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Abstract

This final report to the Department of Energy/National Energy Technology Laboratory for DE-FE0000870 covers the period from 2009 to June, 2013 and summarizes the main research accomplishments, which can be divided in sensing materials innovation, bimodular sensor demonstration, and new understanding and discoveries. As a matter of fact, we have successfully completed all the project tasks in June 1, 2013, and presented the final project review presentation on the 9th of July, 2013. Specifically, the major accomplishments achieved in this project include:

- 1) Successful development of a new class of high temperature stable gas sensor nanomaterials based on composite nano-array strategy in a 3D or 2D fashion using metal oxides and perovskite nanostructures.
- 2) Successful demonstration of bimodular nanosensors using 2D nanofibrous film and 3D composite nanowire arrays using electrical resistance mode and electrochemical electromotive force mode.
- 3) Series of new discoveries and understandings based on the new composite nanostructure platform toward enhancing nanosensor performance in terms of stability, selectivity, sensitivity and mass flux sensing.

In this report, we highlight some results toward these accomplishments.

Table of Contents

Abstract.....	2
1. Executive Summary.....	4
2. New high temperature gas sensing nanomaterials	4
2.1. 3D composite nanowire arrays	4
2.2. 2D composite nanofibrous films	11
3. Demonstration of high temperature bimodular gas sensors	14
3.1. Bi-modular oxygen gas sensor using NiO thin film	14
*3.2. Composite nanowire arrays based bi-modular sensors	15
4. Fundamental understanding on 3S (Stability, Sensitivity and Selectivity).....	18
*4.1. High temperature stability.....	18
*4.2. Sensitivity: sensitizing effect from perovskites	19
*4.3. Selectivity: Pt-CeO ₂ nanofiber sensors in different gases.....	21
5. Conclusions	24
6. Selected publication list, Patents/invention disclosures, conference papers.....	24
7. Other accomplishments.....	26

* *Patentable materials: documented in patent application and invention disclosures, i.e., 1) and 4) in section 6.*

1. Executive Summary

This final report to the Department of Energy and National Energy Technology Laboratory for DE-FE0000870 covers the period from October 1, 2009 to June 1, 2013. Under this project, DOE awarded UConn about \$795,506 to conduct the research and development on a new class of nanowire/film composite nanostructure based sensing materials for high temperature gas detection. Much of the material presented here has already been submitted to DOE/NETL in quarterly technical reports. We had also presented the final project review presentation on the 9th of July, 2013. This report covers three main research accomplishments in this project.

First, we have successfully developed a new class of high temperature stable gas sensor nanomaterials based on composite nano-array strategy in a three-dimensional (3D) or two-dimensional (2D) fashion using metal oxides and perovskite nanostructures. Using a combination of solution and vapor phase methods, various high temperature stable metal oxide/perovskite composite nanowire arrays have been fabricated on solid substrates such as Si, Al₂O₃, and Yttrium-stabilized ZrO₂ (YSZ). Magnetron sputtering or sol-gel process has been used for the seeding process of metal oxides such as ZnO and SnO₂, followed by a hydrothermal decomposition process for nanowire array growth. And then sputtering or sol-gel process will be used for surface deposition of perovskite nanoparticle films surrounding nanowire arrays. On the other hand, through an electrospinning and high temperature post-calcination process, 2D composite nanofibrous films have been fabricated with different composition and distribution. The composition and morphology distributions are controlled via adjusting precursor concentration, electrical field, as well as calcination temperature.

Second, successful demonstration has been achieved on the bimodular nanosensors using 2D nanofilm and 3D composite nanowire arrays using electrical resistance mode and electrochemical electromotive force mode. The bimodular sensing mechanisms are built based on the desired responsiveness in both electrical and electrochemical signal variations upon the nanostructures designed being exposed to different gaseous conditions (gas concentration and species). The two modes of signal variations allowed a cross-check and complementary sensing process of gas species at high temperature. Besides the resistance and electromotive force signals, the nanostructure surface impedance signal has also been successfully extracted as an effective high temperature sensing mode using 2D and 3D composite nanostructures made of metal oxides and perovskites.

Finally, a series of new discoveries and understandings have been achieved based on the new composite nanostructure platform toward enhancing nanosensor performance in terms of stability, selectivity, sensitivity and mass flux sensing. In the stability, the composite strategy involving metal oxide core and perovskite nanoshell proves to be successful to allow higher working temperature than that for metal oxide nanostructure alone, possibly attributed to the synergy effect between metal oxide and perovskite. Both perovskite and noble metal nanoparticles have been found to effectively enhance the nanosensor selectivity, as a result of the selective catalytic filtering or adsorption/spill-over effects on the metal oxide surface. Finally, the perovskite nanoparticle layering on the metal oxide nanowires is found to greatly enhance the sensitivity possibly due to the surface passivation/filtering effect, catalytic surface reaction effect and the p-n junction electronic effect.

In the following sections 2, 3 and 4, we have highlighted some important results and discussions toward these above-mentioned accomplishments.

2. New high temperature gas sensing nanomaterials

2.1. 3D composite nanowire arrays

In this project, we have successfully fabricated various 3D nanorod or nanotube arrays of metal oxides using a combination of solution phase and vapor phase methods. Specifically, sputtering or sol-gel process had been used for deposition of seeds on solid substrates such as Si, YSZ and Al_2O_3 . Based on the seed layer such as ZnO, TiO_2 , SnO_2 , etc., hydrothermal, solvothermal or electrochemical approaches have been used for growth of a large number of binary metal oxide nanowire arrays, such as ZnO, TiO_2 , CeO_2 , Co_3O_4 , Ga_2O_3 , etc.. Furthermore, we used sol-gel process or sputtering process to deposit the nanofilm of perovskites such as $\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$ (LSMO), $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$ (LSCO), and $\text{La}_x\text{Sr}_{1-x}\text{FeO}_3$ (LSFO). The nanowire/film size, thickness, aspect ratio, as well as density distribution are controlled through adjusting the deposition time and atmosphere/precursor conditions.

As an example, we successfully fabricated vertically aligned ZnO and Ga_2O_3 nanorod arrays using a combination of wet chemistry and thermal annealing. The coating of perovskite on the Ga_2O_3 nanorod arrays are being performed. Further, ZnO/LSCO nanorod arrays devices were designed and fabricated with top and bottom electrodes fabricated. Different perovskite materials including LSMO, LMO, LSCO, and LSFO have been deposited on different metal oxide nanostructure templates by radio frequency (RF) magnetron sputtering and post annealing process. The parameters of sputtering process and post annealing process were optimized to improve the quality of perovskite materials. The morphologies, structures and compositions of the metal oxide/perovskite composite nanostructures were investigated. The synthesis of composite nanostructures composed of metal oxide nanocores and perovskite nanofilms is scalable, repeatable and controllable.

