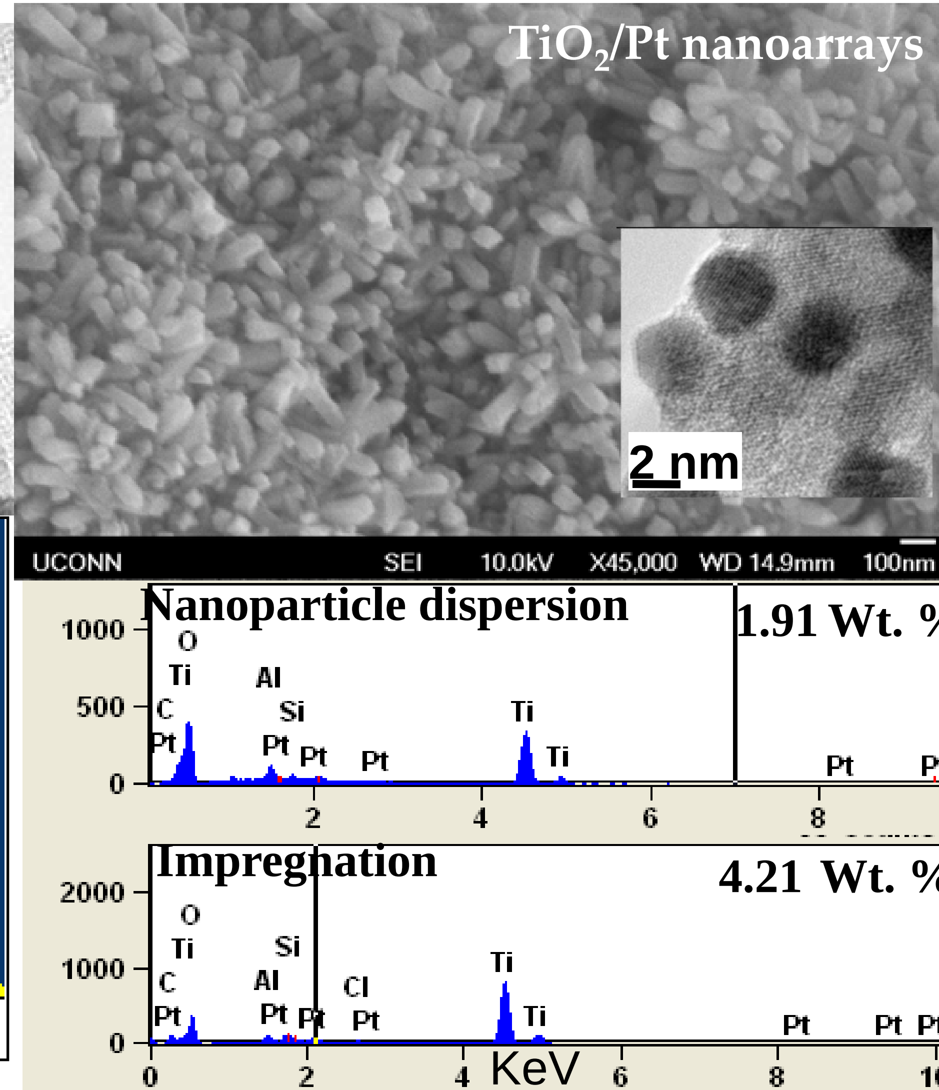

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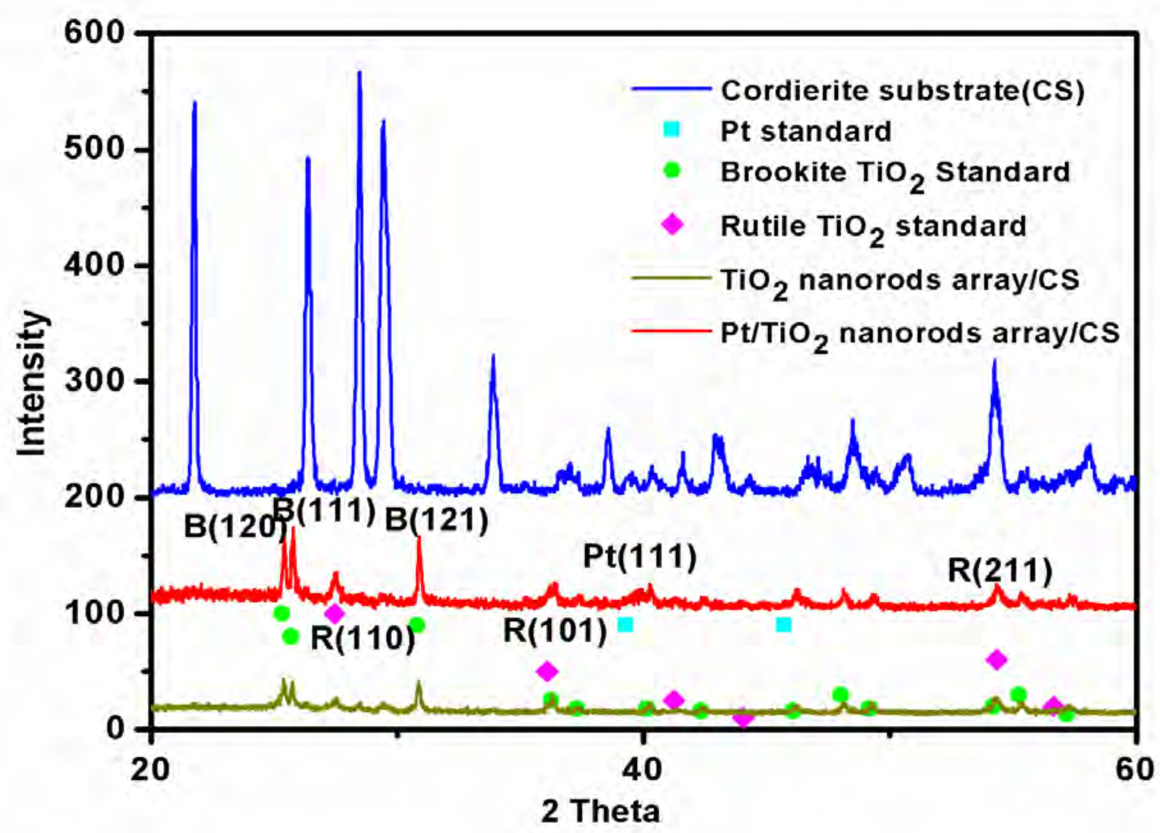
