Final Technical Report

Project Title: Sub-Nanostructured Non-Transition Metal Complex Grids For Hydrogen Storage

Project Period: January 20, 2004 to July 31, 2007

Date of Report: October 27, 2007

Recipient: Cleveland State University

Award Number: DE-FC36-04ER14007

Working Partners: Cleveland State University
Carnegie Mellon University

Cost-Sharing Partners: Cleveland State University

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Executive Summary:

This project involved growing sub-nanostructured metal grids to increase dynamic hydrogen storage capacity of metal hydride systems. The nano particles of any material have unique properties unlike its bulk form. Nano-structuring metal hydride materials can result in:

- ⇨ Increased hydrogen molecule dissociation rate,
- ⇨ Increased hydrogen atom transport rate,
- ⇨ Decreased decrepitation caused by cycling,
- ⇨ Increased energy transfer in the metal matrix,
- ⇨ Possible additional contribution by physical adsorption, and
- ⇨ Possible additional contribution by quantum effects

The project succeeded in making nano-structured palladium using electrochemical growth in templates including zeolites, mesoporous silica, polycarbonate films and anodized alumina. Other metals were used to fine-tune the synthesis procedures. Palladium was chosen to demonstrate the effects of nano-structuring since its bulk hydrogen storage capacity and kinetics are well known. Reduced project funding was not sufficient for complete characterization of these materials for hydrogen storage application. The project team intends to seek further funding in the future to complete the characterization of these materials for hydrogen storage.

Comparison of Accomplishments with Goals:

Following list of milestones are taken from the "Summary of Technical Project Kick-Off Meeting" held between project team and DOE officials before the project start. Milestones up to 4 in the 2nd year of the project were met in this effort. There is still some work that needs to be performed to complete characterization of the hydrogen storage characteristics of nano-structured metal grids. Remaining milestones were not met (were not attempted) as the project received only reduced funding during 2nd year and no additional funding afterwards.

Milestones:

Year 1:

Milestone 1: Fabrication of cathode with layered zeolite where only pathway for cations to reach cathode surface is through zeolite crystal micropores

Milestone 2: Proof of pure metal sub-nanostructured grid growth in the zeolite layer by standard characterization techniques (i.e. HRTEM, SEM, EDAX, STEM AFM/STM, etc) before zeolite removal

Year 2:

Milestone 3: Demonstrate zeolite removal process does not damage the grid

Milestone 4: Improved equilibrium and/or kinetic hydrogen storage characteristics of a pure metal sub-nanostructured grid with after zeolite removal as compared to the bulk pure metal.

(The project accomplished up to this point.)

Milestone 5: Proof of mixed metal complex sub-nanostructured grid growth in the zeolite layer by standard characterization techniques (i.e. HRTEM, SEM, EDAX, STEM AFM/STM, etc) before zeolite removal

Year 3:

Milestone 6: Improved equilibrium and/or kinetic hydrogen storage characteristics of mixed metal complex sub-nanostructured grid after zeolite removal as compared to bulk mixed metal complex

Milestone 7: Demonstrate metal alloy sub-nanostructured grid has durability with limited (10-20) cycles of hydrogenation/dehydrogenation

Milestone 8: Estimate scale-up potential of the zeolite-electrochemical technique based on lab-scale experiments.

Summary of Project Activities:

Background

A major problem with metal hydride systems is the slow kinetics of hydrogen uptake/release due to two reasons; 1) intrinsic reaction rate of the hydrogen molecule dissociation on the external surface of the metal, and 2) slow diffusion of atomic hydrogen in the dense metal phase. In this project, we grew nanostructured metal grids with about 50% porosity. This is expected to increase the overall hydrogen dissociation reaction rate (since the external metal surface area is greatly increased), and decrease the diffusion time constants (since the diffusion path is greatly reduced). In addition, the high mass transfer rates through the pores and hydrogen dissociation dispersed throughout the metal is expected to enhance the energy transfer characteristics. The flexibility of such a grid is expected to lower decrepitation caused by cycling. Hydrogen storage capacity may also increase due to contributions by physical adsorption and through possible quantum effects.

Technical Approach:

The approach in this project to produce nanoporous metals can be simply summarized in three steps:

1. Coat a cathode with nanoporous materials to act as template,
2. Employ electrochemical deposition of metal cations in the pores to grow -nanostructured metal grids,
3. Dissolve the template, leaving the metal grid only.

