**Final Technical Report to the
Department of Energy, National Energy Technology Laboratory**

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Project Title: Three-Dimensional Composite Nanostructures for Lean NO_x Emission Control

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By

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* Patentable materials: documented in patent application and invention disclosures 3 & 5 in section 5.2.

1. Executive Summary

This final report to the Department of Energy (DOE) and National Energy Technology Laboratory (NETL) for DE-EE0000210 covers the period from October 1, 2009 to July 31, 2013. Under this project, DOE awarded UConn about \$1,248,242 to conduct the research and development on a new class of 3D composite nanostructure based catalysts for lean NO_x emission control. Much of the material presented here has already been submitted to DOE/NETL in quarterly technical reports.

In this project, through a scalable solution process, we have successfully fabricated a new class of catalytic reactors, i.e., the composite nanostructure array (nano-array) based catalytic converters. These nanocatalysts, distinct from traditional powder washcoat based catalytic converters, directly integrate monolithic substrates together with nanostructures with well-defined size and shape during the scalable hydrothermal process. The new monolithic nanocatalysts are demonstrated to be able to save raw materials including Pt-group metals and support metal oxides by an order of magnitude, while perform well at various oxidation (e.g., CO oxidation and NO oxidation) and reduction reactions (H₂ reduction of NO_x) involved in the lean NO_x emissions. The size, shape and arrangement of the composite nanostructures within the monolithic substrates are found to be the key in enabling the drastically reduced materials usage while maintaining the good catalytic reactivity in the enabled devices. The further understanding of the reaction kinetics associated with the unique mass transport and surface chemistry behind is needed for further optimizing the design and fabrication of good nanostructure array based catalytic converters. On the other hand, the high temperature stability, hydrothermal aging stability, as well as S-poisoning resistance have been investigated in this project on the nanocatalysts, which revealed promising results toward good chemical and mechanical robustness, as well as S-poisoning resistance. Further investigation is needed for unraveling the understanding, design and selection principles of this new class of nanostructure based monolithic catalysts.

2. Objectives, Accomplishments and Outlook

2.1 Overall Objectives

- Develop a general platform of three-dimensional (3D) composite nanostructure arrays (nano-arrays) monolithic catalysts with a broad spectrum of catalytic materials for emission control;
- Develop a general cost-effective, green and scalable synthesis method for three-dimensional (3D) composite nanostructure arrays (nano-arrays) monolithic catalysts;
- Demonstrate the ability to significantly reduce or eliminate the usage of Pt-group metals (PGM), while achieve good catalytic performance toward emission aftertreatment in automobiles in the developed 3D composite nanostructured monolithic nanocatalysts;
- Investigate the perovskite surface catalytic chemistry using first principle thermodynamics (FPT) and kinetic Monte Carlo (KMC) simulations to help further optimizing the catalytic materials and structure.

2.2 Accomplishments

- Synthesized various 3D metal oxide nano-arrays on monolith substrates;
- Established a general platform of three-dimensional (3D) composite nanostructure arrays (nano-arrays) monolithic catalysts with well-controlled morphology and multi-components;
- Developed a general low-cost, green hydrothermal process which hold the potential to manufacture the high efficient nano-array based monolithic catalysts in a large scale.

- Explored the high efficient PGM free nano-array monolithic catalysts for NO oxidation.
- Fabricated and characterized the PGM and BaO loaded 3D composite nanowire/rod array (such as $\text{ZnO}/(\text{La,Sr})\text{CoO}_3(\text{LSCO})$ and $\text{TiO}_2/(\text{La,Sr})\text{MnO}_3(\text{LSMO})$, etc.) on monolith substrates;
- Investigated the (hydro-)thermal and mechanical stability, CO and NO oxidation performance, S-poisoning resistance, as well as NSR performance of the 3D composite nanostructures;
- Demonstrated ultra-high materials usage efficiency of 3D composite nano-array catalysts in both PGM and metal oxides, excellent thermal and mechanical robustness, as well as tunable catalytic performance, showing their good potential to be used as the next-generation automotive catalysts.
- Developed the reliable surface catalytic phase diagrams of perovskite (such as LaMnO_3) surfaces through the FTP and KMC simulations.