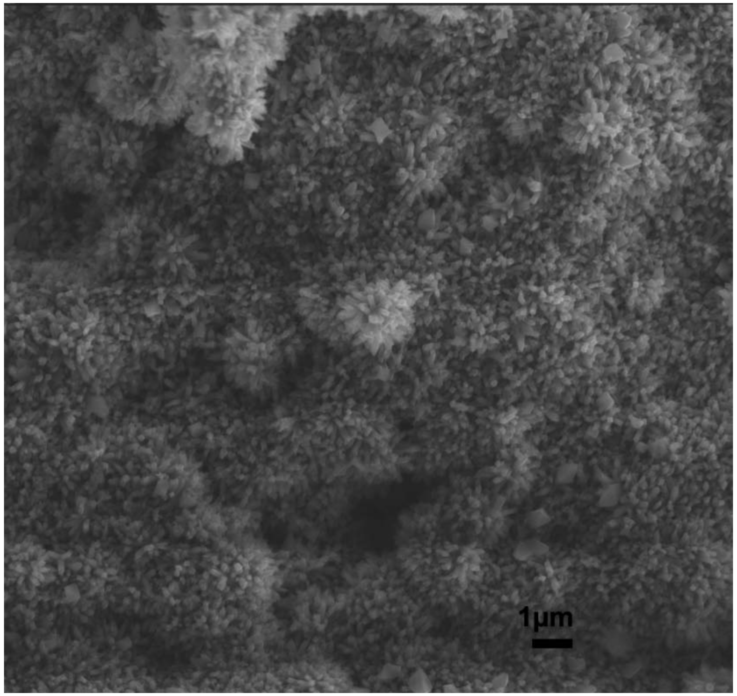
Structure and surface areas of TiO_2 nanoarrays on substrate