The emerging of hierarchical nanostructures such as nanowire arrays has stimulated various important practical applications in energy, environmental, electronic and optoelectronic sectors. Here, we present our early success on the fabrication and utilization of metal oxide/perovskite composite nanowire arrays for chemical sensing.

Fig. 1. Low magnification (a) and high magnification (b) cross-sectional SEM images of ZnO/LSCO core-shell nanorods grown using a combination of hydrothermal and colloidal deposition processes; c) Current-voltage (I-V) measurement of ZnO/LSCO heterostructure in the different humidity. The left inset shows the schematic illustration of the I-V measurement; d) the decreased photocurrent response upon UV illumination compared to the dark.

We have grown ZnO/LSCO core-shell nanorod arrays using a combination of hydrothermal and sol-gel process. Figs. 1 (a) and (b) show the cross-sectional SEM images of ZnO/LSCO composite nanorod arrays. From Fig. 1 (a) we can see that ZnO nanorods grew from the seed layer coated on Si substrate. The width of individual nanorod is very uniform from the tip to the bottom. From Fig. 1 (b) we can see that there are porous layers coated on ZnO nanorods. The LSCO materials were dispersed and coated on the surface of ZnO nanorods during the colloidal deposition.

We have looked into the electronic transport property of ZnO/LSCO core-shell nanorods. The sample was baked at 80 °C overnight before a two-terminal current-voltage (I-V) property measurement. Fig. 1(c) shows the I-V measurement of ZnO/LSCO heterostructure in the different humidity. The inset shows the schematic illustration of the I-V measurement across ZnO nanorod arrays and LSCO nanofilm. Here LSCO layer represents the LSCO nanofilm coated around ZnO nanorod arrays. A good rectifying characteristic have been found in the

fabricated ZnO/LSCO heterostructure, which is similar to that of conventional semiconductor p-n junctions. The relative humidities of background, humidity 1 (HM 1) and humidity 2 (HM 2) were about 9%, 34% and 41%, respectively. The setting temperature of the hot plate was 80 °C. The slope of the I-V curve becomes larger under larger humidity circumstance as a result of decreasing forward resistance. With increasing humidity, H₂O can be physically adsorbed on the nanostructures via hydrogen bonding. The nanostructure's conductance then increases according to Grotthuss's chain reaction, where proton transfer occurs among the hydronium. So with the increasing humidity, the forward resistance of ZnO/LSCO heterostructure decreases. It has been realized lately the water content plays a very important role in gas sensing, where humidity becomes an innegligible factor to be considered during the detection process. This work has set up an important foundation for high temperature sensing where water molecules will have to be taken into account while understanding the chemical sensing process. This work has been highlighted in Journal of Physics D 2011 highlight collections.

Fig. 2. Top view SEM images of as-grown ZnO nanorods (a) and LSMO coated on ZnO nanorods by sputtering as deposited (b). Cross sectional SEM image of LSMO coated around ZnO nanorods by sputtering (c), and by colloidal process.

Another successful example is the ZnO/LSMO composite nanorod arrays, which have also been synthesized through a two-step fabrication process on Si (100) flat substrates. Each composite nanorod is composed of a ZnO nanorod core and a LSMO nanoshell to enable ultra-high specific surface area. Fig. 2 (a) shows a typical top-view low-magnification SEM image of large-area ZnO nanorod array grown using hydrothermal method. A densely packed and well-aligned array of ZnO nanorods grew uniformly over the entire area. These nanorods grew along the [0001] direction as suggested by the hexagonal cross sections revealed from Figs. 2(a) and (b). The average diameter of the nanorods is ~100 nm. Fig. 2 (b) shows a top-view low-magnification SEM image of ZnO nanorod array after LSMO nanofilm deposition by sputtering. The morphology of LSMO on ZnO nanorods by colloidal deposition is very similar to that in Fig. 2 (b). Comparing Figs. 2(a) and (b), large-area ZnO nanorod arrays and LSMO/ZnO nanorod arrays are clearly of similar morphology, which suggests that ZnO nanorods retain their well-

aligned structure after LSMO nanofilm deposition. Figs. 2(c) and (d) show the cross-sectional SEM images of LSMO/ZnO nanorod arrays deposited by sputtering and colloidal deposition, respectively.

It is clearly shown in Figs. 2(c) and (d) that ZnO nanorods grew from the ZnO seed layer coated on Si substrate. The homogeneous coating of all the exposed parts of the nanorods has been achieved in both cases. The nanorods are aligned normal to the substrate despite a little randomness. From Fig. 2 (c) we can see that the width of individual nanorod is thinner and thinner from the nanorod tip to its bottom, which means the thickness of LSMO in the top part is larger than that in the bottom part. This is caused by the deposition process from the top of ZnO nanorod arrays with sputtering. The top part of individual nanorods looks rougher than the bottom part, which might be caused by different annealing effect of LSMO due to different thickness. While from Fig. 2 (d) we can see that the width of individual nanorod is fairly uniform from the nanorod tip to its bottom. Some nanorods are broken due to the cleavage process during the sample preparation.

Figs. 3 (a) and (c) displayed the bright field and dark field TEM images of a typical as-deposited ZnO/LSMO nanorod, respectively. Fig. 3 (a) clearly revealed the mesoporous rough surface of the nanorod. Inset in Fig. 3 (a) shows the SAED pattern of the as-deposited ZnO/LSMO nanorod. The diffusive ring pattern can be found besides the dot pattern that corresponds to ZnO single crystal. Therefore, the crystal structure of LSMO nanofilm coated on ZnO nanorod is polycrystalline but with poor crystallinity. In the dark field image shown in Fig. 3 (c) we can see clearly the core-shell structure of ZnO/LSMO nanorod. Figs. 3 (b) and (d) show the bright field and dark field TEM images of a thermally annealed ZnO/LSMO nanorod, respectively. The LSMO material nanofilm becomes smoother but dispersed after annealing, as indicated through a comparison of Figs. 3 (a) and (b). From the SAED pattern of ZnO/LSMO shown in inset of Fig. 3 (b), the dispersed LSMO nanofilm has very good crystallinity as revealed by scattered dotted pattern in addition to the single set of single crystal ZnO diffraction pattern, instead of a ring pattern. Fig. 3 (d) shows the dark field image of annealed ZnO/LSMO nanorod. Further characterization including high resolution TEM imaging and diffraction analysis are on-going to help further interpret the interface between the core and shell. The insets in Fig. 3 (c) and (d) are the corresponding EDS spectrums spectra to ZnO/LSMO nanorod before and after annealing, respectively. The peaks corresponding to O, Zn, La, Sr, and Mn were identified from both spectrums spectra. The Cu and C peaks come from the carbon-coated TEM Cu grid. The EDS spectra are similar for both as-deposited and annealed ZnO/LSMO composite nanorod.