2.3 Future Directions and outlook

- Further optimize and quantitatively characterize the PGM and Ba based components on 3D composite nano-array based NSR catalysts in terms of configuration, morphology and size;
- Further investigate, understand and improve the PGM and metal oxide interface for further optimization and maximization of 3D composite nano-array catalysts efficiency;
- Further evaluate and improve the thermal, hydrothermal stability and S-resistance of 3-D composite nano-array catalysts;
- Further investigate and understand the relationship between the array configurations, reaction kinetics and catalysts efficiency in the 3-D composite nano-array catalysts system for rational design of next generation high efficient catalysts;

3. Summary of Project Activities

Nowadays, lean-burn engines are attracting more and more attention due to their higher fuel efficiency and lower CO_2 emission than conventional gasoline engines [1-6]. However, under lean-burn conditions, the nitrogen oxide (NO_x) emissions cannot be efficiently reduced over the classical three-way catalysts in the presence of excessive O_2 [1, 4, 7]. The NO_x emissions have multi-fold hazards on the atmosphere, environment and human health, due to the formation of fine particles, ozone smog, acid rain and eutrophication [8]. NO_x storage and reduction (NSR) technology is regarded as one of the most promising exhaust after-treatment technologies for lean-burn gasoline and diesel vehicles. The objective of this project is to develop a new class of oxide-based 3D nano-array based monolithic catalysts for lean burn emission control with drastically reduced materials usage in PGM, and improved catalytic functions.

3.1 Approach

Experimentally, low cost and green wet chemical methods are used to synthesize metal oxide nano-arrays on honeycomb substrates, followed by perovskite coating, PGM and BaO loading through sol-gel processes.[9] Post thermal-annealing is used to improve the crystallinity and stoichiometry of 3D composite nanostructures. Structure, morphology and chemical characterization is carried out using XRD, TEM, SEM, and EDXS. Catalyst evaluation is conducted using temperature programmable reduction (TPR), benchtop tube reactor kinetics testing, thermal and hydrothermal aging testing. Theoretically, the first principles thermodynamics (FPT) and kinetic Monte Carlo (KMC) simulation approaches are used to construct surface phase diagrams of (001) AO- and BO_2 -terminated ABO_3 perovskite surfaces involving gaseous O_2 as the principal source of surface oxygen.[10]

3.2 Result Highlights

In this project, a general platform of three-dimensional (3D) composite nanostructure arrays (nano-arrays) monolithic catalysts with well-controlled morphology was developed. As shown in Figure 1, pristine metal oxide (such as ZnO , TiO_2 , Co_3O_4 , etc.) based monolithic catalysts have been successfully fabricated using low cost and green wet chemical synthesis methods on both cordierite monolith and stainless steel monolith (Figure 1a). Figure 1b shows the photographic image of four types of nano-array based monolithic catalysts including ZnO , TiO_2 , CeO_2 , and Co_3O_4 . Scanning electron microscope (SEM)

topview images of ZnO nanowire array rooted cordierite monolith channels are shown in Figure 1c at low magnification. The as-synthesized Co_3O_4 nanowires ($\sim 10\ \mu\text{m}$ long) in Figure 1d–e exhibited a high uniformity as well as well-aligned and densely packed array characteristics. The closer view electron micrographs in Figure 1f–m revealed the well-defined structural and morphological characteristics of the grown metal oxide nano-arrays on monolith substrates. The as-grown metal oxide nano-arrays can be controlled from nanorod, nanowire, to nanotube and mesoporous nanowires. The mechanical and thermal stability of these monolithic nano-array catalysts were also systematically evaluated and showed excellent performance in both air atmosphere and reactive gases.