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

Y. Guo, Z. Zhang, et al., ***2011****, submitted.*

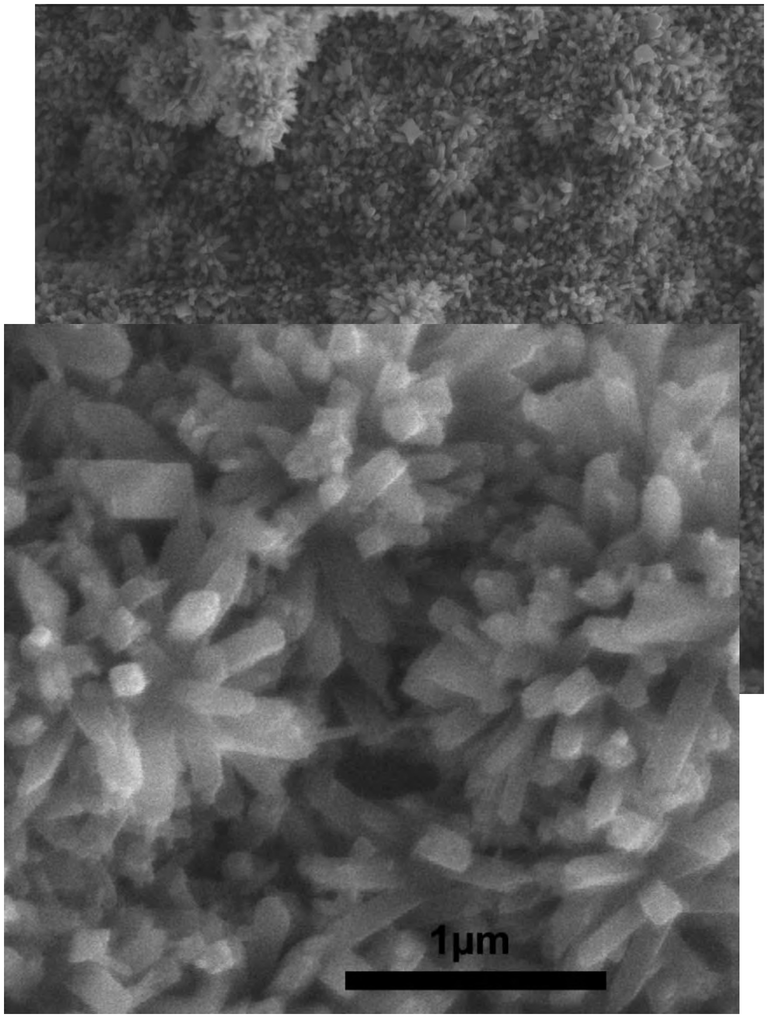
Thermal stability of TiO_2 nanoarrays



Thermal stability of TiO_2 nanorods array at 800^{o}C for 24h

*Y. Guo, Z. Zhang, et al., **2011**, submitted.*

Thermal stability of TiO_2 nanoarrays



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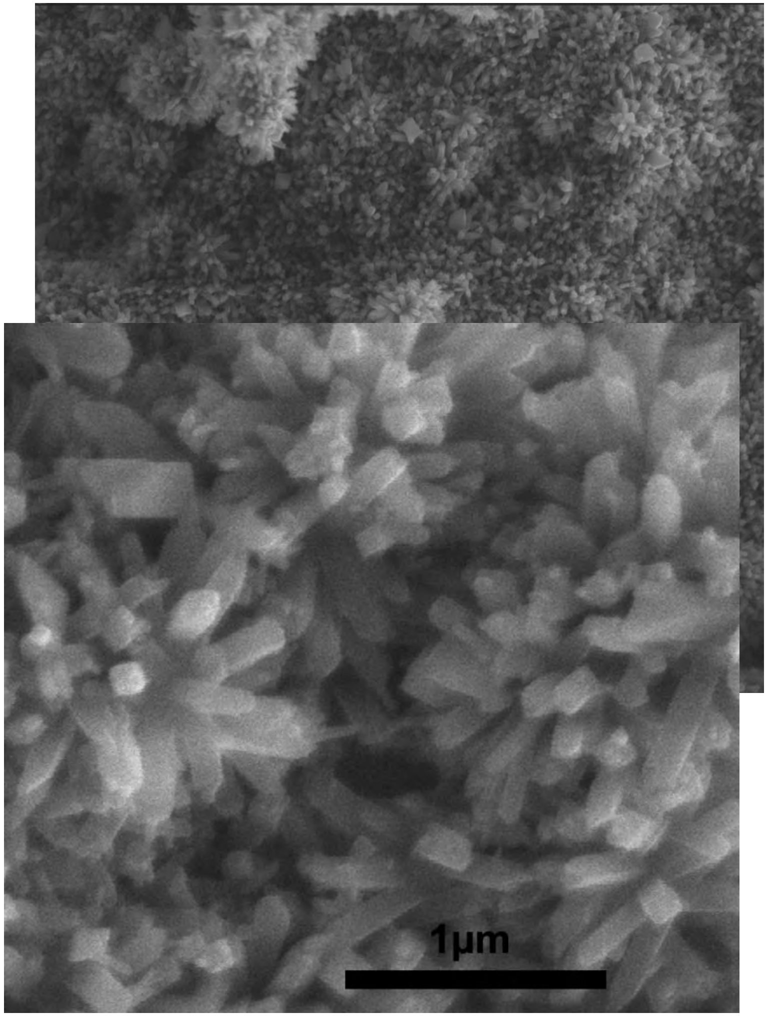