Fig. 3. TEM image of as-deposited ZnO/LSMO composite nanorod: a) and b) bright field, c) and d) dark field. a) and c) correspond to as-deposited ZnO/LSMO, b) and d) correspond to annealed ZnO/LSMO. The insets in a) and b) show the corresponding electron diffraction pattern. The insets in c) and d) show the corresponding EDS spectrum.

Magnetic property of LSMO has been suggested to thickness dependent, including morphology, magnetoresistance and magnetization. To investigate the thickness dependence of magnetization, LSMO nanofilms with various thicknesses have been studied on 3D ZnO nanorod arrays. Fig. 4 shows the M-H hysteresis curve of LSMO nanofilm on ZnO nanorods with various thicknesses represented on flat Si. It is clear that the magnetization increases with the increase of magnetic field for LSMO with all thicknesses until saturation is reached. While the saturation magnetizations decrease with the increasing thickness of LSMO nanofilm, and the thinnest film has the largest saturation magnetization. If nanoparticles of LSMO are small enough, the single magnetic domains will interact with each other, leading to the superparamagnetism. It is worth noting that the 12.5 nm is the thickness of LSMO on flat Si deposited at the same time, which suggests a real LSMO nanofilm on ZnO nanorod side surfaces is much thinner due to the increased surface area. Therefore, the ultrathin nanofilm of LSMO on 3D ZnO nanorod arrays shows the superparamagnetic property. The inset shows the zoom-in M-H hysteresis curves at low magnetic field. The hysteresis curves show that the curve area is nearly zero for 12.5 nm and 25 nm LSMO nanofilms, which indicates a large surface effect with too many Mn^{3+} ions near the

surface to induce a superparamagnetic behavior. When the thickness becomes large, a well-behaved M-H curve was observed for the 50nm LSMO nanofilm on ZnO nanorods substrate, indicating a ferromagnetic behavior of the LSMO nanofilm. In this case, the surface dispersion effect is relatively low, with anisotropic LSMO thin film exhibiting a ferromagnetic behavior like the LSMO nanofilm on 2D Si substrates.

Fig. 4. Typical M-H hysteresis curves of LSMO nanofilms with different thicknesses on 3D ZnO nanorod arrays measured at 80K with magnetic field applied parallel to the film. Inset: the detailed M-H hysteresis curves at low magnetic field.

The BET surface areas of the metal oxide/perovskite composite nanostructures have been measured. Fig. 5 shows the BET surface area measurement of ZnO/LSCO composite nanorod arrays. The LSCO nanofilm was deposited on thick ZnO nanorod arrays as reported before. In order to investigate the temperature dependent surface area, the sample was measured four times after being annealed at different temperatures. As seen from all of panels in Fig. 4, the big negative peak results from the monomolecular adsorption layer of N_2 at liquid nitrogen temperature. The subsequent small positive peaks are due to the desorption of N_2 after removing liquid nitrogen. So the sample under the condition of as-deposited and annealed at different temperature has the similar adsorption-desorption profiles. The calculated surface areas of the of as-deposited samples and those annealed at 600°C, 800°C, 1000°C are 424, 490, 268, and 262 m^2/g . It is reasonable that the specific surface area of sample decreases after high-temperature annealing, since the recrystallization process will happen at high temperature and reduced the surface area. But the surface areas are still retained quite high after 800°C and 1000°C annealings.

Fig. 5. BET surface area measurement was performed on LSCO on thick ZnO nanorod arrays: (a) as-coated sample; (b) annealed at 600°C for 2hrs; (c) annealed at 800°C for 2hrs; (d) annealed at 1000°C for 2hrs.

2.2. 2D composite nanofibrous films

The composite metal oxide nanofibers were prepared by adding two or more metal precursors into a polymer solution, and going through an eletrospinning process. TiO₂/ZnO nanofibers were prepared by electrospinning using a procedure modified from reference. Briefly, 0.2 mL of zinc acetate-saturated ethanol was mixed with 0.2 mL of acetic acid and 0.1 mL of Ti(OiPr)₄. After that, this solution was transferred to 0.5 mL of zinc acetate-saturated ethanol solution containing 0.03 g PVP, followed by 5 min mixing. The mixture was immediately loaded into a plastic syringe equipped with a 23 gauge needle made of stainless steel. The electrospinning conditions were same as that of TiO₂ nanofibers. The collected nanofibers were left in air overnight, followed by calcination in a muffle furnace at 500 °C for 3 h to remove PVP and generate TiO₂/ZnO nanofibers. Similarly, TiO₂/CuO nanofibers have been generated.

Fig. 6. SEM images of (a) TiO₂/ZnO nanofibres; (b) TiO₂/CuO nanofibers.

The composite metal oxide nanofibers generated have a randomly orientated and highly porous 3-dimensional nanofiber-mesh structure, retaining the fiber morphology before calcination (Fig. 6). The final weight percentage of ZnO or CuO is around 10 %. Various components can be

mixed to obtain the preferred properties, with adjustable weight ratio.

Another successful example is the TiO_2/Pt composite nanofibrous film fabrication. 0.2 mL of $\text{Pt}(\text{OAc})_2$ -saturated ethanol was mixed with 0.2 mL of acetic acid and 0.1 mL of $\text{Ti}(\text{O}i\text{Pr})_4$. This solution was then added to 0.5 mL of $\text{Pt}(\text{OAc})_2$ -saturated ethanol solution containing 0.03 g PVP, followed by 5 min mixing. The mixture was immediately loaded into a plastic syringe equipped with a 23 gauge needle made of stainless steel. Electrospinning was conducted at an applied voltage of 20 kV with a feeding rate of 0.3 mL/h and a collection distance of 5 cm. The precursor nanofibers were then calcined in air at 500 °C for 3 h to generate TiO_2 -Pt nanofibers.