Pt nanoparticle loaded metal oxide nano-array monolithic catalysts were also fabricated through colloidal deposition method, as demonstrated in Figure 2. Materials utilization efficiency and catalytic CO oxidation performances were systematically evaluated. [9] The light-off curve and catalytic stability curve were depicted in Figure 2 e and f, respectively. The materials loading and utilization efficiency in both metal oxide and PGM has been improved by an order of magnitude compared to washcoated powder-form monolithic catalysts, i.e., 10 times reduction of PGM and metal oxide usage was achieved (Figure 2g). [9] Comparing with the conventional wash-coated catalysts, the high materials utilization efficiency may be contributed by the ordered macropores between adjacent nanostructures, which form ordered and macroporous channels. These ordered and macroporous channels not only enable optimum metal loading and dispersion during catalyst preparation, but also better expose the active sites and promotes gas–solid interaction by a much shorter diffusion length (Figure 2h). The highly ordered and facet well-defined, well-separated but densely packed high surface area nano-arrays might have helped the enabling of the well-defined, highly efficient, robust and tunable catalysts, which provide a potentially next generation of automotive catalysts.

Based on the general platform of 3D nano-array based monolithic catalysts we had demonstrated, the optimized growth processes were also explored to establish a general low-cost, green method for potential large scale manufacture. Taking ZnO nanorod array as an example, we systematically investigated the morphology and dispersing dependent on various growth parameters including temperature, agitation, concentration, and so on. Mechanical agitation such as ultrasonic vibration during dip-coating and magnetic stirring during the growth process plays a key role to improve mass transport throughout 3D space-confined channels. To fully understand the uniformity control over the nanostructure growth distribution in this hydrothermal process, a simple computational fluid dynamics (CFD) study was employed as shown in Figure 3a and 3b. The computational model is shown in Figure 7a. The CFD results (Figure 3b) showed the real-time predictions of the pressure difference between the ends of each channel. A small oscillating pressure difference between the channel ends was generated by the unsteady motions introduced by the horizontally rotating stirring rod which helped producing a convective flow that flushed the channel with fresh solution about every 2 min. The 1-inch in diameter and 1cm in length ZnO grown monolith sample was fabricated with the mechanical agitation (Figure 3c). SEM investigation (Figure 3d) suggested that densely packed, well controlled ZnO nanorod array were uniformly coated throughout the 1 centimeter long channel. The experimental enhancement of nanostructure seeding and growth uniformity directly proved that mechanical agitation can help enhancing the transport across multiple channels within the cordierite monoliths and, therefore, the nucleation and growth uniformity of ZnO nanostructures. The agitation assisted growth method shed a light on the large scale manufacture of 3-D nano-array based monolithic catalysts.

Active, stable and PGM free catalysts can dramatically reduce the cost of catalysts and have been pursued by scientists and engineers for decades in industrial catalysts. Nano-array catalysts with the high surface area and small size effect are potentially good substitutes for PGM catalysts. In this project, we demonstrated that Co_3O_4 nanowire array based monolithic catalysts showed comparable activity as PGM catalysts with reasonable catalytic stabilities in NO oxidation, which is a crucial step in the NO_x emission control. Figure 4a showed the light-off curves of the Co_3O_4 nano-array-based monolithic catalysts and Co_3O_4 powder form wash-coated monolithic catalysts prepared by different Co precursors, respectively.

Comparing with the powder form catalysts, all the nano-array based catalysts showed enhanced activity at a lower temperature. Especially, both CA and CN samples reach the NO to NO₂ conversion as high as 80% at a relatively low temperature of 275 °C. The catalytic NO conversion performance of CA with varied oxygen concentration were also investigated and showed in Figure 4b. A series of stability characterizations have been conducted on nano-array based monolithic catalysts. Repeated heating and cooling is essential in the automotive catalysts, we investigated the stability of nano-array based catalysts by mimicking the temperature fluctuation by cyclic temperature change from 150 °C to 400 °C (Figure 4c). The maximum NO conversion temperature stayed the same during cooling process and no degradation of catalytic activity was observed. Isothermal catalytic stability of these catalysts was also studied by monitoring the NO conversion change at the temperature where maximum conversion was achieved. As shown in Figure 4d, no activity degradation, weight loss and observable morphology change during the 20 hours' test for all three monolithic catalysts were detected. The new type of noble metal-free monolithic catalysts has been successfully developed by rational assembly of hierarchical Co₃O₄ nano-arrays on three dimensional ceramic and stainless steel substrates, which provide a new avenue to low-cost, high efficient emission control catalysts.

