Final Report for AOARD Grant 10-4056

Silicon Nanotips and Related Nano-systems Involving Fluid and Carrier Transport and their Micro-devices for Power and Sensing Applications

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Abstract:

A number of micro-/nano-devices using arrayed silicon nanotips (SiNTs), ZnO nanorods and related advanced nano-composites as their key components have been developed. These devices possess specific attributes such as architecture- and/or surface/interface-controlled properties. For any targeted functionality, different treatments for the surface or interface are required for best optimizing the resultant physical/chemical properties. On-chip approach to fabricate micro-/nano-fluidic devices involving fluid and carrier transport, such as the electrochemical power and sensing has been employed. Joint project with AFRL and US-based scientists on ionic-liquid fuel injector for space vehicle has been proposed during this period of time and approved recently.

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14. ABSTRACT
This is the report of a project to develop a number of micro-/nano-devices using arrayed silicon nanotips, zinc oxide nanorods, and related advanced nano-composites as their key components.

15. SUBJECT TERMS
Nano-Materials, Fluid Dynamics, Silicon Nano Tips, On-chip Fabrication

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Introduction

Over the last few years, my group has devoted substantial efforts to the development in arrayed Si nanotips (SiNTs), in their bare form for anti-reflection, and their related advanced nano-composites for various applications, such as optoelectronics, sensing and energy. Our emphases have been placed on novel designs using the inherently high surface area and large aspect ratio of the SiNTs. The latter geometric property is unique, which gives rise to tunable and large local field, and thus is advantageous for electric-field driven devices. For instance, a significantly reduced threshold voltage has been demonstrated in the arrayed SiNTs/ZnO light emitting diodes (LED). The high surface area of the SiNTs and, in fact, any arrayed one-dimensional nanostructures resembling the structure of SiNTs, has offered an opportunity in designing high-performance devices controlled by hetero-junctions or surface-dominant properties. For instance, nano-structured system with well-controlled surface structures can give better catalytic activity and subsequent charge (or energy) transfer; by blending electro-/photo-active donor and/or acceptor or making hybrid heterojunctions, one can fabricate high-efficiency electrochemical, optoelectronic or photovoltaic devices. As will be exemplified below, novel designs using the inherently high surface area and large aspect ratio of these nanostructures have shown unique properties and device performance unmatched by their bulk counterparts.

Categorized Summary of Research Outcomes

(1) O_2 plasma-activated CuO-ZnO inverse opals as high-performance methanol microreformer:

We have successfully demonstrated an easy route to fabricate a novel CuO-ZnO catalyst with well-defined inverse opal nanostructure (Figure 1) on the inner surface of microchannels, via direct synthesis, for microreformer applications. The 3-dimensional ordered macro-porous nano-architectures have distinct advantages in terms of enhanced catalytic activities since they posse a high specific surface area as well as enable effective transport of reactant molecules to the active sites. As shown in Figure 2, the CuO-ZnO inverse opal obtained in this study, when operated at a low-reaction temperature of only 230°C, yields complete conversion of methanol, high hydrogen production rate (300 mmol g_{cat}^{-1} h^{-1}), low CO formation (130–170 ppm), and outstanding stability (after

continuous 80 h of operation), making it exceedingly promising toward methanol reforming reaction (MRR). Detailed surface bonding analyses for the CuO-ZnO inverse opal by x-ray photoelectron spectroscopy (XPS), as shown in Figure 3, indicate that the O_2-plasma treatments generate oxygen vacancies (V_o), producing active entities for MRR in the nano-architectures. The present results prove that the catalytic performance of Cu-ZnO catalysts for MRR can indeed be improved through control not only of hierarchical pore-channel networks but also of V_o induced by O_2-plasma treatment. These efforts open up new opportunities in the development of highly active and selective nanoarchitectures for a wide range of different catalytic reaction systems.

