Flame Synthesis of Iron Oxide Nanowires for Direct Coal Chemical Looping Combustion, and Tungsten Oxide Nanowires for Enhanced Photoelectrochemical Water Splitting

Link Energy Fellowship Final Report

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2009-2011 Link Energy Fellow

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1. Introduction

High-aspect ratio nanomaterials such as nanowires (NWs) composed of earth abundant metal oxides are technologically important materials for future energy conversion and storage devices. Highly anisotropic materials such as NWs often outperform the commonly used isotropic polycrystalline or particulate films in applications that place complex and multifunctional demands on the materials because NWs contain two different length scales (small diameter, large length) that can be independently tailored to match the characteristic lengths of disparate physical processes. Moreover, arrays of NWs fixed perpendicularly to electrically conductive substrates have further benefits over particulate films since they are better able to exchange current with the substrate, and are resistant to agglomeration.

Despite these advantages, the applications of metal oxide NWs are limited because conventional synthesis methods cannot achieve the scalable, rapid, controllable and economical synthesis of high-quality metal oxide NWs. In the present work, two novel methods for the flame synthesis of metal oxide NWs are developed, and the resulting nanowires tested for two promising, emerging energy conversion technologies: 1) Direct Coal Chemical Looping Combustion, and 2) Photoelectrochemical water-splitting. These synthesis methods are rapid, atmospheric, controllable and scalable, result in highly pure and crystalline materials, and could greatly extend the applicability of metal oxide nanowires to large-scale energy conversion and storage problems.

2. Results

Two novel methods for the flame synthesis of metal oxide NWs and related nanomaterials are developed and investigated. Both methods are rapid (µm/min axial growth rate), atmospheric, controllable and scalable, and result in highly pure and crystalline materials. Simultaneously, these methods allow the growth of metal oxide NWs on diverse, technologically relevant, and often delicate substrates. The first method is flame-heated solid phase diffusion growth, in which a metal substrate is rapidly heated to high temperatures by a flame, and metal oxide NWs grow by metal diffusion out of the substrate in the hot, oxidative post-flame environment (Fig. 1A). The second is flame vapor deposition, in which the flame oxidizes and evaporates metals at high temperatures to produce large concentrations of oxide vapors that condense onto cooler substrates in the form of NWs and other nanostructures (Fig. 1B). In each method, the chemical composition, growth rate and morphology (shape, packing density and alignment) of the nanostructures can be finely controlled by tuning flame parameters such as the fuel/air ratio and temperature, and substrate parameters such as surface energy and temperature. To date, α-Fe_2O_3 and CuO

NWs have been grown by flame-heated solid phase diffusion,[1] while $W_{18}O_{49}$,[2, 3] WO_3,[2, 3] γ-Fe_2O_3,[4] and ZnO NWs, and MoO_3 nanobelts[5] have been grown by flame vapor deposition.
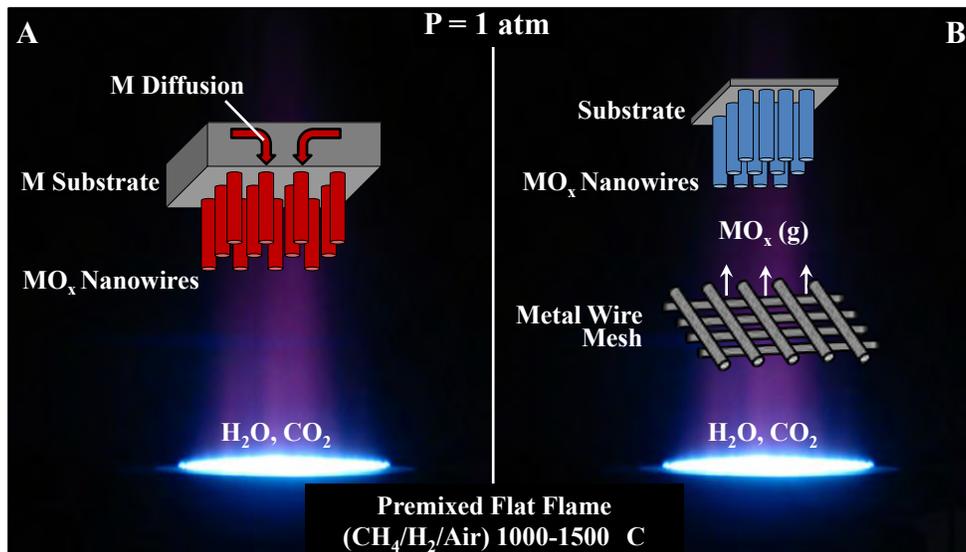

Figure 1. Novel flame synthesis methods for metal oxide nanowires: A) Flame-heated solid phase diffusion, and 2) Flame vapor deposition.