The resulting nano-structured materials were to be characterized extensively by microscopy (optical, SEM, HTEM), chemical analysis (EDAX), and surface area analysis and by hydrogen uptake capacity and rate measurements.

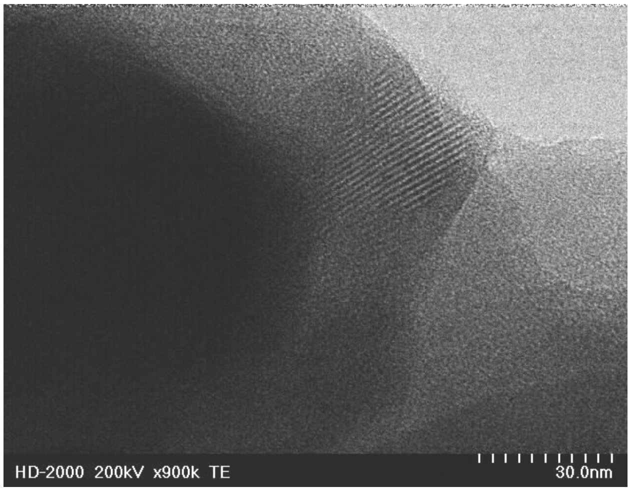
Accomplishments

The cathode must be completely covered with the nanoporous template to allow metal ion transport only through the pores to achieve the main goal of this project. Cathode preparation is the single most challenging task. Initially zeolites were used as nanoporous templates then moving on to mesoporous silica, polycarbonate films and anodized alumina. Initially common metals such as copper and nickel were used to tune the electrochemical deposition process, later palladium was used to show the effect of nanostructuring since bulk palladium hydrogen uptake capacity and kinetics is well known. Several techniques were proposed/tried to make a cathode completely covered with nanoporous template. These techniques can be categorized into three main approaches:

1. Physical compaction of nanoporous materials on cathode conductors,
2. In-situ growth of nanoporous materials on cathode conductors, and
3. Coating a cathode conductor layer on a nanoporous membrane.

In each case, nanostructured metals were electrochemically grown in the porous structure under carefully controlled conditions (temperature, electrolyte composition, current density, polarity, etc.). The resulting materials were initially characterized by microscopy (optical, SEM, HTEM) and elemental analysis (EDAX) without removal of the template. Later in the project, the template material was removed using appropriate solution chemistry (mostly high pH alkaline solutions) to yield the nanostructured metal phase only.

Physical compaction involved coating metal conductors (wire mesh, solid and sintered metal plates) with hydrothermal synthesized nanoporous templates (zeolites faujisite and silicalite and mesoporous silica) in a high-pressure press sometimes using a binder material (such as bentonite). Electrodeposited particles showed nano-phase growth in the nanoporous template. Two examples for faujisite and mesoporous silica are shown in Figure 1. Physical compaction approach was abandoned after two quarters due to the problems of delamination of the template layer off the cathode surface during electrodeposition and undesirable deposition of large size (mm size) metal in the macropores. Nevertheless, the existence of the nano-phase confirmed that electrochemical growth is feasible if an "acceptable" cathode can be prepared.



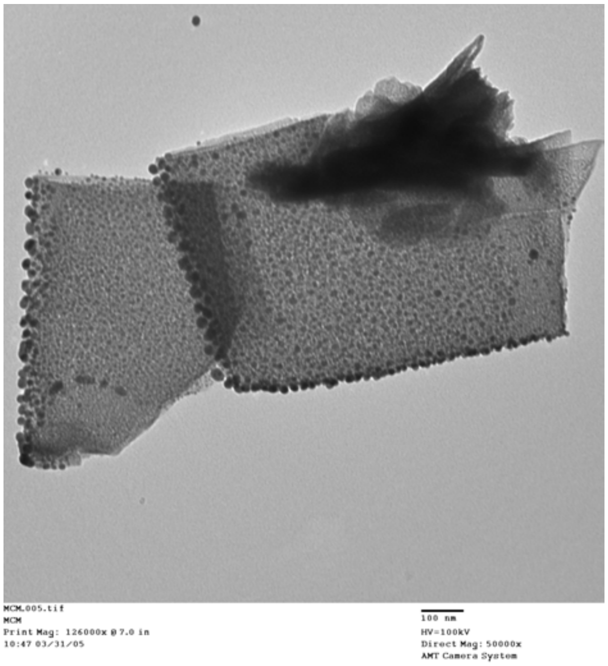


Figure 1. Metal nanophase grown in faujisite (left) and mesoporous silica (right) with physically compacted cathode