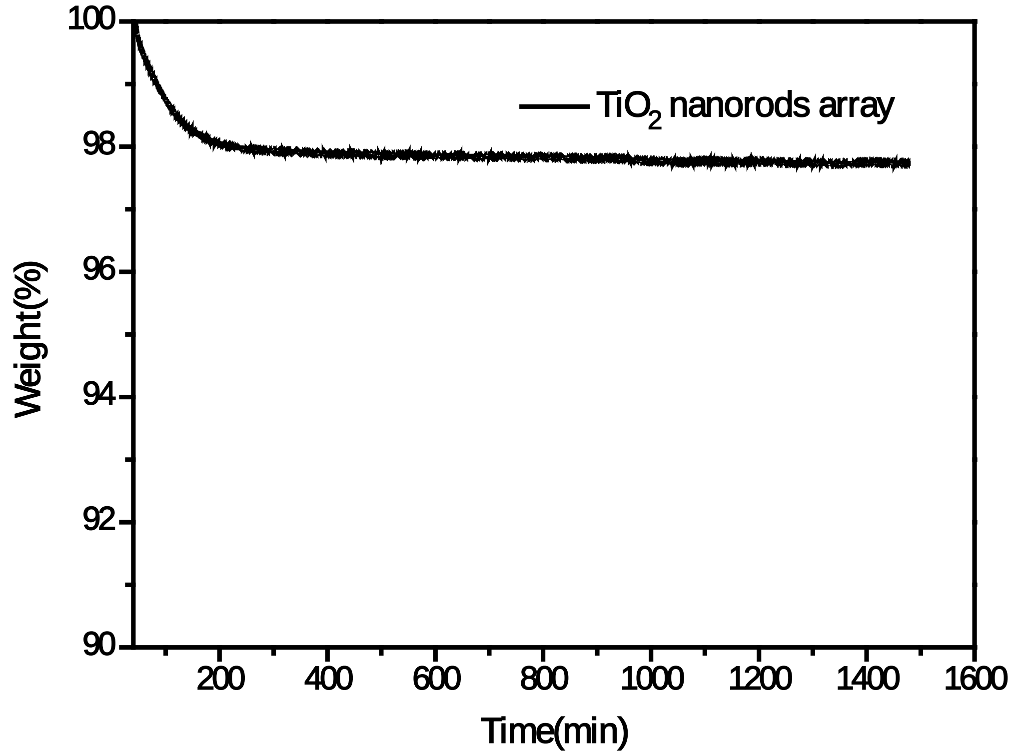

Thermal stability of TiO_2 nanorods array at 800°C for 24h

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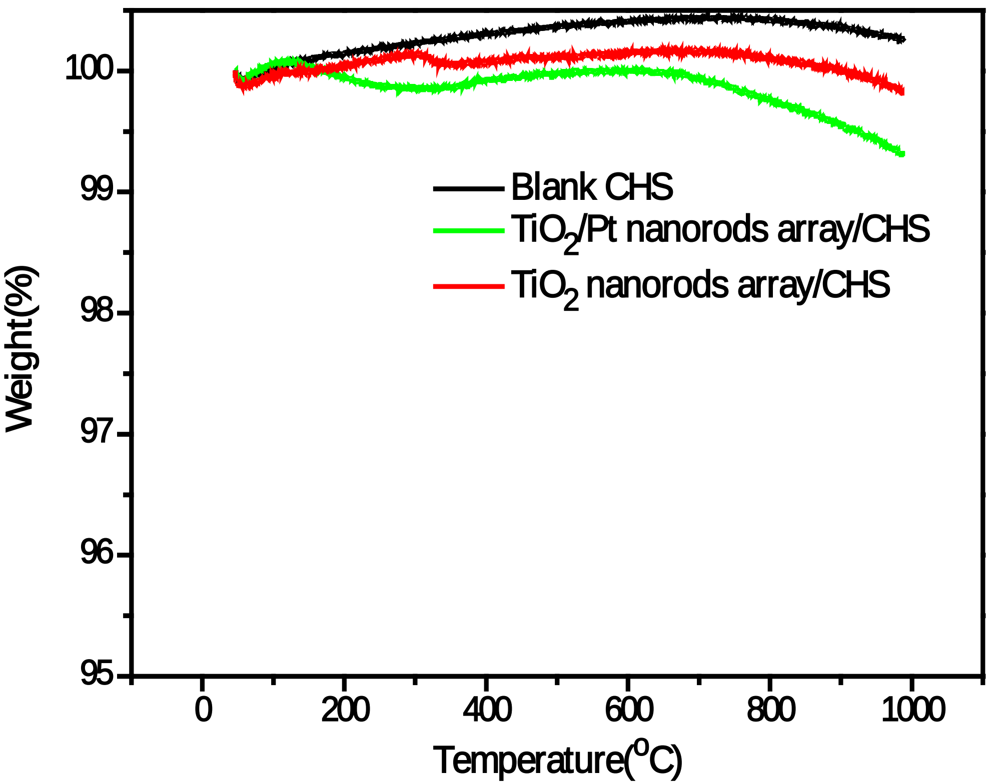
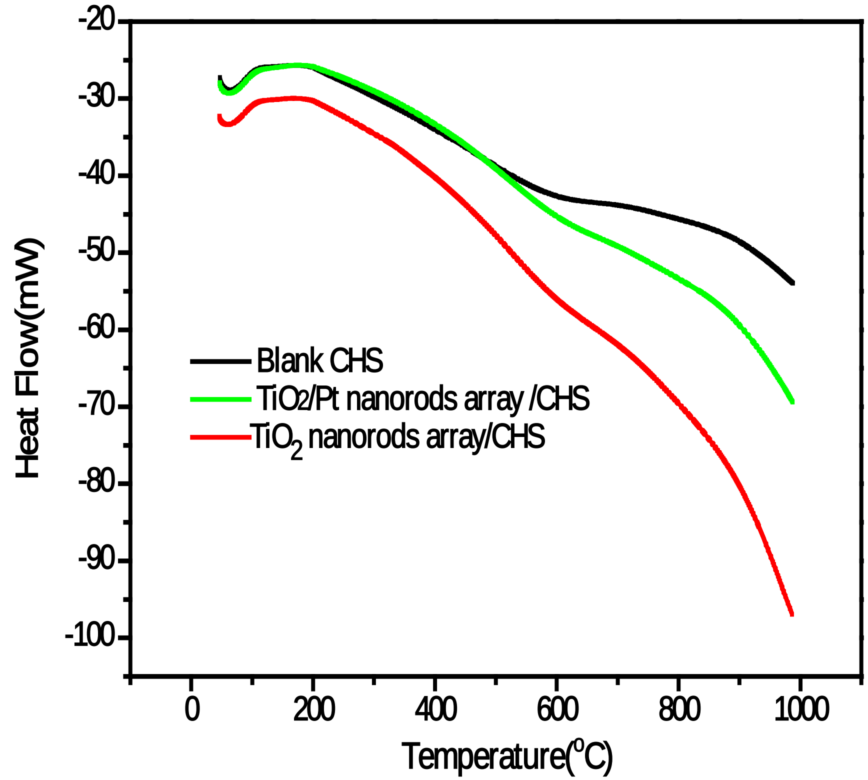
Thermal stability of TiO_2 nanoarrays under oxidative atmosphere