2.1. Results for Direct Coal Chemical Looping Combustion with α-Fe₂O₃ NWs

Direct Coal Chemical Looping Combustion (DC-CLC) allows us to use our abundant coal resources in a way that facilitates the economical sequestration of carbon dioxide. Coal is conventionally combusted in air, and the resulting product stream contains mostly nitrogen, a harmless gas, and very little carbon dioxide. The carbon dioxide can then be captured only at great expense, with the entire stream sequestered, or carbon dioxide separated from nitrogen for sequestration. Instead, in DC-CLC, coal is combusted by reaction with metal oxides, rather than with air, producing a concentrated stream of carbon dioxide that is economical to sequester. The metal oxides, once they have given up their oxygen, are shuttled to an air reactor to be re-oxidized, before being sent back to react with more coal, in a cycle. CLC has been demonstrated for gaseous fuels using a fluidized bed of solid metal oxide particles, but its direct application to solid coal fuel remains a challenge, in large part because of the difficulty in separating the unreacted solid coal from the solid metal oxide particles.

In this work, the fluidized bed was replaced with a fixed bed of flame-synthesized metal oxide (α-Fe₂O₃) NWs[1] to avoid the issue of separation, and provide extremely high surface areas for enhanced reaction rates. To demonstrate the viability of this idea and simulate the DC-CLC process, the α-Fe₂O₃ NWs were subjected to reduction tests in hydrogen gas (Fig. 2A-B-C) and violent mechanical degradation tests by immersion in a fluidized bed of sand (Fig. 2A-D-E). The tests revealed that the NWs are efficient oxygen carriers, being completely reduced to iron, and then completely re-oxidized to α-Fe₂O₃ without any change in morphology. However, during the mechanical degradation tests, a significant fraction of the NWs were fractured by collision with sand particles, resulting in a loss of material, though the NWs could

be regenerated by oxidation. To mitigate mechanical fracture, NWs of increasing thickness and, hence, fracture resistance, were grown by increasing the growth temperature (Fig. 3A-C).[1] It remains to be seen whether these NWs will better survive the fluidized coal environment.
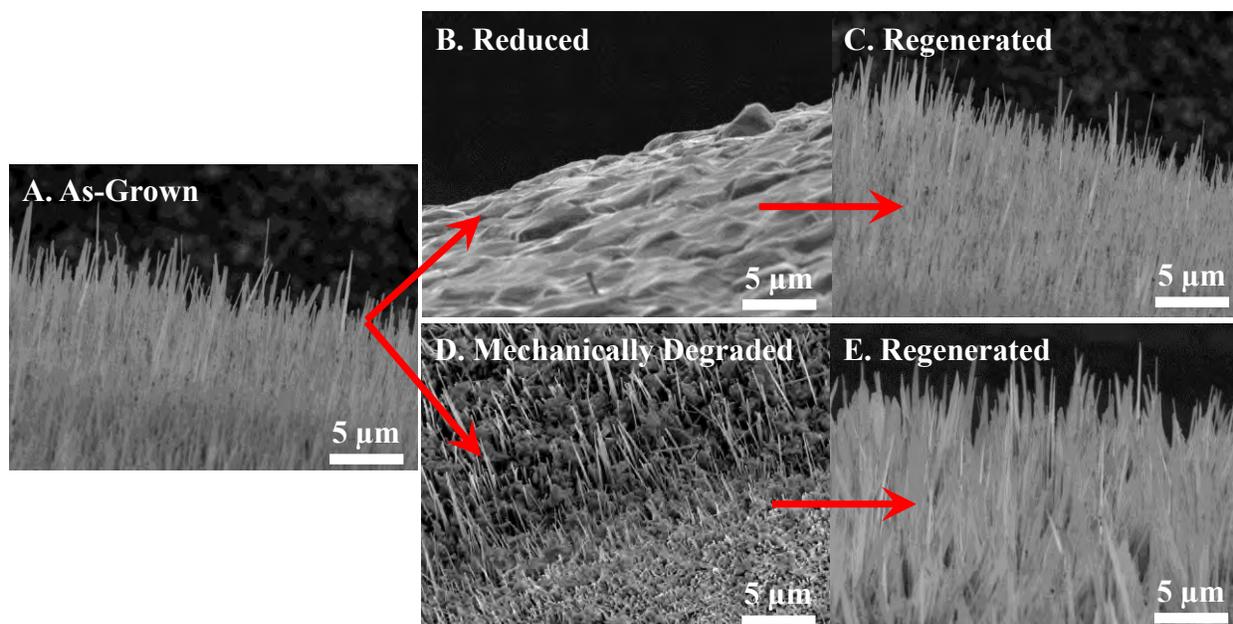