Considerable effort was devoted to the second approach; in-situ growth of nanoporous templates on cathode plates. In particular, faujisite, silicalite and mesoporous silica were grown in-situ over stainless steel, sintered copper and anodized titanium conductors. It was necessary to treat the metallic surfaces before in-situ growth to increase the adhesion of the nanoporous templates. This pre-treatment essentially formed a metal-oxide layer to promote adhesion without completely eliminating the metallic cathode surface necessary for charge transfer during the electrochemical growth. Electrodeposition of metals was then performed in the pores of these coated cathodes. This approach completely circumvented the two problems encountered before; template delamination and undesirable macro metal particle growth. The nano-phase formation was confirmed with HTEM (see Figure 2) and with EDAX analysis. Unfortunately despite our efforts, the thickness of the in-situ growth layer was very small (1-10 μm) which prevented the synthesis of nano metals in any substantial quantity.

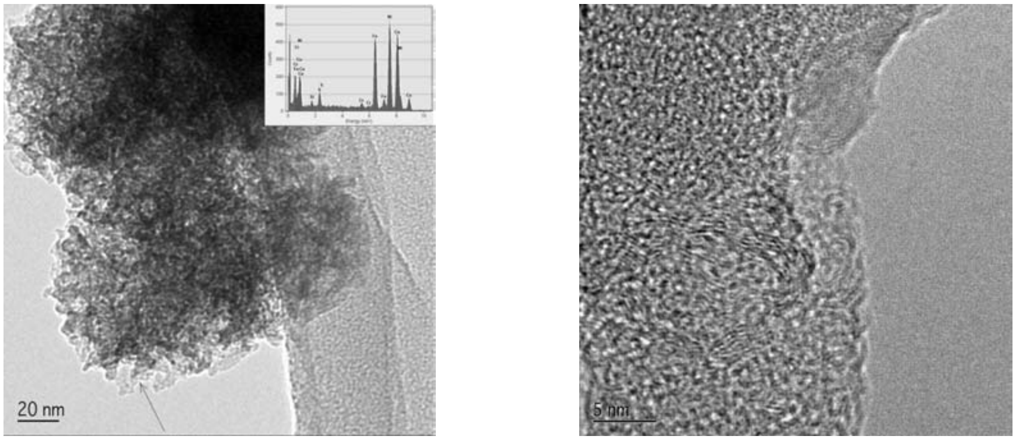


Figure 2. Nano metal grown with templates grown in-situ over cathode conductors

The final approach proved to be most productive for nano-phase electrochemical metal growth. In this approach, a nanoporous material already in a membrane form is made into a cathode by coating an electrically conducting layer on one side. Two types of membranes were utilized; 1) track-etched polycarbonate films (PCF), and 2) anodized alumina (AA).

The PCF membranes were used to perfect the electrodeposition conditions since they are readily available with various pore sizes from 15 nm to 100,000 nm. We utilized 15 to 1,000 nm range in our experiments. One such nano-metal growth with 100 nm characteristic diameter is shown in Figure 3 as an example. Although PCF membranes were very useful to tune electrodeposition conditions at nano scale, once again they suffer from limited yield since the pore density is low.