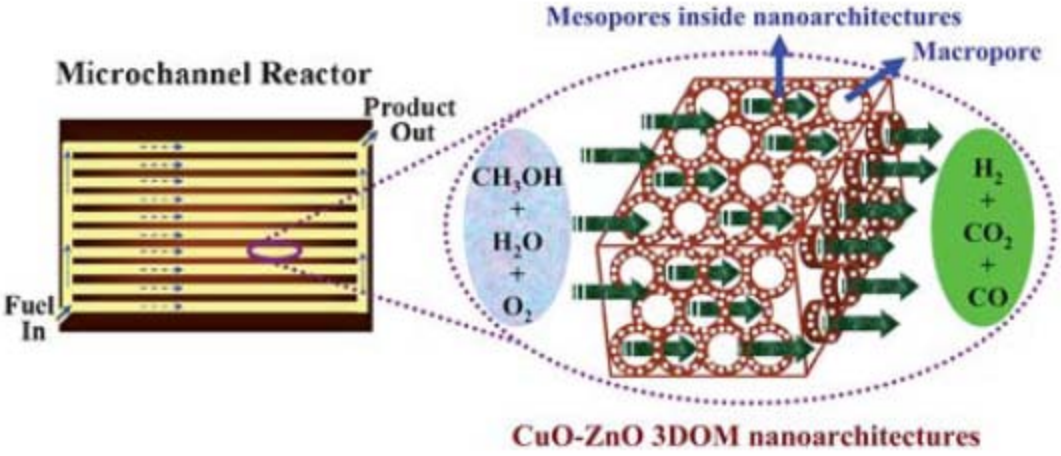

Fig. 1 Schematic diagram of the novel catalyst CuO-ZnO inverse opals fabricated on the inner surface of the microchannel reactor.

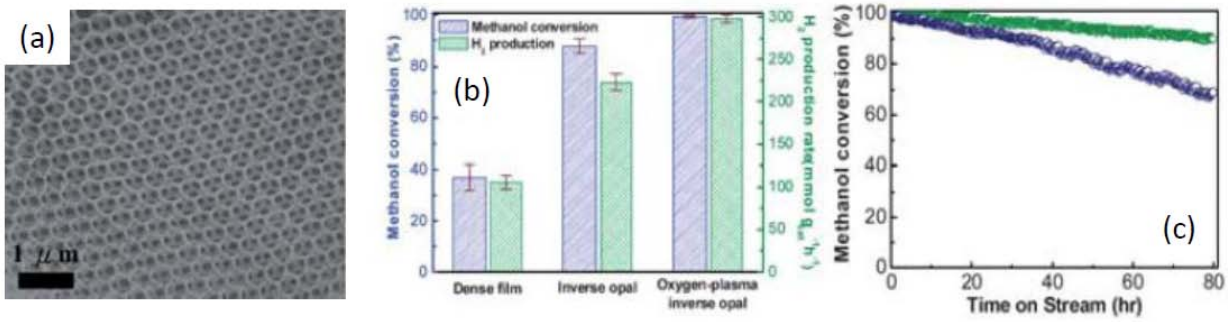

Fig. 2 (a) SEM image of the CuO-ZnO inverse opal. (b) Rates of methanol conversion and H2 production for Cu-ZnO catalysts with dense film, inverse opal, and O2-plasma treated inverse opal nanostructures, respectively. (c) Stability tests of MRR with O2-plasma treated Cu-ZnO inverse opal for plasma exposure time of 10 min (green diamond) and commercial catalysts (blue circle).