Figure 2. Evolution of morphology of the α-Fe_2O_3 nanowires during simulated DC-CLC, monitored by scanning electron microscopy (SEM): A. as-grown α-Fe_2O_3 nanowires, B. after reduction, C. regenerated after reduction, D. after mechanical degradation, and E. regenerated after mechanical degradation.
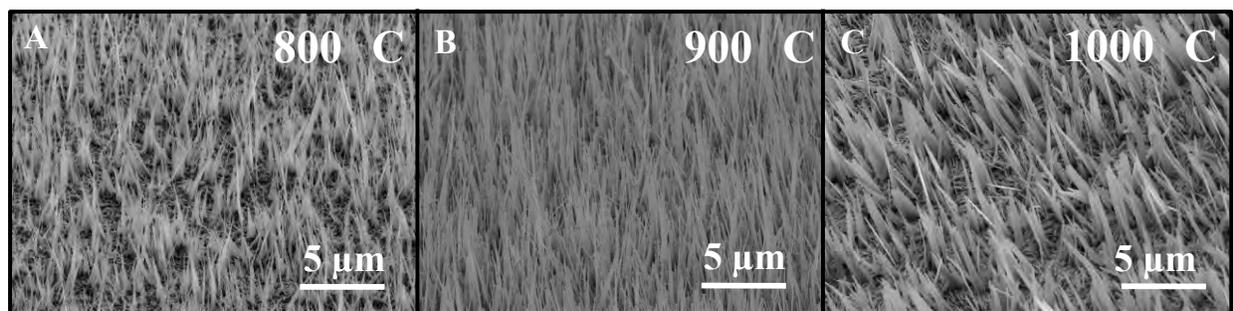

Figure 3. Control of α-Fe_2O_3 nanowire morphology for fracture resistance. Nanowires of increasing thickness and, hence, fracture resistance, are grown with increasing temperature in the range of 800-1000°C (A-C).

2.2 Results for Photoelectrochemical Water-Splitting with WO_3 NWs

Photoelectrochemical (PEC) water-splitting is an economical means for the production of hydrogen from sunlight and water. Hydrogen is an important feedstock for the production of fertilizers and the hydrocracking of petroleum, besides its potential use as an energy carrier. While most of our hydrogen comes from the stream reforming of natural gas, renewable and clean hydrogen production from water using solar energy is an attractive alternative. This is conventionally done through a coupled photovoltaic (PV)-electrolyzer system, but the high costs of such systems has meant that solar hydrogen production

accounts for only 5% of all the hydrogen produced today. PEC water-splitting is cheaper than PV-electrolysis because the functions of light absorption, charge generation and electrochemical reaction are all integrated into a single material that is simply immersed into water to form a fully functioning device (Fig. 4A), resulting in major material and fabrication cost savings. Moreover, if the PEC material is shaped in the form of NWs, the efficiency of hydrogen production can be improved by tuning the length of the NWs to match the light absorption depth of the material, while tuning the diameter to match the charge transport length.