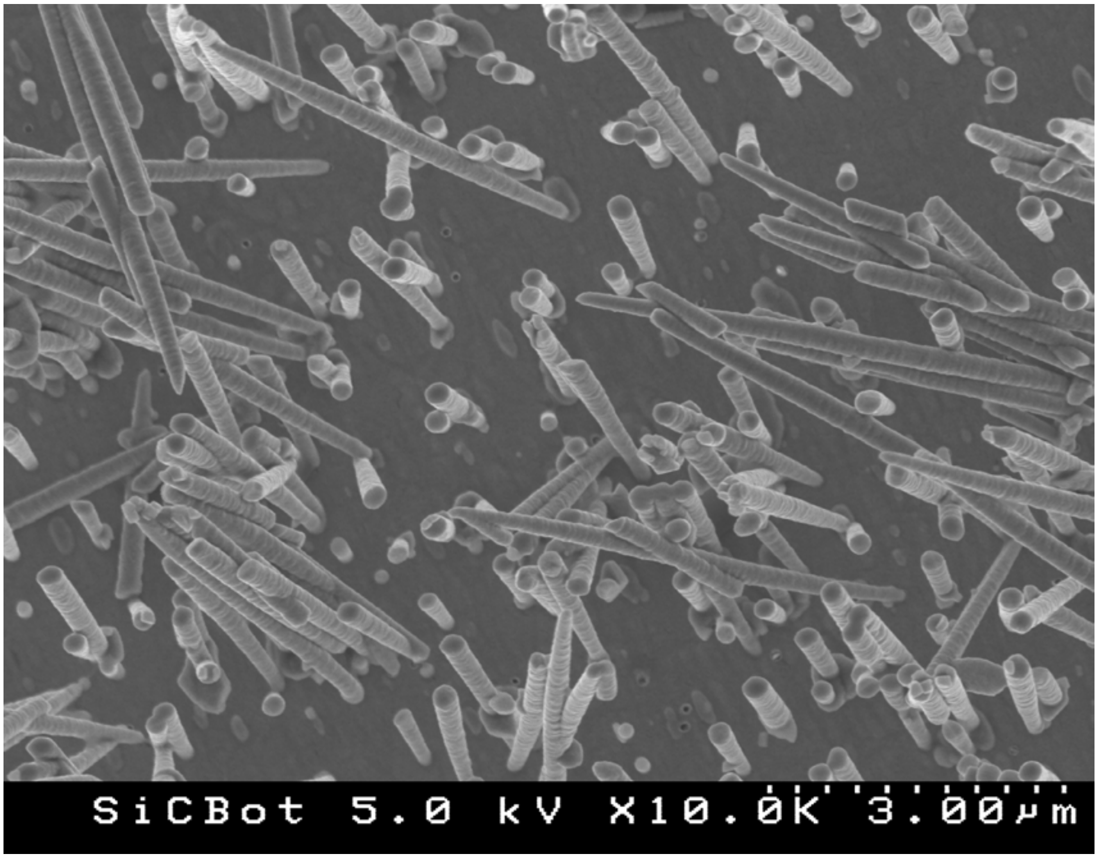


Figure 3. Metal nano-cylinders grown in track-etched polycarbonate films

Anodized alumina is prepared by etching aluminum plates at high voltage, which produces very high-density parallel pore structure on the surface. Anodization is followed by removal of any metallic phase left under the porous structure and opening of pore bottoms. These membranes are commercially available as Anodisc® (see Figure 4).

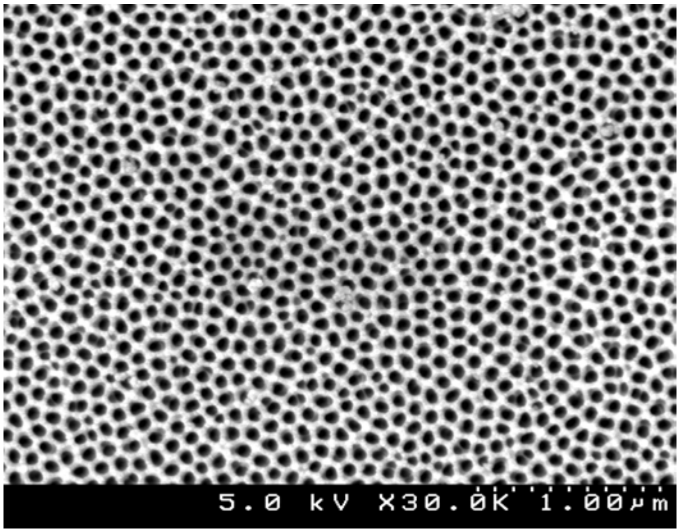


Figure 4. Commercial anodized alumina (Anodisc®) membrane with 200 nm pores

The pore diameter of commercial membranes is about 200 nanometer somewhat larger than the desired size. Also, the commercial membranes have some irregularity in their structure with pore splitting and/or convergence which is not the ideal conditions for electrochemical nanoporous metal growth. We have synthesized anodized alumina membranes in our labs to overcome these problems. The pore size is controlled between 20-200 nm and the pores are completely straight in our membranes which are later used for electrochemical metal growth. Figure 5 compares the crossections of commercial and lab synthesized anodized alumina membranes.