*Multi-components nano-array based 3-D composite nano-array monolithic catalysts were also developed in this project. Using pristine ZnO nanorod array as template, both ZnO/LSCO/Pt nanorod and ZnO/LSCO/BaO/Pt nano-array NSR catalysts were made by dip-coating method. Figure 5a shows the low magnification top-view SEM image of as prepared ZnO/LSCO/Pt nano-array catalysts. Zoom-in SEM image (inset of Figure 5a) indicated that nanorods are densely packed with a rough surface as a result of an overcoated layer of LSCO/Pt on ZnO nanorods. On the basis of ZnO/LSCO/Pt catalysts, different preparation methods have been found to influence the nano-array catalysts' catalytic performance. It is found that sequentially deposited ZnO/LSCO/Pt nano-array shows higher NO conversion efficiency throughout the temperature range (Figure 5b). Three cycles of NO oxidation were performed on the sequential deposited catalysts to evaluate the stability of as-prepared catalysts (Figure 5c). The first test displayed a lower NO conversion efficiency than the other two, which may be induced by the impurity adsorbates on the catalyst surface. After burning the surface contamination in the first cycle, the second and third tests show almost the same profiles; demonstrating good catalytic stability of ZnO/LSCO/Pt. Considering the identical Pt mass loading controlled for these two samples, certain amount of Pt may immerse in between LSCO layer and ZnO core during the co-loading process, leading to fewer Pt active sites exposed and compromised its catalytic performance. Therefore, the sequential deposition method may be a good process for preparing high efficient nano-array based monolithic catalysts.

*Sulfur resistivity of as-prepared Pt/LSCO/ZnO nano-array based monolithic catalysts was also evaluated. Figure 5d was the NO conversion plots on the Pt/LSCO/ZnO/CH catalyst before and after SO₂ adsorption. After 3 cycles of NO oxidation tests, the conversion rate of the catalyst had no obvious change, which indicated that the catalyst has a very good stability for NO oxidation. After 5h of SO₂ adsorption, the conversion rate of the catalyst just changes from 65% to 63%. Even after 15h poisoning, the conversion rate is ~ 55%. This indicated that the catalyst had a good S poisoning resistance. Further investigation was conducted on the effect of S poisoning on the catalyst morphology by SEM, which shows no obvious change even after 15 h poisoning. The EDX results indicated no obvious change in other elements except S, which shows 0.2 at%, before and after 15 h poisoning.

*Water steam is generally involved in a lot of industrial process and sometimes could seriously decrease the catalyst performance. Therefore, the hydrothermal stability of ZnO based nano-array catalysts had been studied using two types of experiments. One is under extreme condition with 100% steam vapor at 120 °C. The structure and morphology analyses after 24 hours aging in boiling deionized water suggested that both the array structure and surface morphology of ZnO, ZnO/LSCO and ZnO/CeO₂ retain very well with no visible morphology change, which suggests as-prepared ZnO nano-array monolithic catalyst is very stable in 100% steam vapor environment. On the other hand, the hydrothermal aging was also

conducted at high temperature under 10% steam vapor at 500 °C for 24 hours. Little decrease on NO oxidation performance has been observed, which may be attributed to the passivation of silica layer on the surface.

*The NSR performance was investigated on the as-prepared ZnO/LSCO/BaO/Pt nano-array monolithic catalysts. Figure 5e reveals a NO₂ breakthrough after just a few seconds and the NO₂ outlet concentration reaches to a maximum of 160ppm in about 10 min after NO₂ breakthrough. In a typical storage and reduction cycle (Figure 5f), after NO₂ outlet concentration reaches to a maximum and stable for 10 min, reducing gas (H₂) were induced to the system to start the “rich phase”. NO₂ outlet concentration reaches a peak upon introduction of H₂ and then decreases to undetectable level in 10 min. The study on the structure and storage/reduction performance relationship is on-going. The distribution of BaO particles on the nano-array monolith may have played an important role in the NSR performance.