Fig. 7. Typical SEM images of (A) TiO_2 -PVP nanofibers; (B) TiO_2 - $\text{Pt}(\text{OAc})_2$ -PVP nanofibers; (C) TiO_2 nanofibers and (D) TiO_2 -Pt nanofibers obtained after calcination. Insets: Histograms showing the size distributions of nanofibers and each size distribution was obtained from 50 randomly selected nanofibers.

SEM was first employed to investigate the morphology of the precursor nanofibers and the corresponding calcined products. Fig. 7 A and B presents the typical SEM images of electrospun TiO_2 -PVP and TiO_2 - $\text{Pt}(\text{OAc})_2$ -PVP composite nanofibers. Since $\text{Ti}(\text{O}i\text{Pr})_4$ can be rapidly hydrolyzed by moisture in the air, amorphous TiO_2 is presented in the electrospun nanofibers. After calcinations in air at 500 °C, the PVP was completely degraded and the calcined samples remained the nanofibrous structures (Figs. 7 C and D). However, a decrease in their average diameter was observed, which could be attributed to the loss of PVP, the crystallization of TiO_2 , and/or the decomposition of $\text{Pt}(\text{OAc})_2$. In addition, the surfaces of calcined nanofibers were not as smooth as the precursory nanofibers. As presented in Fig. 7 C and D, TiO_2 nanofibers, which were composed of bigger nanoparticles, possessed rougher surface than that of TiO_2 -Pt nanofibers. Size distribution calculated from 50 randomly selected nanofibers was shown in the inset of Fig. 7.

Fig. 8. Typical TEM images of (A) a TiO_2 nanofiber and (B) a TiO_2 -Pt nanofiber; inset: the corresponding SAED pattern. EDX analysis of (B) TiO_2 nanofibers and (D) TiO_2 -Pt nanofibers. C and Cu peaks in EDX come from the copper-carbon grid of TEM.

Fig. 8A and C shows typical TEM images for single TiO_2 nanofiber and TiO_2 -Pt nanofiber, respectively. One can see that numerous black dots are present in the TiO_2 -Pt hybrid nanofiber. The condensation of Pt nanoparticles may be the major reason for the formation of these black dots. The insets of Fig. 8A and C display corresponding selected area diffraction pattern, indicating the polycrystalline structure of the nanofibers. Furthermore, EDX analysis was conducted with Tecnai T12 TEM to reveal the difference of compositions in the TiO_2 nanofibers and TiO_2 -Pt hybrid nanofibers. Well-formed peaks for Pt can be observed in the EDX pattern of the TiO_2 -Pt composite nanofibers (Fig. 8D), while no Pt is found in the TiO_2 nanofibers (Fig. 8B).

We have successfully fabricated NiO-CdO composite nanofibers with very high transparent conductivity. 0.4 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (fixed at 0.4 g) and 0.1 g $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 1.6 g water and then mixed with a 2.8 g solution consisting of 0.4 g PVP and 2.4 g ethanol. The electrospinning and calcination steps were the same with the fabrication of NiO-Pt. Fig. 9 presents the I-V curve of ITO coated, CdO coated and pristine glass slides. The curve of CdO coated glass slide shows a slope which is larger than 1/3 of that of ITO coated glass slide. This result indicates the excellent conductivity of CdO nanofibers. We expect the incorporation of CdO into NiO would also improve the sensitivity of glucose detection.

Fig. 9. Plots of current versus applied potential obtained with ITO coated glass slide, CdO coated glass slide and pristine glass slide.

Fig. 10. (A) SEM image of NiO-CdO nanofibers. (B) TEM images of a NiO-CdO nanofiber. (C) SAED pattern of NiO-CdO hybrid nanofibers.

The typical SEM image of NiO-CdO nanofibers shown in Fig. 10A exhibits quite different morphology with that of pristine NiO nanofibers, with a bigger average diameter of 105 nm and rougher surface. As the TEM image shows (Fig. 10B), the surface of NiO-CdO nanofiber is not as uniform as that of pristine NiO nanofiber, and the defects in the nanofiber are obvious. Fig. 10C presents the SAED pattern of the hybrid nanofiber, which is an indication of the polycrystalline structure.

We have extended the fabrication to metal oxide/noble metal hybrid nanofibers and binary metal

oxide system. NiO/CuO, NiO/Co₃O₄, Co₃O₄/CuO, Co₃O₄/Mn₂O₃, ZnO/Mn₂O₃ binary systems have been already synthesized and will be characterized.

Based on binary metal oxide nanofibers, we have successfully deposited perovskite nanofilms using sol-gel process. For example, by immersing Fe₂O₃ nanofibrous film in La_{0.67}Sr_{0.33}MnO₃ (LSMO) hydrogel for 30 min, and then annealed under atmosphere at 800 °C for 3 h, Fe₂O₃ /LSMO nanofibrous film was successfully fabricated. The TEM image shown in Fig. 11 clearly demonstrates the uniform coating layer of LSMO on the surface of Fe₂O₃ nanofiber with a thickness of around 10 nm.

To fabricate LSMO nanofibers, we used the precursory solution prepared by dissolving La(NO₃)₃·6H₂O, Sr(NO₃)₃ and Mn(NO₃)₂·4H₂O according to the corresponding molar ratio in PVP/DMF solution. Then the precursory nanofibers were fabricate using electropinning and were collected on Si wafer. The precursor was then calcined under air atmosphere at 800 °C for 3 h for the formation of LSMO.

Fig. 11. A typical TEM image of a single LSMO-coated Fe₂O₃ nanofiber.

Fig. 12. Typical SEM images of LSMO nanofibers at low (A) and high (B) magnification.

The SEM images of the as-prepared LSMO nanofibers is shown in Figs. 12A and B, presenting an average diameter of around 100 nm and rough surfaces. The small diameter and the rough surface can provide large surface area, which can further offer more active catalytic site. Meanwhile, the porous structure can minimize the hindrance for mass transfer.

3. Demonstration of high temperature bimodular gas sensors

3.1 Bi-modular oxygen gas sensor using NiO thin film

Based on the previous research of potentiometric sensor, a novel configuration of bimodular sensor was investigated. For the potentiometric mode, the Pt wires were connected to the sensing electrode (NiO film) and reference electrode (Pt), respectively. Open circuit potential was

obtained between NiO film and Pt film as electromotive force (EMF) signal. For the amperometric mode, two Pt wires were mounted on the surface of NiO film, the initial volts was chosen at 1 V. Fig. 13 shows bimodular sensor configuration.