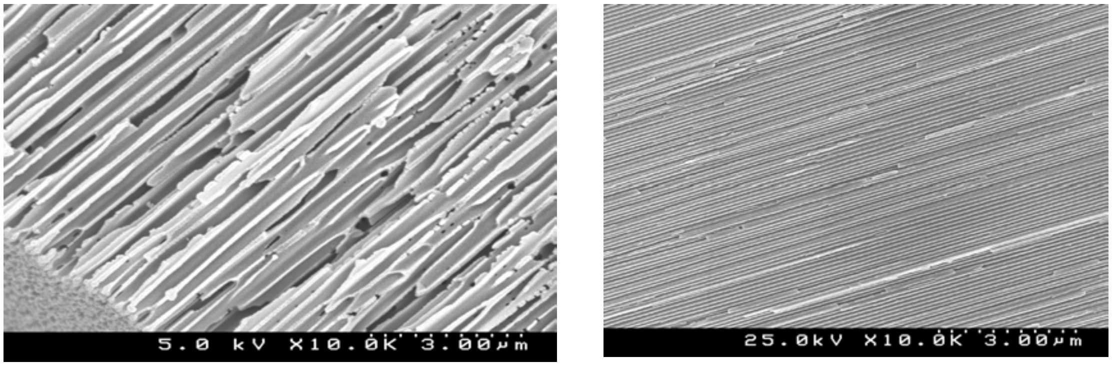


Figure 5. Anodized alumina templates for nanoporous metal growth: left-commercial Anodisc®, right-lab synthesized

The anodized alumina membranes are “glued” on conductor cathode plates using silver paint to enable metal electrodeposition. The alumina is then removed with high pH alkaline solution after the nano-porous metal is grown. The anodized alumina membranes have a very high pore density thus resulting in a dense metal nano-phase. Examples for 200 nm palladium are shown in Figure 6.