** Patentable materials: documented in patent application and invention disclosures 3 & 5 in section 5.2.*

Furthermore, first principles methods were successfully employed enabling us to simulate the steady-state catalytic interaction of oxygen with LaMnO₃ (001) surface under varying levels of oxidative environment.[10] In the work, density-functional theory (DFT) together with transition-state theory was first used to obtain the energetics and activation barriers of various relevant elementary surface processes. The results were subsequently used in kinetic Monte Carlo (kMC) simulations to explicitly account for the correlations, fluctuations, and spatial distributions of the oxygen ad-atoms and ad-molecules at the surface of the catalyst under steady-state conditions. As shown in Figure 6, DFT–GGA-calculated relaxed geometries of O₂ ad-molecules in monodentate (panels a and b, respectively) and bidentate (panels c and d, respectively) binding modes on the surface Mn-on-top site were depicted. The calculation results suggested that the bidentate binding modes were predicted to be less energy favorable by 0.24 eV compared with the monodentate modes. The calculated (*p*, *T*) surface phase diagram based on purely thermodynamic arguments and the kMC method based equilibrium surface phase diagrams for the surface are computed and found to be in reasonable agreement with each other. In addition to the thermodynamics, the kMC based approach has allowed us to describe the kinetics related effects (such as influence of thermal and chemical history and surface preparation on sample's behavior) and meta-stable regions on the (*p*, *T*) phase diagram. We find that the results from our model are in good agreement with available temperature programmed desorption experiments in the literature.[11, 12]

3.3 Conclusions

In this project, main accomplishments are listed as follows:

- Established a general platform of three-dimensional (3D) composite nanostructure arrays (nano-arrays) monolithic catalysts with well-controlled morphology and multi-components;
- Developed a general low-cost, green hydrothermal process which hold the potential to manufacture the high efficient nano-array based monolithic catalysts in a large scale.
- Explored the high efficient PGM free nano-array monolithic catalysts for NO oxidation.
- Fabricated and characterized the PGM and BaO loaded 3D composite nanowire/rod array (such as ZnO/(La,Sr)CoO₃(LSCO) and TiO₂/(La,Sr)MnO₃(LSMO), etc.) on monolith substrates;
- Investigated the (hydro-)thermal and mechanical stability, CO and NO oxidation performance, S-poisoning resistance, as well as NSR performance of the 3D composite nanostructures;
- Demonstrated ultra-high materials usage efficiency of 3D composite nano-array catalysts in both PGM and metal oxides, excellent thermal and mechanical robustness, as well as tunable catalytic performance, showing their good potential to be used as the next-generation automotive catalysts.
- Developed the reliable surface catalytic phase diagrams of perovskite (such as LaMnO₃) surfaces through the FTP and KMC simulations.

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5. Products developed under the award and technology transfer activities

5.1. Selected Publications and Presentations

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39. S. Glod, Z.H. Zhang, Y.B. Guo, P.-X. Gao, *ZnO Nanowire Arrays Coated With La_{1-x}Sr_xCoO₃ Perovskite Nanoparticles for DOC and DeNO_x Integration*, Materials Science & Technology 2011 conference, Columbus, OH, Oct. 18, 2011.
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41. P.-X. Gao, et al., *Thermal and chemical stability of metal oxide/perovskite/metal nano-interfaces: An investigation of modeled ZnO/(La,Sr)CoO₃/Pt nanowire based catalyst*, DoE Catalysis Science program meeting, Annapolis, MD, Oct. 2, 2011.
42. P.X. Gao, *Multi-functional Composite Nanowires for Energy, Environmental and Biomedical Applications*, Institute of Materials Science Associates Program Annual Meeting, University of Connecticut, Storrs, CT, May 18, 2011.
43. P.X. Gao, *Three-dimensional Composite Nanostructures for Lean NO_x Emission Control*, DOE Vehicle Technology Program Annual Merits Review Meeting, Washington, D.C., May 12, 2011.
44. P.X. Gao, *Hierarchical Oxide-based Nanoarchitectures for Energy, Environmental and Sensing Applications*, SPIE Photonics West: Oxide based Materials and Devices, San Francisco, CA, January 25, 2011.
45. P.X. Gao, *Three-dimensional Composite Nanostructures for Lean NO_x Emission Control*, DOE Vehicle Technology Program Annual Merits Review Meeting, Washington, D.C., June 10, 2010.
46. P.X. Gao, *Three-dimensional Composite Nanostructures for Lean NO_x Emission Control*, DOE HQ, Washington, D.C., March 31, 2010.
47. P.X. Gao, *Hierarchical Composite Nanostructures for Energy, Environmental and Sensing Applications*, Materials Science and Engineering Program, Worcester Polytechnic Institute, Worcester, MA, March 19, 2010.
48. Y.B. Guo, H.Y. Gao, Z. Ren, and P.X. Gao, *ZnO nano-array based emission control catalysts*, North American Catalysis meeting in Detroit, June 5-10, 2013. (Poster)