Fig. 13 Bimodular sensor configuration

In this new configuration, the oxygen sensing behavior for the potentiometric and amperometric modes was examined at 600°C simultaneously and independently. As shown in Fig. 14, both potentiometric and amperometric modes displayed repeatable, fast and reversible responses to oxygen concentration change. This is the first demonstration of bi-modular high temperature sensor in one device.

Fig. 14 Sensing behavior to 500ppm O₂ at 600 °C for the potentiometric(a) and amperometric(b) sensor

*3.2. Composite nanowire arrays based bi-modular sensors

Fig.15 (a) shows the top-view SEM image of large area as-grown ZnO on YSZ substrate. ZnO nanorod arrays (NRAs) have been grown on YSZ substrate (Fig.15 (a)). The ZnO NRAs are vertically aligned on YSZ substrate, very similar to that grown on silicon (Si) substrate. Fig.15 (b) shows the zoom-in top-view SEM image of ZnO NRAs. The top plane of the nanorods exhibit hexagonal shape, which indicates that the as-grown ZnO nanorods on YSZ are single crystalline. The average diameter of the nanorods is about 100nm. To improve the thermal stability, LSCO thin film was coated around the ZnO nanorods by sputtering. After coating and annealing the composite structure retains the morphology of ZnO NRAs, and the morphologies

and structures didn't change much after the sensor test at high temperatures up to 1000°C only that the side wall surface became a little rough.

Fig. 15. SEM images of ZnO NRAs grown on YSZ substrate. (a) and (b) correspond to different magnifications.

Both amperometric and potentiometric signals have been recorded upon different content of gases at different high temperatures. Different gases with different contents balanced by nitrogen (N_2) were introduced into the test chamber. Fig. 16 shows the response upon different content of CO gas at 500°C (a) and 800°C (b) in the form of both open output voltage and current signals of LSCO/ZnO/YSZ based sensor. Both the currents and the open circuit voltages of LSCO/ZnO/YSZ sensor increase upon the introduction of CO into the test chamber at both 500°C and 800°C. The sensitivity, response time and recovery time of open circuit voltage signals are higher than that of current signals measured at 500°C as can be seen from the figure. For example, the response time at 120ppm CO is 25 second for voltage signal, while 81 second for current signal. So potentiometric method is more effective than amperometric method for high temperature CO detective. When measured at 800°C, both current and voltage signals have quicker response and recovery than that at 500°C, especially for current signals for higher CO content. For example, the response time at 120ppm is 20 second for voltage signal, and 45 second for current signal.

Fig. 16. Bi-modal responses in the form of current signals (black) and open circuit voltage signals (blue) of ZnO/LSCO/YSZ composite NRAs based sensors on the different content of CO at two different high temperatures: 600°C (a) and 800°C (b).

Then NO₂ has been tested at 800°C using LSCO/ZnO/YSZ based sensor as shown in Fig. 17 (a). Both the potentiometric and amperometric technique were employed to detect the response NO₂ concentration with ppm levels. The contents of NO₂ are 2, 3, 4 and 5ppm balanced by N₂. For NO₂ detection, there are background noises in both current and voltage signals, but the base lines are stable as can be seen from Fig. 17 (a). The responses of the currents increase linearly with the increase of the contents of NO₂. The voltage signals show much quicker response than that of current signals. The voltages decrease very fast upon the introduction of NO₂ gas, but then the voltages increase slowly. Before the termination of NO₂ gas, the voltage signals have already recovered to their baselines. And after the NO₂ gas was terminated, voltage signals increase suddenly, and then recover to its baseline slowly. So as a total, the performance of voltage response is not as normal as that of current response when measured at 800°C for NO₂ detection.

Then different contents of oxygen (O₂) have been tested by LSCO/ZnO/YSZ sensor at high temperatures as can be seen in Fig.17 (b). For the O₂ sensing behaviors, the current signals show good sensitivity, response and recovery except that there is a little abnormal behavior for 200ppm O₂. And the response increase nearly linearly with the increase of contents. But the sensitivity of voltage signals is relatively small as can be seen from the blue curve in Fig.17 (b). And the sensing behavior of open circuit voltage for O₂ at 800°C is similar with that for NO₂ at 800°C. The voltage decreases very fast upon the introduction of O₂ gas, and then increase slowly. And it increase suddenly with the termination of O₂ gas, and then recovery to it baseline slowly. The reason for such phenomena is not very clear at the present time. Then the potentiometric method has been performed at 1000°C as can be seen from the red curve in Fig.17 (b). The sensitivity is much higher than that measured at 800°C. The sensing behavior measured at 1000°C is normal, and the response is fast.

Fig. 17. Response of the current and open circuit voltage signals of LSCO/ZnO/YSZ based sensors on NO₂ (a) and O₂ (b).

4. Fundamental understanding on 3S (Stability, Sensitivity and Selectivity)

*4.1. High temperature stability

LSCO thin films were deposited on ZnO nanorod arrays template by sputtering and the post annealing process was performed to enhance the crystalline. Fig. 18 (a) shows the XRD pattern of the ZnO/LSCO composite nanorod arrays. The inset in (a) is the SEM morphologies.

ZnO peaks correspond to (10 $\bar{1}$ 0), (0002), (10 $\bar{1}$ 1), and (10 $\bar{1}$ 2) planes can be found clearly. The as-grown ZnO nanorod arrays have hexagonal wurtzite structure. The peak at 33° correspond to LSCO (110) plane (JCPDS 04-013-1000), which indicates LSCO thin film deposited around ZnO nanorod has perovskite structure. The inset in Fig.4 (a) shows the top view SEM image of ZnO/LSCO composite nanorod arrays. The composite arrays retained the SEM morphology of ZnO nanorod arrays except that ZnO nanorods were coated with a LSCO thin film. Fig.18 (b) shows the temperature-programmed reduction (TPR) measurement of ZnO/LSCO samples with different thickness of LSCO thin films deposited on ZnO nanorod arrays. Using a heating ramp of 10 K min⁻¹, the TPR peaks were found to be located at 545, 573, 597, and 541 °C for the thickness of LSCO 20nm, 50nm, 100nm, and 150nm. The peaks correspond to the reduction of ZnO nanorod arrays. it is clearly that with slight increase of LSCO thickness, the reduction temperature of ZnO shifted to the higher temperature region, which may suggest the chemical stability increase of ZnO as the additional LSCO film may behave as either a gas diffusion barrier or a ZnO pinning layer hindering the nanoscale ZnO surface from the H₂ reduction process (oxygen removal from ZnO lattice).

