

FINAL PROJECT REPORT

Richard M. Crooks

11 April, 2007

Project Title: From First Principles Design to Realization of Bimetallic Catalysts for Ultrahigh Selectivity

Sub-Project Title: Synthesis and Characterization of Dendrimer-Encapsulated Bimetallic Catalysts

Award No.: DE-FG02-05ER15683

Principal Investigator: Richard M. Crooks
Department of Chemistry and Biochemistry
The University of Texas at Austin
1 University Station, A5300
Austin, TX 78712-0165
Ph. 512-475-8674, Fx. 512-475-8651, e-mail: crooks@cm.utexas.edu

Students supported: Orla M. Wilson
Heechang Ye
Ye Hu

Postdocs supported: Robert W. J. Scott

Collaborators: Jinguang G. Chen & Douglas J. Buttrey (Univ. of Delaware)
Anatoly Frenkel (NSLS)
Ian M. Anderson (Oak Ridge National Laboratory)

Project Dates: 09/15/2005 – 09/14/2006

Report Dates: 09/15/2003 – 9/14/2006

3-year Budget: \$306,450

Objectives

Overall Research Objectives. The overall objective of this project was to synthesize and characterize structurally well-defined, bimetallic catalysts. These materials, which we call dendrimer-encapsulated nanoparticles (DENs) are synthesized within dendrimer templates by coordination of metal ions to the interior tertiary amines of the dendrimer, followed by reduction. This approach yields monometallic and bimetallic nanoparticles that have a high degree of uniformity in size, structure, and composition.

Specific Objectives. The specific objectives of this project are to evaluate the homogeneous and heterogeneous catalytic activity of bimetallic nanoparticles prepared by the dendrimer templating approach. We are particularly interested in the effect of nanoparticle size, composition, and structure on catalytic rates and product distributions.

Important Note. This grant was transferred from Texas A&M University to The University of Texas in Austin at the end of the second year of the three-year term. The original grant number was DE-FG02-03ER15471. This final reports includes accomplishments, publications, and presentations during the entire three year period of DE-FG02-03ER15471 and DE-FG02-05ER15683.

Brief Summary of Accomplishments

(A) Synthesis, Characterization, and Fundamental Properties of Bimetallic DENs. AuAg alloy and core/shell bimetallic DENs were synthesized and characterized. Selective extraction was used as a structural characterization tool for these bimetallic nanoparticles. This is significant because there are few easily accessible methods for structure elucidation of bimetallic nanoparticles in this size regime. As a first step towards the synthesis of catalytically active, bimetallic heterogeneous materials we reported the incorporation of Au and Pd monometallic DENs and AuPd bimetallic DENs into amorphous titania networks. The compositional fidelity of the original DENs, and to some extent their size, is retained following dendrimer removal. Gas-phase catalytic activity for CO oxidation is higher for the bimetallic catalysts than for the corresponding Pd-only and Au-only monometallics.

(B) Electrocatalysts based on dendrimer-encapsulated nanoparticles. Platinum dendrimer-encapsulated nanoparticles (DENs) were prepared within fourth-generation, hydroxyl-terminated, poly(amidoamine) dendrimers and immobilized on glassy carbon electrodes using an electrochemical immobilization strategy. X-ray photoelectron spectroscopy, electron microscopy, and electrochemical experiments confirm that the Pt DENs are about 1.4 nm in diameter and that they remain within the dendrimer following surface immobilization. The resulting Pt DEN films were electrocatalytically active for the oxygen reduction reaction (ORR). The films are also robust, surviving up to 50 consecutive cyclic voltammograms and sonication. Monometallic Pd DENs were also prepared and found to have little catalytic activity for the ORR. However, PtPd bimetallic DENs had catalytic activity nearly identical to that found for Pt-only DENs. This indicates an overall catalytic enhancement for the bimetallic electrocatalysts.

Potential Impact

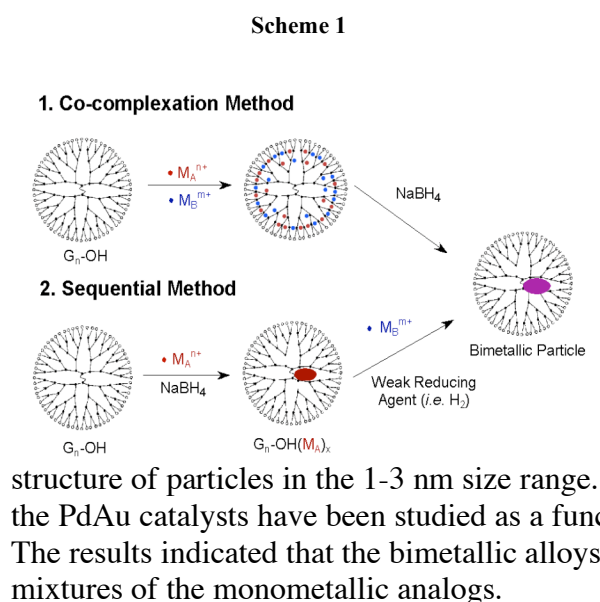
The field of catalysis is central to the DOE mission. In this research we are addressing two specific aspects of catalysis science. First, we are developing new methods for the synthesis and characterization of bimetallic catalysts that are monodisperse in size, composition, and structures. Second, we are testing these materials for their catalytic efficiency. A specific example is the PtPd electrocatalysts described in this report. These materials have direct applications to fuel cell technologies.