49. Y.B. Guo, H.Y. Gao, Z. Ren, and P.X. Gao, *Synthesis and emission control properties of ZnO/(La,Sr)CoO₃(LSCO) core-shell nanowire array based monolithic catalysts*, North American Catalysis meeting in Detroit, June 5-10, 2013. (Oral)
50. P.X. Gao, Y.B. Guo, and Z. Ren, *Ultra-efficient, Robust and Well-defined Metal Oxide Nano-Array based Monolithic Catalysts for Emission Control*, ACS Spring National meeting, New Orleans, April 7, 2013. (Oral)
51. S. Glod, Y.B. Guo, Z.H. Zhang, Z. Ren, and P.X. Gao, *Size and Shape Effects in Composite Nanorod Array Based Catalysts for Emission Control*, CMOC symposium 2013, New Haven, CT, March 13, 2013. (Oral)
52. P.X. Gao, Y.B. Guo, and Z. Ren, *Ultra-efficient, Robust and Well-defined Nano-array based Catalytic Devices for Emission Control*, EMC meeting, Orlando, Jan. 23, 2013. (Oral)
53. S. Glod, Y.B. Guo, Z.H. Zhang, Z. Ren, and P.X. Gao, *Structure and catalytic performance in automotive catalysts based on ZnO/(La,Sr)CoO₃ composite nanorod arrays*, MRS Fall meeting, Boston, Nov. 2012. (Oral)
54. Z. Ren, Y.B. Guo, Z.H. Zhang, C.H. Liu, and P.X. Gao, *Ultra-efficient PGM-free Catalytic Nanoreactors for NO Oxidation*, MRS Fall meeting, Boston, Nov. 2012. (Oral)
55. K.T. Liao, Z. Ren, P. Shimpi, P.X. Gao, *Cu-Sn alloying via low temperature solution process*, CMOC symposium 2012, Storrs, CT, April. 11, 2012. (oral)
56. Z. Ren, Y.B. Guo, G. Wrobel, P.X. Gao, *Three- Dimensional (3D) Multi-component Koosh Ball Structures*, CMOC symposium 2012, Storrs, CT, April. 11, 2012. (poster)
57. Z.H. Zhang, Y.B. Guo, N. Freedman, and P.X. Gao, *CeO₂ Nanowire Arrays on 2D and 3D substrates for Lean NO_x Automobile Emission Control*, Materials Research Society 2011 fall meeting, Boston, MA, Nov. 30, 2011. (oral)
58. Z. Ren, Y.B. Guo, G. Wrobel, P.X. Gao, *ZnO Nanowire Growth Array Growth on Three-Dimensional (3D) Spherical Substrate: Facile Synthesis of Multi-component Koosh Ball Structures*, Materials Research Society 2011 fall meeting, Boston, MA, Nov. 28, 2011. (poster)
59. Z. Ren, Y.B. Guo, D. Knecht, P.X. Gao, *Synthesis of Fe₃O₄/SiO₂ Core-shell Structured Microspheres*, Materials Science & Technology 2011 conference, Columbus, OH, Oct. 17, 2011.
60. S. Glod, Z.H. Zhang, Y.B. Guo, P.X. Gao, *ZnO Nanowire Arrays Coated With La_{1-x}Sr_xCoO₃ Perovskite Nanoparticles for DOC and DeNO_x Integration*, Materials Science & Technology 2011 conference, Columbus, OH, Oct. 18, 2011.
61. P.X. Gao, P. Shimpi, H.Y. Gao, W.J. Cai, and G. Wrobel, *Multifunctional Composite Nanostructures for Energy and Environmental Applications*, The 4th International Symposium for Advancement of Chemical Science: Challenges in Renewable Energy, MIT, Boston, July 5-8, 2011.
62. Y.B. Guo, H.Y. Gao, Z. Ren, and P.X. Gao, *Anisotropic surface control of catalytic and sensing properties in metal oxide-based composite nanowires*, North American Catalysis meeting in Detroit, June 5-10, 2011.
63. Y.B. Guo, H.Y. Gao, Z. Ren, and P.X. Gao, *Synthesis and multifunctional environmental catalysis properties of TiO₂/(La,Sr)MnO₃(LSMO) composite nanostructures*, North American Catalysis meeting in Detroit, June 5-10, 2011.
64. W.J. Cai, and P.X. Gao, *Reversible catalytic multi-gas sensing based on single crystalline metal oxide-hybrid nanowires*, North American Catalysis meeting in Detroit, June 5-10, 2011.
65. W.J. Cai, and P.X. Gao, *Synthesis and characterization of SnO₂-based nanowires for energy and environmental applications*, North American Catalysis meeting in Detroit, June 5-10, 2011.