In this work, arrays of WO_3 NWs grown by flame vapor deposition[3] outperformed WO_3 NW arrays grown by conventional methods such as hydrothermal[6] and chemical vapor deposition (CVD)[7] synthesis, for PEC water-splitting. Specifically, the high concentration of tungsten oxide vapors generated in the atmospheric flame allowed the growth of NWs with higher packing density, and correspondingly higher light absorption, than is possible by the other methods. The photocurrent plotted in Fig. 4B for NWs grown by the various methods, is proportional to the water-splitting rate. As seen in the plot, WO_3 NWs grown by flame vapor deposition split water at approximately twice the rate at which the hydrothermal and CVD NWs did, for the same applied bias and incident light intensity of one sun.
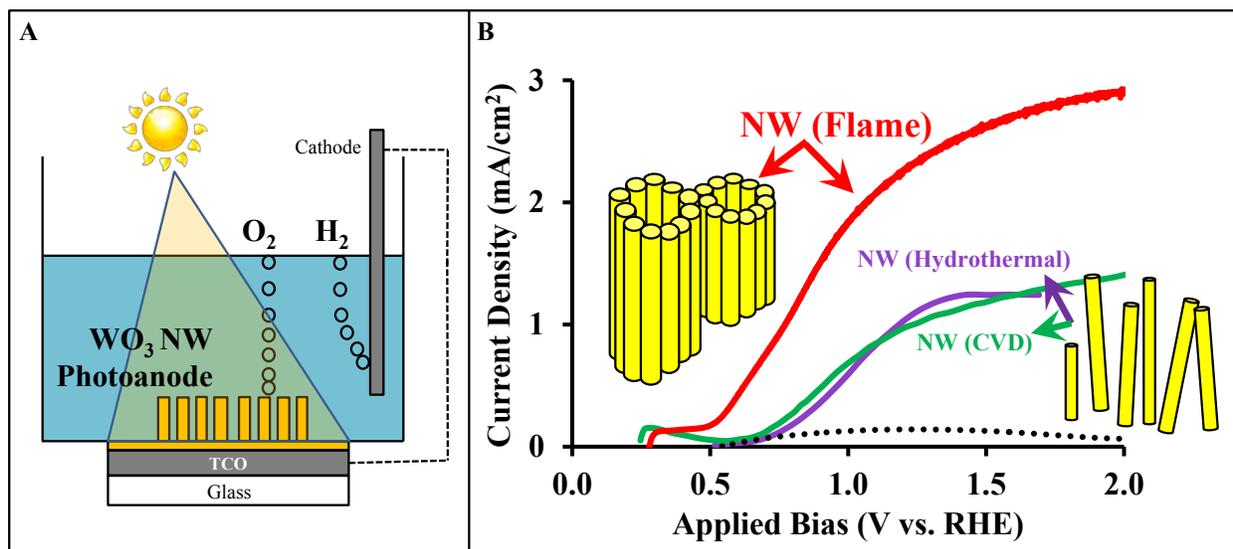

Figure 4. A. Photoelectrochemical (PEC) water-splitting by an array of WO_3 nanowires (NWs). B. PEC water-splitting performance of WO_3 NWs grown by flame vapor deposition, compared to that of those grown by hydrothermal and chemical vapor deposition (CVD) methods. The current density plotted on the y-axis is proportional to the water-splitting reaction rate, and the illumination is one sun.

3. Significance, Impact and Future Directions

The energy challenges facing humanity can only be solved if economically viable alternatives to conventional energy sources and conversion methods are developed. The first technology discussed here, direct coal chemical looping combustion, allows us to use a conventional fuel source while minimizing the damage to our environment in the process. The second technology, PEC water-splitting, may dramatically reduce the environmental cost of important industrial processes and enable the large-scale capture and storage of solar energy at lower cost than today's solar cells, electrolyzers and batteries. The

common innovations in both technologies, and the keys to future energy conversion and storage technologies, are novel materials and synthesis techniques. Material morphology, purity, and crystallinity are inextricably linked to synthesis methods, and the development of economical, rapid, versatile and scalable synthesis methods for high quality materials is of paramount importance. The flame synthesis methods described herein extend our ability to grow highly tailored nanomaterials at large scales, and may play a vital role in enabling the next generation of highly efficient energy conversion and storage materials. The material shape control strategies developed here from a knowledge of fundamental physical and chemical processes will enable increased complexity and versatility in future materials grown by similar methods, and may allow the functionalities of truly earth-abundant materials to be fully exploited.