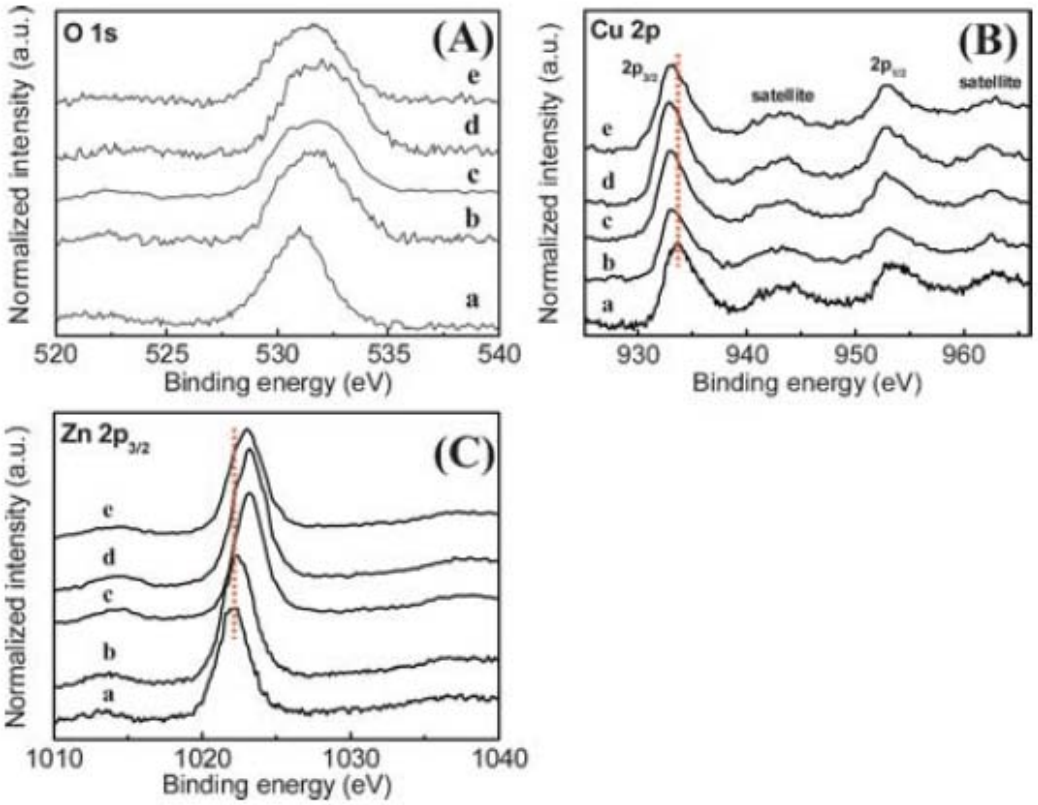

Fig. 3 XPS spectra of (A) O 1s, (B) Cu 2p, and (C) Zn 2p3/2 transitions for CuO-ZnO 3DOM nanoarchitectures after O2-plasma treatment for (a) 0, (b) 3, (c) 5, (d) 10, and (e) 15 min, respectively.

(2) Label free sub-picomole level DNA detection with Ag nanoparticle decorated Au nanotip arrays as surface enhanced Raman spectroscopy platform

Label free optical sensing of adenine and thymine oligonucleotides has been achieved at the sub-picomole level using self assembled silver nanoparticles (AgNPs) decorated gold nanotip (AuNT) arrays. As shown in Figure 4, the platform consisting of the AuNTs not only aids in efficient bio-immobilization, but also packs AgNPs in a three dimensional high surface area workspace, assisting in surface enhanced Raman scattering (SERS). The use of sub-10nm AgNPs with optimum inter-particle distance ensures amplification of the chemically specific Raman signals of the adsorbed adenine, thymine, cytosine and guanine molecules in SERS experiments. High temporal stability of the Raman signals ensured reliable and repeatable DNA detection even after three weeks of ambient desk-top conservation. This facile architecture, being three dimensional and non-lithographic, differs from conventional SERS platform.