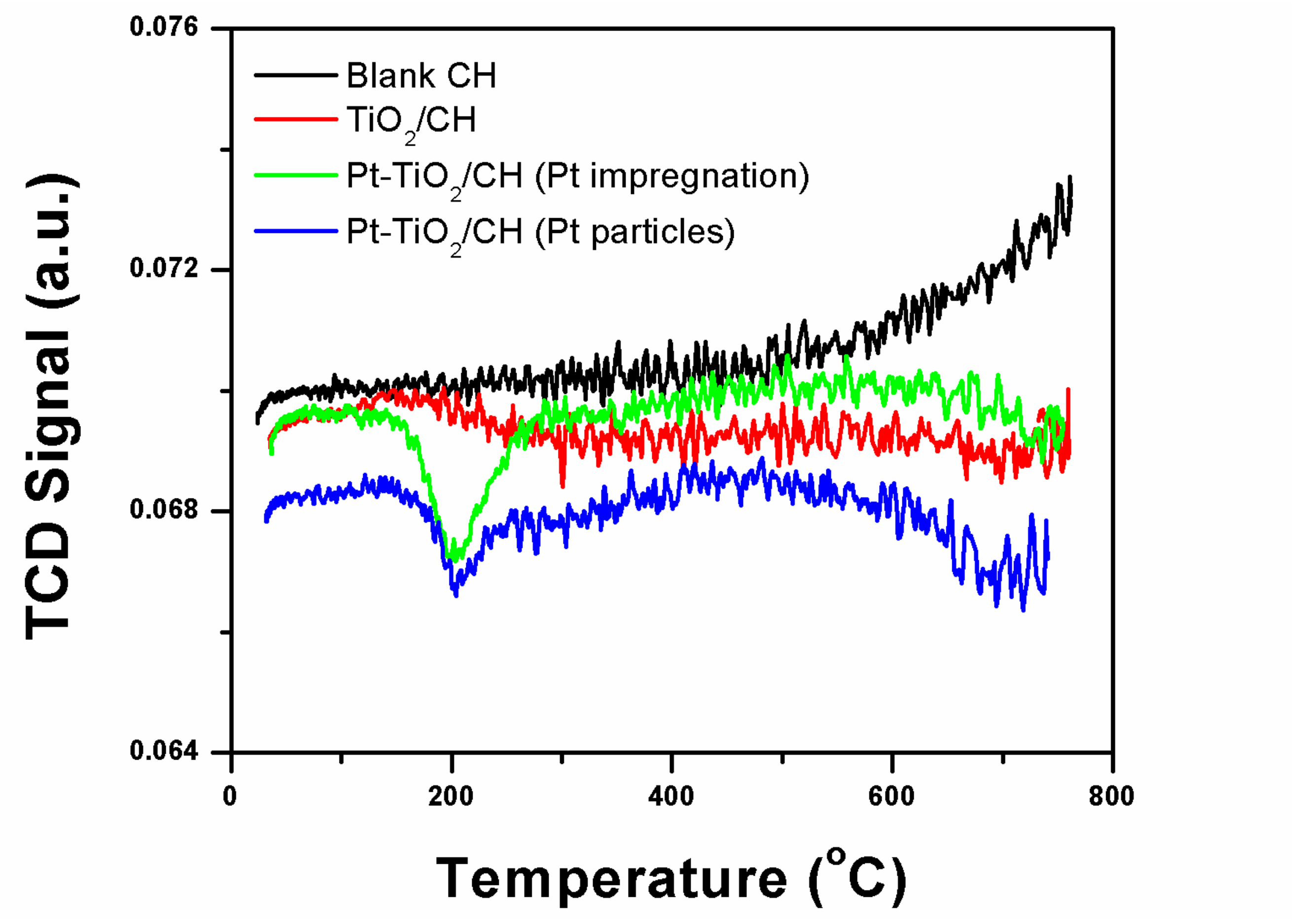




TGA and DSC of TiO_2 nanorods array on substrates

Y. Guo, Z. Zhang, et al., ***2011****, submitted.*

Thermal stability of TiO_2 nanoarrays under reductive atmosphere

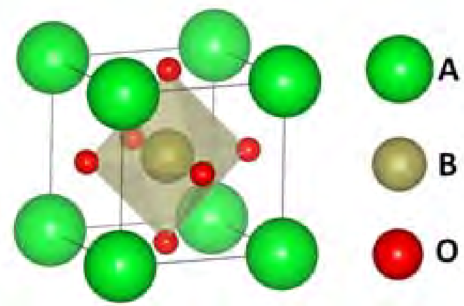


TPR-H_2 of Pt coated TiO_2 nanoarrays on substrates.