5.2 Special Recognitions & Awards/Patents Issued

1. K.T. Liao, Z. Ren, Z.H. Zhang, P.-X. Gao, *Free standing Cu-Sn alloying via low temperature solution process*, CMOC symposium 2012, Storrs, CT, April. 11, 2012. (Best student oral presentation award)

2. Z. Ren, Y.B. Guo, G. Wrobel, P.-X. Gao, *Hierarchical Koosh Ball Nanoarchitectures: Towards Multifunctional and Three Dimensional Integration of Nanoscale Building Blocks*, CMOC symposium 2012, Storrs, CT, April 11, 2012. (Best student poster award)
3. P.-X. Gao, Y.B. Guo, Z. Ren, Z.H. Zhang, "Metal oxide nanorod arrays on monolithic substrates", US non-provisional patent filed, PCT filed, 2012.
4. P.-X. Gao, Z.H. Zhang, "Temperature-programmed-reduction Fabrication Method for Tubular Structure Devices", US non-provisional patent filed, PCT filed, 2013.
5. P.-X. Gao, Y.B. Guo, and Z. Ren, "Ultra-efficient, robust and well-defined nano-array based monolithic catalysts," Invention Disclosure 12-079, University of Connecticut, 2012.

5.3 Networks or Collaborations Fostered

1. Industrial collaborative partnership expanded from 1 (Honda Research Institute) to 4 including catalyst supplier Umicore Autocatalyst USA and substrate supplier Corning Inc, and manufacturer United Technologies Corporation through United Technologies Research Center (UTRC);
2. Catalysis research collaboration established with two Department of Energy National Laboratories including Brookhaven National Lab (BNL) and Oak Ridge National Lab (ORNL) through successfully securing four user programs with the National Synchrotron Light Sources (NSLS), the Center for Functional Nanomaterials in BNL, and the Center for Nanophase Materials Science in ORNL, particularly targeting for catalyst stability, functionality, and activity understanding.
3. In addition, we have initiated the collaboration with the Emissions and Catalysis group in the Fuels, Engines, and Emissions Center at ORNL.

5.4 Technology Transfer

1. Start-up: 3D Nano-array Technology LLC was started in January 2013, it is in discussion with the University of Connecticut for licensing agreement of one of the patents filed by P.-X. Gao et al. through this project.

Acronyms

List all acronyms used in the report and explain what they stand for.