References

1. Rao, P. M.; Zheng, X. L. Rapid Catalyst-Free Flame Synthesis of Dense, Aligned alpha-Fe_2O_3 Nanoflake and CuO Nanoneedle Arrays. *Nano Lett.* **2009,** 9, (8), 3001-3006.
2. Rao, P. M.; Zheng, X. L. Flame synthesis of tungsten oxide nanostructures on diverse substrates. *P. Combust. Inst.* **2010,** 33, 1891-1898.
3. Rao, P. M.; Cho, I. S.; Zheng, X. Flame Synthesis of WO_3 Nanotubes and Nanowires for Efficient Photoelectrochemical Water-Splitting. *P. Combust. Inst.* **2012,** 34, *in press*.
4. Rao, P. M.; Zheng, X. L. Unique Magnetic Properties of Single Crystal gamma-Fe_2O_3 Nanowires Synthesized by Flame Vapor Deposition. *Nano Lett.* **2011,** 11, (6), 2390–2395.
5. Cai, L. L.; Rao, P. M.; Zheng, X. L. Morphology-Controlled Flame Synthesis of Single, Branched, and Flower-like alpha-MoO_3 Nanobelt Arrays. *Nano Lett.* **2011,** 11, (2), 872-877.
6. Su, J.; Feng, X.; Sloppy, J. D.; Guo, L.; Grimes, C. A. Vertically Aligned WO_3 Nanowire Arrays Grown Directly on Transparent Conducting Oxide Coated Glass: Synthesis and Photoelectrochemical Properties. *Nano Lett.* **2011,** 11, (1), 203-208.
7. Chakrapani, V.; Thangala, J.; Sunkara, M. K. WO_3 and W_2N nanowire arrays for photoelectrochemical hydrogen production. *Int. J. Hydrogen Energy* **2009,** 34, (22), 9050-9059.

9. Kim, D. R.; Lee, C. H.; Rao, P. M.; Cho, I. S.; Zheng, X. Hybrid Si Microwire and Planar Solar Cells: Passivation and Characterization. *Nano Lett.* **2011,** 11, (7), 2704-2708.

10. Feng, Y. Z.; Cho, I. S.; Rao, P. M.; Cai, L. L.; Zheng, X. Sol-Flame Synthesis: A General Strategy To Decorate Nanowires with Metal Oxide/Noble Metal Nanoparticles. *Nano Lett.* **2012**.

11. Rao, P. M.; Cho, I. S.; Zheng, X. Flame Synthesis of WO_3 Nanotubes and Nanowires for Efficient Photoelectrochemical Water-Splitting. *P. Combust. Inst.* **2012,** 34, *in press*.

12. Feng, Y. Z.; Cho, I. S.; Cai, L. L.; Rao, P. M.; Zheng, X. Sol-Flame Synthesis of Hybrid Metal Oxide Nanowires. *P. Combust. Inst.* **2012,** 34, *in press*.

13. Cai, L. L.; Rao, P. M.; Feng, Y. Z.; Zheng, X. Flame Synthesis of 1-D Complex Metal Oxide Nanomaterials. *P. Combust. Inst.* **2012,** 34, *in press*.

Report on Utilization of Discretionary Funds

The fellow is an active participant in the meetings of the scientific societies of the materials and combustion research communities. As such, the fellow used the discretionary funds for travel to and from the semiannual Materials Research Society (MRS) meetings, and the biennial International Symposium on Combustion. The support of the Link Foundation Energy Fellowship was acknowledged in each of these presentations.

Impact of the Fellowship on the Fellow's Academic and Professional Development

In applying for the Link Foundation Energy Fellowship, I thought about new energy ideas that were both innovative and impactful. This search brought into sharp focus the energy problems we face as a society, and the daunting challenge of supplying energy to an ever-growing, ever more energy-hungry population. At the same time, I was overwhelmed and encouraged by the diversity and number of possible energy solutions being researched around the world. Winning the Fellowship solidified my growing commitment to working on environmentally friendly energy supply, turning it into what I am sure will be a lifelong passion and mission. Moreover, I expect that the prestige of the Fellowship will have a lasting impact on my opportunities for professional development.