Fig. 18 Characterization of ZnO/LSCO composite nanorod arrays: (a) XRD pattern of the composite arrays. The inset in (a) is a top view SEM image of ZnO/LSCO nanorod arrays. (b) The TPR spectra of ZnO/LSCO samples with different LSCO film thickness.

On the other hand, in order to test the thermal stability of the surface area of such composite nanostructures, the surface areas were tested for the composite nanostructures treated at different high temperatures. The BET measurements of ZnO/LSCO composite nanorod arrays have been discussed. The surface area will decrease when annealed at 800 and 1000°C when compared with the as-deposited one, but the surface area is still very high, as shown earlier in Fig. 5. So the perovskite nanoparticle shells have helped elevate the thermal and chemical stability of ZnO nanowire arrays.

*4.2 Sensitivity: sensitizing effect from perovskites

Fig. 19 shows the XRD of GaOOH NRs (a), β -Ga₂O₃ NRAs (b), and LSFO/ β -Ga₂O₃ (c) NRAs. The insets in (a), (b) and (c) are the corresponding SEM images. GaOOH NRAs were grown on Si/SiO₂ substrate by hydrothermal method. Before the growth, SnO₂ layer that would be used for seed layer was deposited on Si followed by 900°C annealing. Gallium Nitrate was used as precursor for the synthesis. As seen from XRD patterns, there are diffraction peaks from pure GaOOH (JCPDF #06-0180). And the GaOOH NRAs have prefer orientation corresponding to (111) plane. β -Ga₂O₃ NRAs can be obtained by the annealing process at 1000°C for 4hrs. From Fig.4 (b), the diffraction peaks of β -Ga₂O₃ NRAs can be found, and there is not any peaks corresponding to GaOOH. This indicates that all GaOOH has been transferred to Ga₂O₃ through annealing. Then 5nm LSFO film have been sputtered and coated on β -Ga₂O₃ NRAs. But XRD didn't show any LSFO phase peaks as can be seen from Fig.19(c), and Fig.19 (c) is almost same with Fig. 19(b). The reason is that the sputtered LSFO is too thin, and even thinner after coated around nanorods. So peaks corresponding to LSFO are hardly to be detected by XRD. From SEM images GaOOH NRAs show diamond top surface, and the morphology retained after annealing and deposition of LSFO film. For compare, β -Ga₂O₃ NRAs were also decorated with platinum (Pt) particles for sensor test.

Fig. 19. X-ray diffraction (XRD) patterns of (a) GaOOH nanorods arrays, (b) β -Ga₂O₃ nanorods arrays, (c) β -Ga₂O₃ /LSFO nanorods arrays. The insets in (a), (b) and (c) are the corresponding SEM images

Fig. 20 (a) shows the combined response curves of the pure Ga₂O₃, Pt/Ga₂O₃ and LSFO/Ga₂O₃ on different contents of CO measured at 500°C, respectively. From Fig.5 (a) we can see that the coating of LSFO thin film and the decoration of Pt particles increased the sensitivities largely. The calculated sensitivities on different CO concentrations have been compared in Fig.20 (b). LSFO coating can improve sensitivity about 5 times, and the decoration of Pt particles can increase sensitivity to 10 times (both compared with pure Ga₂O₃). Though the sensitivities were increased a lot, the response time become longer as can be seen from Fig.20 (c). LSFO increased response time, and Pt particles increased response time even longer. If the measurement temperature was increased to 800°C which is not shown here, the response time can be reduced, but the sensitivity will also be reduced. Spillover effect can explain the enhancement of sensitivity when decorated by Pt particles. And the enhancement of sensitivity by LSFO coating can be explained by electronic sensitization.

Fig. 20. Carbon monoxide gas sensing test results: (a) Current-time characteristics of β -Ga₂O₃ ; β -Ga₂O₃ /LSFO ; β -Ga₂O₃/Pt composite nanorod tested at 500 °C with N₂ as background atmosphere; (b)

Sensitivity versus CO concentrations characteristics of $\beta\text{-Ga}_2\text{O}_3$; $\beta\text{-Ga}_2\text{O}_3$ /LSFO ; $\beta\text{-Ga}_2\text{O}_3$ /Pt composite nanorod tested at 500 °C ; (c) Response Time versus CO concentrations characteristics of $\beta\text{-Ga}_2\text{O}_3$; $\beta\text{-Ga}_2\text{O}_3$ /LSFO ; $\beta\text{-Ga}_2\text{O}_3$ /Pt composite nanorod tested at 500 °C

* 4.3 Selectivity: Pt-CeO₂ nanofibrous film sensors in different gases

Selectivity has been an especially important performance requirement in the high temperature chemical and physical sensing in the fossil fuel-burned power plants, which greatly demand the capability to selectively characterize precisely of the multiple gas species either oxidative or reductive. One of the challenges has been the selective detection of oxidative gas such as O₂ in reducing atmospheres; the other is the CO detection in multiple reducing gas species. The following example clearly demonstrates that through Pt doping in CeO₂ nanofibrous film (NF) sensors, the selective detection of CO could be achieved in multiple gas species such as O₂, NO, CO₂, SO₂, CH₄, etc.

Pt-CeO₂ NF based sensing device was fabricated on an Al₂O₃ screw and impedance spectroscopy was introduced to detect O₂ and CO at 800 C°. Then, we measured the impedance spectra of the as-prepared sensor in varied concentrations of NO, CO₂ and SO₂ at 800 °C.

Fig. 21. Impedance spectra (Nyquist -plots) of Pt-CeO₂ NFs based sensor in different gas mixture of (a) O₂ balanced by N₂, (b) CO balanced by N₂, (c), NO, CO₂ and SO₂ balanced by N₂, from 0.1 Hz to 1 MHz with amplitude of 0.5 V.

The AC-impedance experiment was conducted with amplitude of 0.5V and frequency from 10⁶ – 0.1 Hz. In each typical experiment, the sensor was kept in the targeted gas mixture for at least 30 min to reach the stable status after changing a different gas. As shown in Figs. 21(a) and (b) that with increasing concentrations of O₂, the radius of the semicircular arc greatly increase, while impedance magnitude $|Z|$ of the sensor in CO/N₂ mixture dramatically dropped by 2 decades and the shape of the spectra also shrank to only a portion of the semicircular arc. These results indicate that the sensor is sensitive to both O₂ and CO. The impedance spectra in different concentrations of SO₂, CO₂ and NO were also measured, which are very similar to the one of N₂, as shown in Fig. 21C. CO₂ and NO showed weak oxidizing property, while SO₂ exhibited a

weak reducing behavior; and the sensor only show limited sensitivity towards these three gases.