CH	Ceramic honeycomb
KMC	Kinetic Monte Carlo
LSMO	(La,Sr)MnO ₃
LSCO	(La,Sr)CoO ₃
LMO	LaMnO ₃
NSR	NO _x Storage and Reduction
FPT	First Principles Thermodynamics
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
EDXS	Energy-dispersive X-ray Spectroscopy
XRD	X-ray diffraction

Figure Captions

Figure 1. Schematic illustration of 3-D configured nano-array catalysts, and typical morphology and structure of metal oxide nano-arrays on monoliths. (a) Schematic nano-array assembly process on typical cordierite and stainless steel monoliths. (b) Selected nano-array rooted monoliths (left to right: ZnO nanorod arrays on stainless steel, and TiO₂ nanorod arrays, CeO₂ nanotube arrays, and Co₃O₄ porous nanowire arrays on cordierite). SEM images of metal oxide nano-array on monoliths: (c) Low magnification view of cordierite monolithic channels grown with ZnO nanorod arrays; inset: Zn and Al element map of a single monolith channel from EDXS. (d) and (e) Top and cross-sectional views of

Co₃O₄ porous nanowire arrays on cordierite monolith. (f) and (j), (g) and (k), (h) and (l), and (i) and (m), are, respectively, ZnO nanorod arrays, TiO₂ nanorod arrays, CeO₂ nanotube arrays, Co₃O₄ porous nanowire arrays on cordierite monoliths and their corresponding TEM images. Scale bars in all the insets are 2 nm.

Figure 2. CO oxidation over Pt-loaded metal oxide nano-array based monolithic catalysts. Low magnification TEM images of individual Pt nanoparticle loaded metal oxide nanostructure and its high magnification HRTEM lattice image (inset): (a) ZnO nanorod; (b) TiO₂ nanorod; (c) CeO₂ nanotube; and (d) Co₃O₄ nanowire. Scale bars in all the insets are 2 nm. (e) CO oxidation conversion as a function of temperature over Pt-loaded (CeO₂, ZnO, Co₃O₄, and TiO₂) nano-array monolithic catalysts; (f) Catalytic stability of Pt-loaded (CeO₂, ZnO, Co₃O₄, and TiO₂) nano-array monolithic catalysts; (g) Materials utilization efficiency of nano-array catalysts and classical-powder washcoated catalysts; (h) A schematic transport model of nano-array catalysts and traditional nano-powder catalysts.

Figure 3. (a) Scheme of the hydrothermal process experimental setup and CFD computational model. (b) Recorded instantaneous pressure difference (ΔP) between the front and back ends of the monolithic channel (1 mm $\times$ 1 mm $\times$ 10 mm) and the resulting velocity in the channel from CFD modeling. (c) Photograph of a typical 1 inch diameter and 1cm thick cordierite monolith substrate. (d) SEM images of ZnO nanorod array at different spot of a 1-cm monolith channel.

Figure 4. (a) NO oxidation performance of catalytic Co₃O₄ nano-arrays and powders prepared from different precursors; (b) catalytic NO conversion performance of CA with varied oxygen concentration. (c) Catalytic NO oxidation performance with repeated heating and cooling; (d) NO oxidation efficiency and weight measurement during long term steady investigation at 275 °C for CA and CN and 325 °C for CC; (e–f) SEM images of CN, CA and CC respectively after all stability tests.

***Figure 5.** Typical top view low magnification (a) and zoom-in SEM images (inset in (a)) of as-prepared ZnO/LSCO/BaO/Pt nano-array monolithic catalysts; NO conversion plots on the ZnO/LSCO/Pt catalysts: (b) NO oxidation on ZnO/LSCO/Pt catalysts made by co-loading and colloidal sequential methods; (c) NO oxidation stability of colloidal deposited ZnO/LSCO/Pt; (d) NO conversion plots on the Pt/LSCO/ZnO/CH catalyst before and after SO₂ adsorption. (e) NO₂ storage profile and (f) a full cycle NSR profile of ZnO/LSCO/BaO/Pt Nanorods based monolithic catalysts.

Figure 6. Top and side views of DFT–GGA-calculated relaxed geometries of O₂ ad-molecules in monodentate (panels a and b, respectively) and bidentate (panels c and d, respectively) binding modes on the surface Mn-on-top site. Red, green, and purple spheres represent O, La, and Mn atoms, respectively.

** Patentable materials: documented in patent application and invention disclosures 3 & 5 in section 5.2.*

Figure 1

Figure 2

Figure 3

Figure 4

*Figure 5

Figure 6