*Y. Guo, Z. Zhang, et al., **2011**, submitted.*

O ad-atoms on perovskites:
Geometry, electronic structure and energetics

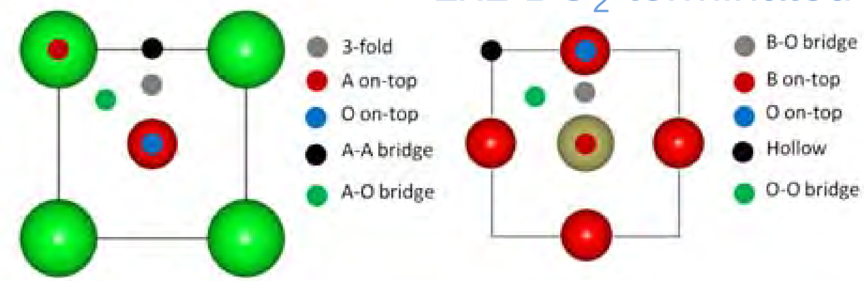
$PbTiO_3$ v/s $LaMnO_3$



Perovskite crystal structure

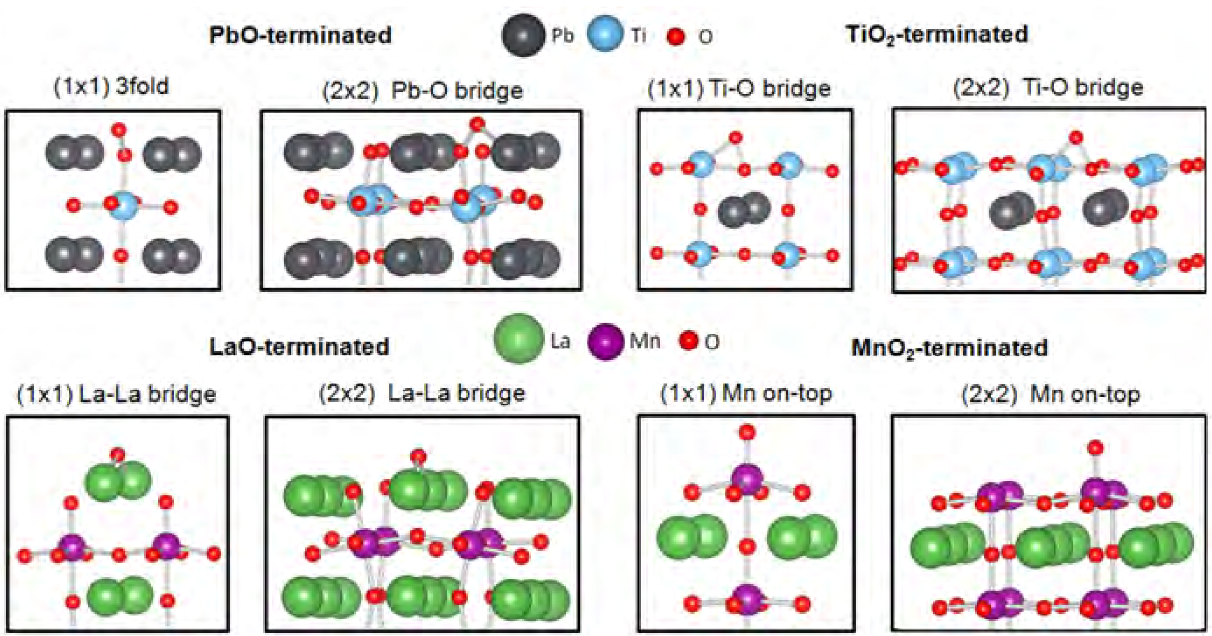
1x1 AO-terminated

1x1 BO_2-terminated



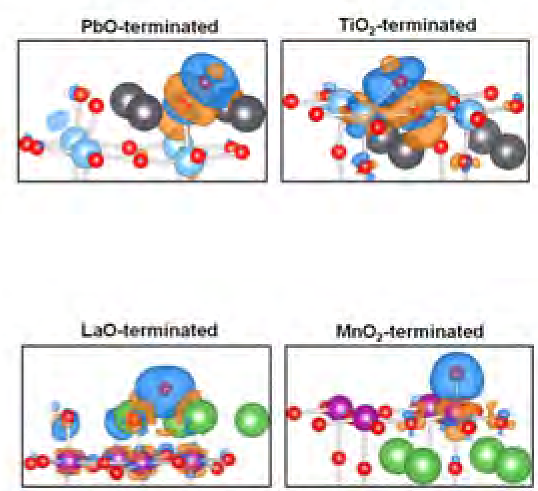
Various O adsorption sites on the (001) surfaces