Fig. 22. Impedance vs. frequency profiles of Pt-CeO₂ nanofibrous film-based sensor in different gas atmosphere at 800 °C.

The impedance spectroscopy data of the sensor in different gas atmospheres can be also presented as $\log |Z|$ was plotted vs $\log$ frequency, as shown in Fig. 22. Since the sensor only show limited sensitivity towards NO, CO₂ and SO₂, the impedance spectra of the sensor in these three gas mixtures also overlapped between 10^4 - 10^6 Hz, as same as in O₂/N₂ mixture. Therefore, we can eliminate all the interference from O₂, NO, CO₂ and SO₂ by measuring impedance at a fixed frequency which located between 10^4 - 10^6 Hz. The sensitivity of Pt-CeO₂ NFs-based sensor towards different gases at fixed operating frequency of 10^5 Hz is summarized in Fig. 22. To compare the sensitivity of both reducing and oxidizing gas, the sensitivity was defined as $|\log (Z_g/Z_0)|$, where Z_0 is the initial impedance of the sensor in high purity nitrogen and Z_g is the measured real-time impedance upon exposure to different gas mixture. As presented in Fig. 23, the sensor exhibited good sensitivity and selectivity toward CO at the selected operating frequency of 10^5 Hz.

Fig. 23. Summarized sensitivity of the sensor in different gases (N₂, O₂, CO, NO, CO₂ and SO₂).

The real-time gas detection of Pt-CeO₂ NFs-based sensor based on AC impedance was carried out at high operating temperature 800 °C with a fixed frequency of 10⁵ Hz. Fig. 24(a) represents typical impedance modulus responses of the sensor as a function of time upon periodic exposure to CO (with concentrations from 20 ppm to 100 ppm) balanced in high purity N₂. The sensor showed good sensitivity at the operating frequency of 10⁵ Hz towards CO. Upon exposure to 100 ppm CO, the modulus $|Z|$ of the sensor quickly dropped 10 times smaller than the $|Z|$ in N₂. By purging with carrying gas, the response of Pt-CeO₂ NFs-based sensor can be completely recovered and the sensor responses towards three-time exposure of 100 ppm CO showed good reproducibility. The CO concentration dependent behavior was revealed by calibration curve presented in Fig. 24(b), which shows a linear relationship between $\log |Z|$ and $\log C_{CO}$ (concentration of CO). The sensitive, fast, reversible, reproducible and selective responses upon exposure to CO/N₂ mixture suggest that Pt-CeO₂ NFs based impedancemetric sensor is suitable for application of high temperature CO detection.

Fig. 24. (a) real-time CO detection of the Pt-CeO₂ NFs based sensor at operating frequency of 10⁵ Hz at 800°C; (b) Calibration curve for CO responses.

5. Conclusions:

We have successfully fabricated high temperature stable 3D nanowire and 2D nanofibrous film composites, based on which we have demonstrated a new class of high temperature bi-modular gas sensors. The composite nanomaterials design and selection for the enhancement of high temperature stability, sensor selectivity and sensitivity was successfully validated through right combination of nanostructures and materials entities. The understanding on the sensor materials sensitivity, selectivity and stability is gained, particularly on the nanostructure composite strategy as a promising approach for designing stable, sensitive and selective sensors at high temperature. A couple of typical example sensors include the composite nanowire arrays of ZnO/LSCO, Ga₂O₃/LSFO, and nanofibrous composite of Pt/CeO₂, which have been successfully demonstrated at the high temperature.

*** Patentable materials: documented in patent application and invention disclosures 1) and 4) in section 6.**

6. Selected publication list, Patents/invention disclosures, conference papers, etc.

Journal publications/book chapters/proceedings (> 30):

- 1) Z. Ren, Y.B. Guo, Z.H. Zhang, C.H. Liu, and P.X. Gao, *J. Mater. Chem. A*, 2013, 1, 9897-9906.
- 2) Z.H. Zhang, H.Y. Gao, W.J. Cai, C.H. Liu, Y.B. Guo, and P.-X. Gao, *J. Mater. Chem.*, 2012, 22, 23098.
- 3) W.J. Cai, H.Y. Gao, D.S. Kim, P.X. Gao, "Hierarchical Self-assembly of Semiconductor Nanowires for Electronics, Energy and Environment Applications", Chapter in *Encyclopedia of Semiconductor Nanotechnology*, Ahmad Umar Eds, American Scientific Publisher, Stevenson Ranch, CA, 2012, in press. (invited)
- 4) P.X. Gao, P. Shimpi, et al., *Int. J. Mole. Sci.*, 2012, 13(6), 7393-7423. (invited review)
- 5) X.Y. Liu, Y. Ding, L.C. Zhang, P.X. Gao, Y. Lei, *RSC Advances*, 2012, 2, 5193-5198.
- 6) M. Staruch, H.Y. Gao, P.X. Gao, and M. Jain, *Adv. Funct. Mater.*, 2012, 22, 3591-3595.
- 7) X.Y. Liu, Y. Ding, H.Y. Gao, P.X. Gao, Y. Lei, *RSC Advances*, 2012, 2, 3872-3877.
- 8) Z. Ren, Y.B. Guo, G. Wrobel, D. Knecht, H.Y. Gao, Z.H. Zhang, P.X. Gao, *J. Mater. Chem.*, 2012, 22, 6862-6868.
- 9) G. Wrobel, M. Piech, P.X. Gao, and S. Dardona, *Crys. Grow. Design*, 2012, dx.doi.org/10.1021/cg301002s.
- 10) P.X. Gao, J.Y. Liang, X.D. Wang, J. Yang, *Sci. Adv. Mater.*, editorial, 2012, 4, 781-783.
- 11) G. Wrobel, M. Piech, S. Dardona, P.X. Gao, *Sci. Adv. Mater.*, 2012, 4, 819-824.
- 12) P. Shimpi, K.-T. Liao, H.J. Lin, P.X. Gao, *Sci. Adv. Mater.*, 2012, 4, 837-842.
- 13) P.X. Gao, and Gang Liu, "Helical Nanostructures: Synthesis and Potential Applications," Chapter 7 in *Three Dimensional Nanoarchitectures: Designing the Next Generation Devices*, Weilie Zhou et al. Eds, Springer, New York, NY, 2011, 167-204. (invited)
- 14) Y.B. Guo, Z.H. Zhang, H.Y. Gao, Z. Ren, and P.X. Gao, *Catalysis Today*, 2011, DOI:10.1016/j.cattod.2011.10.027.
- 15) W.Z. Jia, L. Su, X.P. Li, L.C. Zhang, Z.Y. Gu, P.X. Gao, Y. Lei, *RSC Advances*, 2011, 1, 1500-1505.
- 16) K.-T. Liao, P. Shimpi, and P.X. Gao, *J. Mater. Chem.*, 2011, 21 (26), 9564-9569.
- 17) P. Shimpi, S. Yadav, R. Ramprasad, and P.X. Gao, *J. Phys. Chem. C*, 2011, 115, 7372.
- 18) H.Y. Gao, M. Staruch, M. Jain, P.X. Gao, P. Shimpi, Y.B. Guo, W.J. Cai, and H.-J. Lin,

Appl. Phys. Letts, 2011, 98, 123105.