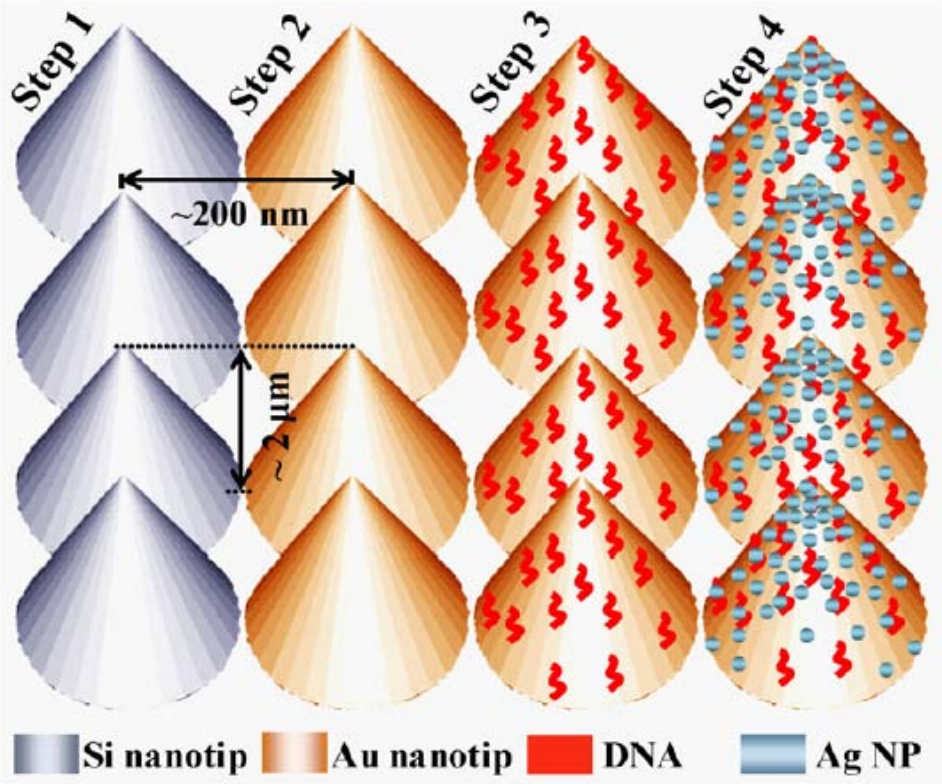

Fig. 4 A schematic of the pathway for generating the SERS platform. Step 1: the as-grown silicon nanotip array template; Step 2: Au coating of the SiNT array to generate the AuNT array for efficient DNA immobilization; Step 3: immobilization of DNA molecules on the AuNT array; Step 4: silver nanoparticle (AgNP) deposition for efficient Raman signal enhancement.

(3) Giant Room Temperature Electric-field-assisted Magnetoresistance in $La_{0.7}Sr_{0.3}MnO_3$/n-Si Nanotips Heterojunctions

An on-chip approach for fabricating heterojunctions of ferromagnetic/semiconductor–nanotips is demonstrated (Figure 5). The high-density array of Si nanotips (SiNTs) is employed as a template for depositing $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) rods with a pulsed-laser deposition method. Compared with the planar LSMO/Si thin film, the heterojunction shows a larger magnetization, a higher Curie temperature (Figure 6), and an enhancement of room temperature magnetoresistance (*MR*) ratio up to 20% under 0.5 T and a bias current of 20 μA. The *MR* ratio is found to be tunable, which increases with increasing external bias and the aspect ratios of the nanotips. Electric-field-induced metallization, in conjunction with nanotip geometry, is proposed to be the origin for the giant *MR* ratio.

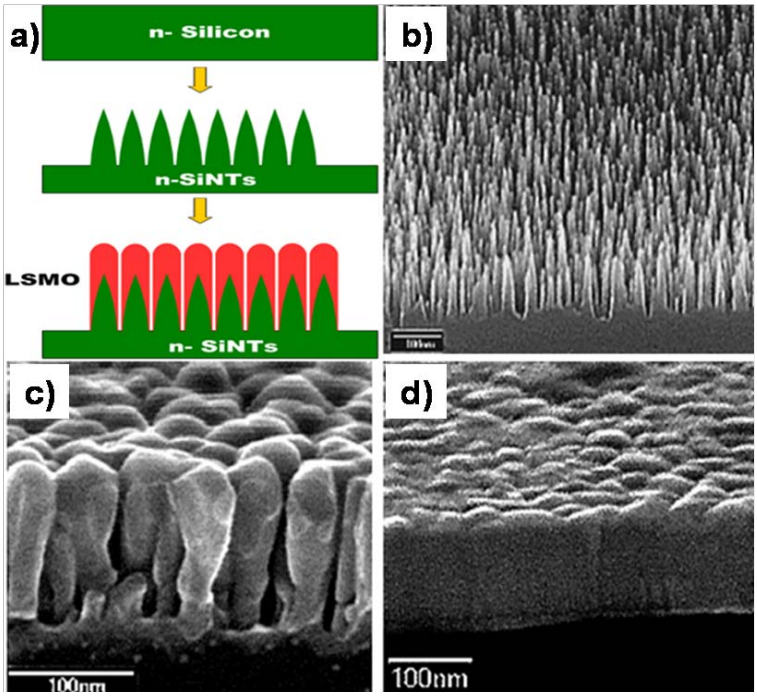

Fig. 5 (a) Schematic drawing of side view structure for the LSMO/SiNTs heterojunction. (b) and (c) are SEM images of Si-NTs and LSMO/SiNTs, respectively. (d) SEM image of LSMO film grown on planar Si wafer.