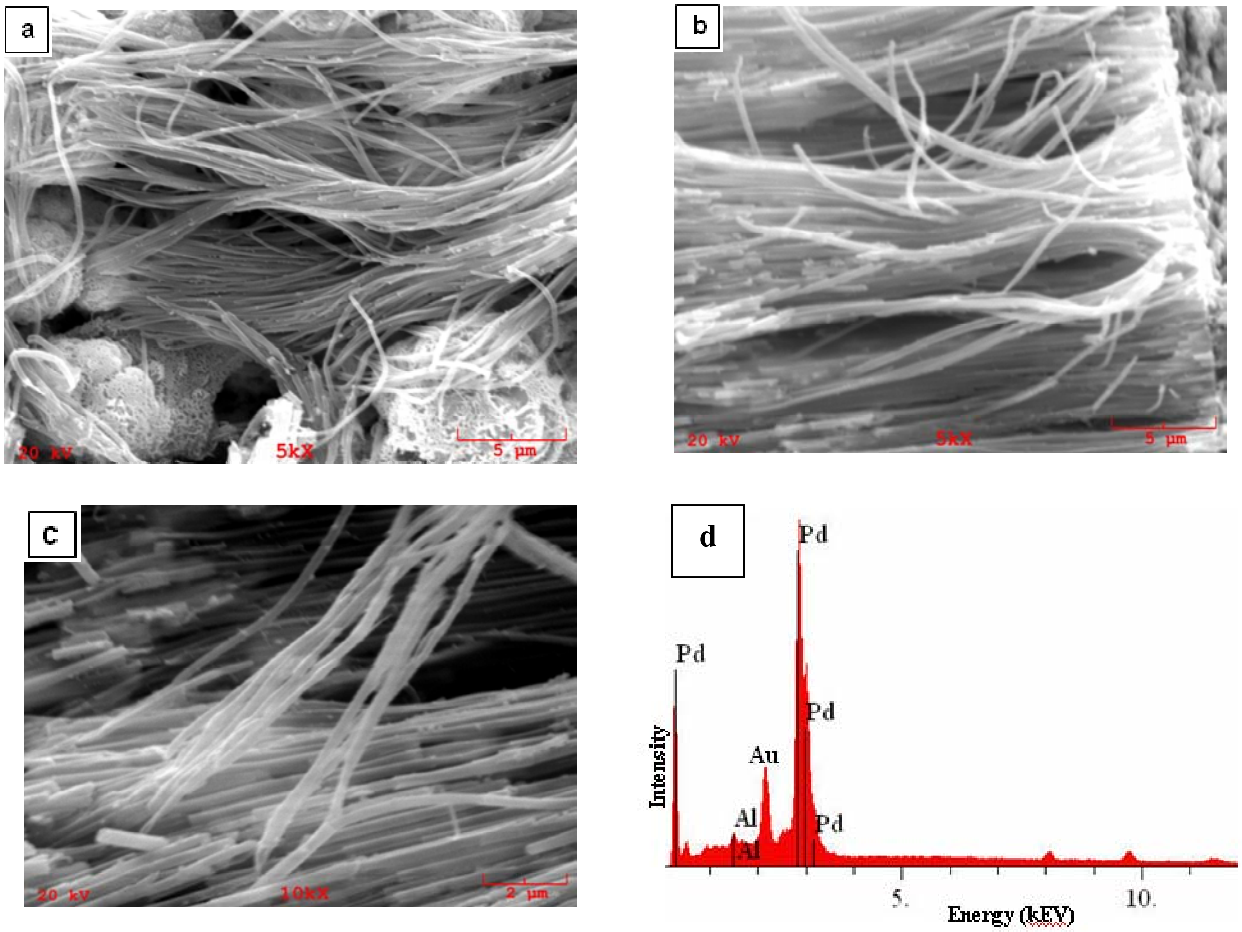


Figure 6. 200 nm nanoporous palladium grown in anodized alumina. a) Partially removed alumina is visible as particles, b) the structure is held together by van der Waals forces and slight over-growth on the top (right) of the membrane even after complete removal of alumina template, c) self-standing strands of palladium fibers, d) EDAX analysis of palladium fibers after treatment shows mainly palladium, some gold (sputtered for imaging) and very small amount of residual aluminum, no other elements are observed.

As might be noticed in Figure 6, the electrodeposition conditions have been optimized completely for palladium growth which was the first metal to be evaluated for the effect of nanostructuring on hydrogen storage. Palladium is the ideal candidate to demonstrate effect of nano structuring of metals for hydrogen storage application since its hydrogen storage capacity and kinetics is well established as a bulk material. We now can produce gram quantities of palladium nano-wire bundles (20-200 nm diameter) for hydrogen storage evaluation. Unfortunately, we do not have the resources to completely characterize the hydrogen storage performance as initially planned since we received about half of the funding requested in the proposal. Most of this work was performed in the no-cost extension periods of this project over the past 18 months, as DOE did not provide any new funds since fiscal year 2006. We intend to seek further funding to complete the hydrogen storage characterization.

Products Developed:

No commercial products or patents resulted from this project. The project progress was reported to DOE in regular quarterly and yearly reports at annual review meetings. In addition, the project was presented to USCAR hydrogen tech storage team. Thus, all the general deliverables have been delivered.

There were seven presentations in national and international meetings where DOE was acknowledged as a financial sponsor. We intend to publish some of the findings in journals in the near future with due acknowledgement of DOE sponsorship. We do not foresee any patent applications based on the findings in this project. The presentations to date are:

1. Asli Ertan and Orhan Talu, “Hydrogen Storage Equilibrium and Kinetics of Palladium Nanowires Grown in Anodized Alumina,” AIChE Annual Meeting, Salt Lake City, Utah, November 2007

2. Aniket Sonalkar and Orhan Talu, “Permeation in Mesoporous Silica-Anodized Alumina Composite Membranes,” AIChE Annual Meeting, Salt Lake City, Utah, November 2007

3. Orhan Talu, “KEYNOTE LECTURE: Adsorptive Storage,” 9th Int. Conf. On Fundamentals of Adsorption, Giardini Naxos, Italy, May 2007

4. Asli Ertan, Surendra N. Tewari and Orhan Talu, “Different Methods for Mesoporous Silica Synthesis and Their Effects on Surface Properties,” AIChE Annual Meeting, Cincinnati, Ohio, October 2005

5. Pradeep Kodumuri, Orhan Talu and Surendra N. Tewari, “In-Situ Growth of Zeolites and Mesoporous Silica on Metal Substrates,” AIChE Annual Meeting, Cincinnati, Ohio, October 2005

6. Chandrashekhar Pendyala, Surendra N. Tewari and Orhan Talu, “Study of Growth Mechanisms of Metallic Nanowire Arrays in Porous Substrates,” AIChE Annual Meeting, Cincinnati, Ohio, October 2005

7. Orhan Talu, “Sub-Nanostructured Non-Transition Metal Complex Grids for Hydrogen Storage,” DOE Hydrogen Program Review, Washington, D.C., May 2005