- 19) P.X. Gao, P. Shimpi, et al., Hierarchical Composite Nanowires for Energy, Environmental and Sensing Applications, *Proceedings of SPIE Photonics West*, San Francisco, CA, Jan. 22-27, 2011. (invited)

Patents and Invention Disclosures:

- 1) Yu Lei and Y.X. Liu, Impedancemetric high temperature gas sensor selectively towards reducing gas based on electrospun nanofibers, US Provisional Patent (in processing), 2013.
- 2) P.X. Gao, H.J. Lin, Nanowire array based flow sensors, UConn Invention disclosure filed, 2013.
- 3) P.X. Gao, H.J. Lin, Nanowire-based mass flux sensors, UConn Invention disclosure filed, 2013.
- 4) P.X. Gao, H. Gao, and H.J. Lin, Perovskite sensitizing of nanowire based chemical sensors, UConn invention disclosure filed, 2012.
- 5) Y. Lei, Y. Ding, Y. Wang, Non-Enzymatic Glucose Sensing Using Novel Metal Oxide-Metal Composite Nanofibers, US patent pending, PCT filed, 2011.

Selected Conference Papers (>35):

- 1) K.-T. Liao, P. Shimpi, and P.X. Gao, MRS Fall Meeting, Boston, November, 2011.
- 2) Z.H. Zhang, N. Freedman, Y.B. Guo and P.X. Gao, MRS Fall Meeting, Boston, November, 2011.
- 3) H.J. Lin, H.Y. Gao, and P.X. Gao, MRS Fall Meeting, Boston, November, 2011.
- 4) Z. Ren, Y.B. Guo, D. Knecht, and P.X. Gao, MS&T 2011 meeting, Columbus, OH, Oct. 2011.
- 5) Y.X. Liu, Y. Ding, H.Y. Gao, P.X. Gao, Y. Lei, High temperature oxygen sensors based on novel CeO₂ nanofibers. American Institute of Chemical Engineers 2011.
- 6) Y.X. Liu, Y. Ding, H.Y. Gao, P.X. Gao, Y. Lei, "High Temperature Oxygen Sensors Based on Metal Oxide Nanofibers", 220th ECS Meeting, 2011.
- 7) P.X. Gao, DoE catalysis science program meeting, Oct. 2011.
- 8) P.X. Gao, 4th International Symposium for Advancing chemical Science for Renewable Energy Symposium, MIT, Boston, MA, 7/2011.
- 9) W.J. Cai, P.X. Gao, 22nd North America Catalysis Meeting, June, 2011 (R. J. Stokes Student Travel Award)
- 10) P. Shimpi, P.X. Gao, Connecticut Microelectronics and Optoelectronics Symposium, Storrs, CT, 4/ 2011.
- 11) G. Wrobel, M. Piech, P.X. Gao, and S. Dardona, ASM-Hartford chapter Student Paper competition, Storrs, CT, 4/7/2011. (1st place)
- 12) K.T. Liao, Z. Ren, P. Shimpi, P.X. Gao, Cu-Sn alloying via low temperature solution process, Connecticut Microelectronics and Optoelectronics Consortium (CMOC) symposium 2012, April 11, 2012. (Best student paper award)
- 13) X.C. Sun, H.Y. Gao, Y.X. Liu, P.X. Gao, Y. Lei, High temperature potentiometric type gas sensors. 2012 CMOC Symposium, April 11, 2012.
- 14) Z. Ren, Y.B. Guo, G. Wrobel, P.X. Gao, Three-Dimensional (3D) Multi-component Koosh Ball Structures, CMOC symposium 2012, April 11, 2012. (best student poster award)

- 15) H.J. Lin, H.Y. Gao, and P.X. Gao, Electrical sensitization effect of (La,Sr)FeO₃(LSFO) nanoparticles over semiconductor Ga₂O₃ nanorods in high temperature gas detection, MRS Fall meeting, Boston, Nov. 2012. (poster)
- 16) P.X. Gao, Scalable 3-D Nanostructure Array Integration: A Nanomaterials Roadmap toward Ultrahigh Efficiency, Robustness, and Multi-functionality, Center for Functional Nanomaterials, Brookhaven National Lab, Upton, Nov. 6, 2012.
- 17) P.X. Gao, 3D Hierarchical Nanostructure Array Integration for Energy and Environmental Applications, nano3D-Kassel 2012 Research Conference, Kassel, Germany, Oct. 18, 2012.
- 18) P.X. Gao, Scalable 3D Nano-Array Integration for Sustainable Energy and Environmental Applications, Institute of Solid State Physics, University of Jena, Jena, Germany, Oct. 17, 2012.
- 19) P.X. Gao, H.J. Lin, and H.Y. Gao, Perovskite Nanoparticle enhanced Nanorod Array based Gas Sensors at High Temperature, EMC meeting, Orlando, Jan. 23, 2013.

7. Other accomplishments

- 1) 4 postdocs and 9 graduate students have been involved in this grant, with 6 of them having graduated with Ph.D. degrees in either Materials Science and Engineering or Chemical Engineering, 3 on-going with Ph.D. study.
- 2) Selected honors and awards of involved graduate students: 1 outstanding graduate student award, MSE program, UConn, 2011; 2 Doctoral Dissertation Fellowship awards, UConn; 1 Outstanding Graduate Scholar Award, Graduate School, UConn, 2009-2012; 3 conference best paper awards, Connecticut Microelectronics and Optoelectronics Consortium (CMOC) symposia; 1 R. J. Stokes student travel Award, 22nd North America Catalysis Meeting, June, 2011.