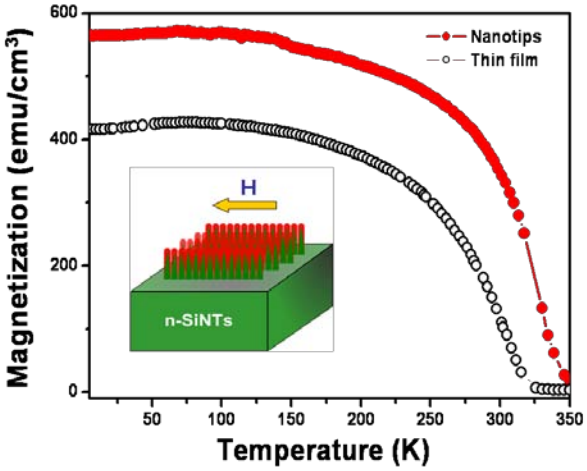

Fig. 6 Magnetizations as a function of temperature under a magnetic field of 100 Oe are shown for the planar LSMO/Si-wafer (open circle in black) and the LSMO/SiNTs array (solid circle in red). The inset presents the measurement configuration, in which the applied magnetic field is in parallel with the sample plane.

List of Publications: Please list any publications, conference presentations, or patents that resulted from this work.

I. Selective Project-related Publications

Overall, 18 papers were published during this project period of time. Financial support from the AFOSR/AOARD has been indicated explicitly in the following 6 papers.

(1) 'Anti-reflecting and Photonic Nanostructures', S. Chattopadhyay*, Y. F. Huang, Y. J. Jen, A. Ganguly, K. H. Chen and L. C. Chen*, an invited review article in A. G. Cullis and S. S. Lau, Eds., *Materials Science and Engineering Review 69*, pp. 1-35, Elsevier, 2010. [Front cover]

(2) 'Correlating Defect Density with Carrier Mobility in Large-Scaled Graphene Films: Raman Spectral Signatures for Estimation of Defect Density', Jeong-Yuan Hwang, Chun-Chiang Kuo, Li-Chyong Chen*, and Kuei-Hsien Chen*, *Nanotechnology 21*, 465705 (2010).

(3) 'O_2 Plasma-activated CuO-ZnO Inverse Opals as High-performance Methanol Microreformer', Yan-Gu Lin, Yu-Kuei Hsu, San-Yuan Chen, Li-Chyong Chen* and Kuei-Hsien Chen*, *J. Mater. Chem.* 20, 10611 (2010).

(4) 'Catalytic Performance of Plate-type Cu/Fe Nanocomposites on ZnO Nanorods for Oxidative Steam Reforming of Methanol', Chien-Cheng Li, Ran-Jin Lin, Hong-Ping Lin, Ching-Chun Chang, Yu-Kai Lin, Li-Chyong Chen*, Kuei-Hsien Chen*, *Chem. Comm. 47*, 1473 (2011).

(5) 'Label Free Sub-picomole Level DNA Detection with Ag Nanoparticle Decorated Au Nanotip Arrays as Surface Enhanced Raman Spectroscopy Platform', Hung-Chun Lo, Hsin-I Hsiung, Surojit Chattopadhyay*, Hsieh-Cheng Han, Chia-Fu Chen*, Jih Perng Leu, Kuei-Hsien Chen and Li-Chyong Chen*, *Biosens. Bioelectron. 26*, 2413 (2011).

(6) 'Giant Room Temperature Electric-field-assisted Magnetoresistance in $La_{0.7}Sr_{0.3}MnO_3$/*n*-Si Nanotips Heterojunctions', C. W. Chong, Daniel Hsu, J. G. Lin*, L. C. Chen*, W. C. Chen, K. H. Chen and Y. F. Chen, *Nanotechnology* 22, 125701 (2011).

II. Selective Project-related Invited Talks at International Conferences

[AFOSR/AOARD has been indicated explicitly in the following presentations.]

(1) International Symposium on Low Carbon and Renewable Energy Technology, ISLCT 2010 (November 15-18, 2010), on *"GaN for photo-electrochemical water splitting"*, Jeju, Korea

(2) IVESC-NanoCarbon 2010 (October 14-16, 2010), on "*On-chip synthesis of graphene, carbon nanotube and related hybrids for electrochemical energy applications"*, Nanjing, China

(3) Asia Pacific Conference of Chemical Engineering Congress, APCChE (October 5-8, 2010), **Keynote Speaker**, on "*Graphene, carbon nanotube and related hybrids for electrochemical energy applications'*, Taipei, Taiwan

(4) SPIE-Optics and Photonics (August 1-5, 2010), Symposium OP202: Solar Energy and Technology, on "*GaN for photo-electrochemical water splitting*", San Diego, USA