Relaxed geometry of O ad-atom covered surfaces



Difference electron density plots

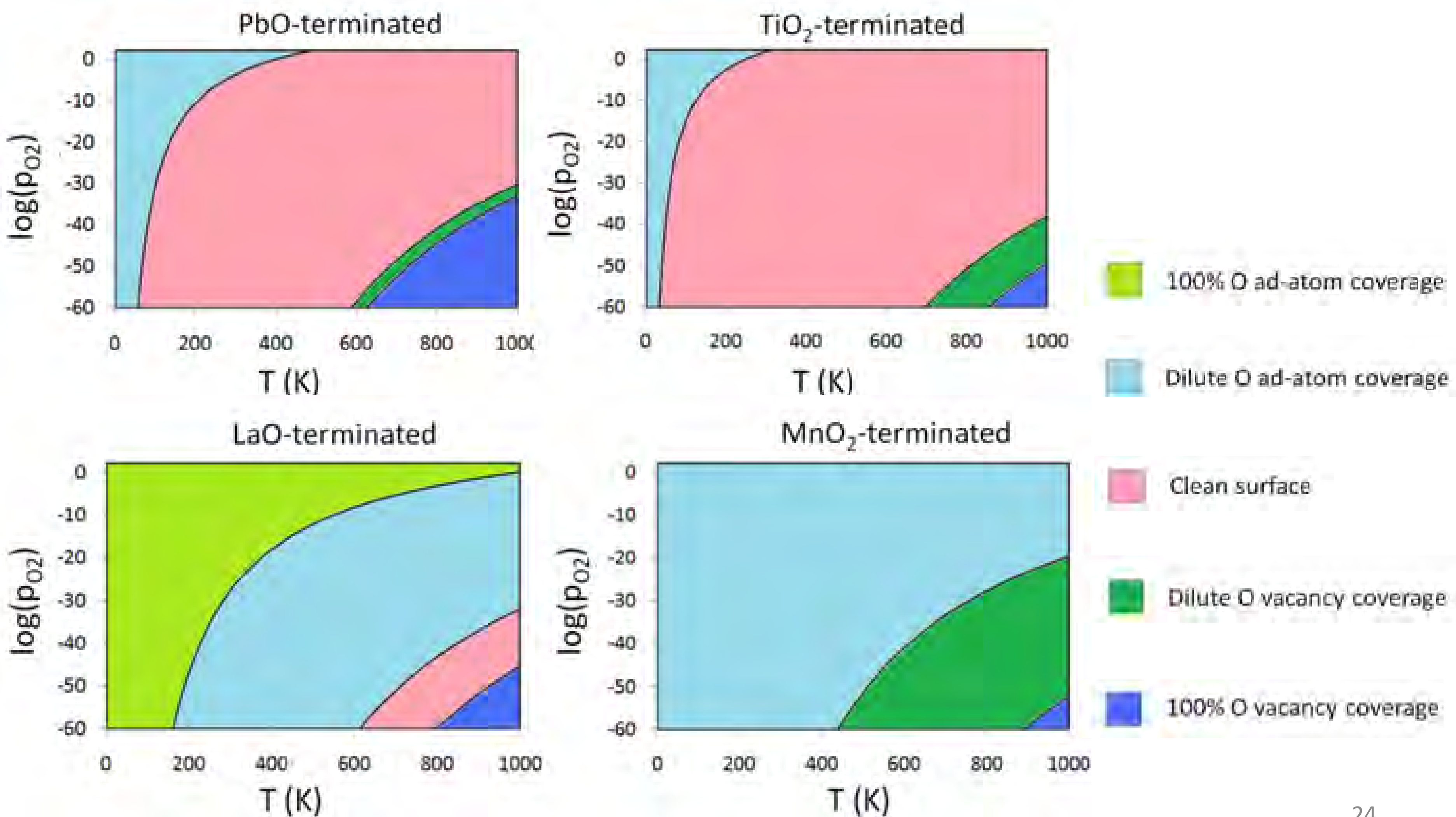
$[\Delta\rho = \rho_{Oad} - \rho_{clean} - \rho_O]$



G. Pilania and R. Ramprasad, Surface Sci. ***2010.***

(p,T) surface phase diagrams:

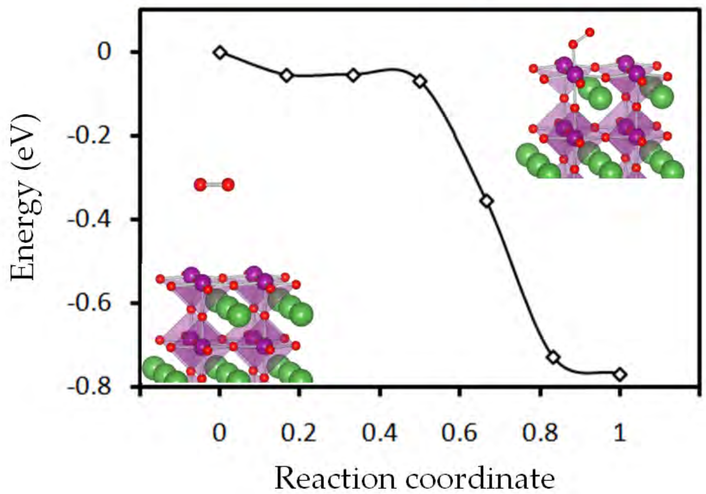
Thermodynamic stability of Clean and Oad atom or vacancy covered surfaces



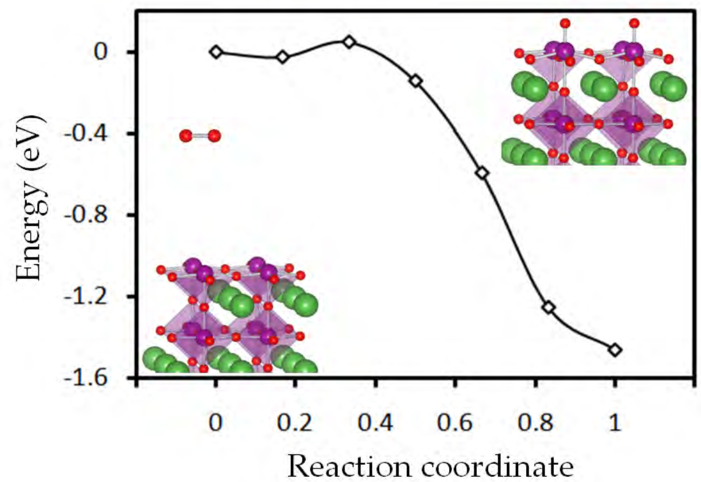
Based on DFT calculations within LDA approximation

Computed reaction barriers

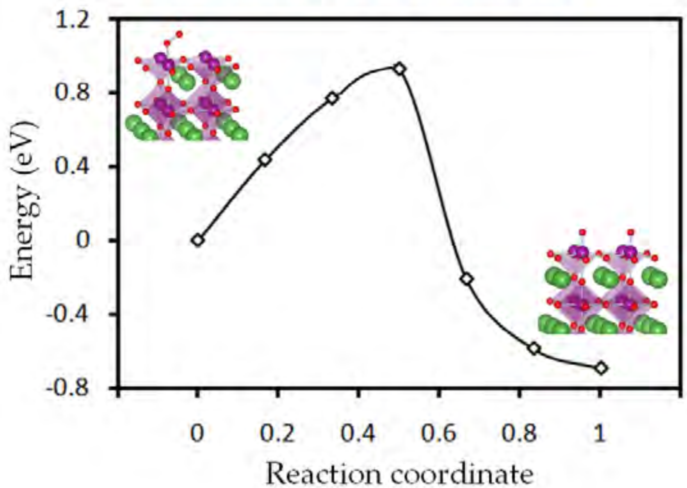
Molecular adsorption



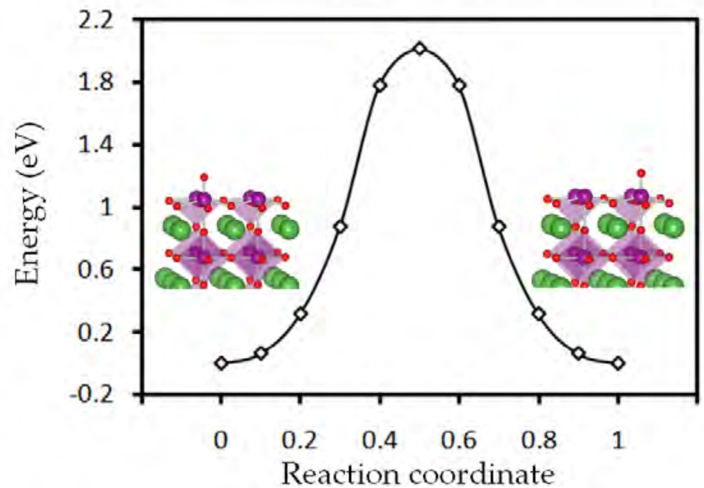
Dissociative adsorption



Surface Dissociation



Surface Diffusion



Collaborations

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

Future work

1) Conduct systematical synthesis optimization of 3D composite nanowire arrays.
2) Continue the metal (oxide) loading/doping study on 3D composite nanowire arrays.
3) Evaluate the catalytic performance of 3D composite nanowire arrays on the NO_x storage and reduction performance.
4) Calculate reaction barriers for various elementary steps involved in the oxygen dynamics on the perovskite crystal surfaces associated with incorporation of NO_x interactions.

Acknowledgements

- Postdoc: Drs. Y. Guo, Z. Zhang, H. Gao, and G. Liu
  Graduate students: W. Cai, P. Shimpi, G. Pilania, C. Chung, S. Glod, Z. Ren
- Co-PIs: Drs. P. Alpay and R. Ramprasad (UConn), Dr. C. Brooks (HRI, Ohio)
- Project officers: K. Howden, M. Ursic
- DOE/NETL, UConn Research Foundation, UConn - New faculty start-up funds, ACS-PRF, Honda Research Institute

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