Detailed Summary of Accomplishments

(A) Synthesis, Characterization, and Fundamental Properties of Bimetallic DENs.

Dendrimer-encapsulated nanoparticles (DENs) are synthesized within dendrimer templates by coordination of metal ions to the interior tertiary amines of the dendrimer, followed by reduction. This approach yields monometallic and bimetallic nanoparticles with unprecedented uniformity in size, structure, and composition. In this project we have focused on the catalytic properties of these materials, and specifically on correlating these properties to the atomic composition of nanoparticles in the 1.0 - 2.5 nm diameter range.

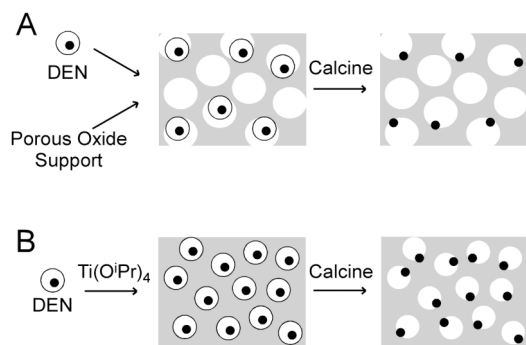
We have synthesized alloy and core/shell DENs using the two approaches illustrated in Scheme 1. The co-complexation method, which we have used to prepare PdPt, PdAu, and AuAg bimetallic DENs, leads to random alloys. The second approach, which we call the sequential method, leads to core/shell nanoparticles. We



We have used this method to prepare [Au](Pd) and [Pd](Au) DENs (brackets indicate the core metal and parentheses indicate the shell metal). More recently, we used the same strategy to synthesize [Au](Ag) and [AuAg](Au) core/shell DENs. All of these materials have been characterized by UV-vis spectroscopy, TEM, single-particle EDS, elemental analysis, and XPS. In addition, we have developed a new analytical method for determining the structure of core/shell DENs.

This is an important development, because there are very few analytical tools for assessing the structure of particles in the 1-3 nm size range. Finally, the hydrogenation of allyl alcohol using the PdAu catalysts have been studied as a function of the elemental composition of the DENs. The results indicated that the bimetallic alloys were substantially more active than corresponding mixtures of the monometallic analogs.

As a first step towards the synthesis of catalytically active, bimetallic heterogeneous materials we recently reported the incorporation of Au and Pd monometallic DENs and AuPd bimetallic alloy DENs into amorphous titania networks. For the monometallic catalysts, two approaches



Scheme 2

were investigated. First, preformed Au DENs were deposited onto commercial solid-oxide supports via wetness impregnation (Scheme 2A). While this is the usual method for preparing heterogeneous catalysts incorporating bimetallic nanoparticles, the resulting nanoparticles are rarely monodisperse in size or composition and often consist of a mixture of monometallic and bimetallic nanoparticles. Such materials are less than ideal candidates for fundamental studies that attempt to correlate catalyst structure and function. Our second approach involved the incorporation of Au and Pd DENs into an

amorphous titania network prepared using sol-gel chemistry (Scheme 2B). Addition of titanium isopropoxide to methanolic solutions of Au and Pd DENs, and the subsequent hydrolysis and condensation of the alkoxide precursor results in the DEN incorporation. The latter approach is especially interesting, because in this case both the inside and the outside of the dendrimer act as templates: the exterior of the dendrimer templates pores within the sol-gel matrix, and the interior templates the metal nanoparticles. In both cases, the dendrimer could be removed by calcination to leave behind just the metal nanoparticles. While the wetness impregnation method led to a four-fold increase in the average Au nanoparticle size following calcination at 500 °C, the size increase with the sol-gel method was only 40%. However, a further increase in the calcination temperature to 550 °C to ensure complete removal of the dendrimer led to the particle size increasing from 2.7 ± 0.6 nm to 4.4 ± 0.8 nm. After calcination at 500 °C the average size of the titania/Pd DEN composite was 3.0 ± 0.6 nm. We believe that the post-calcination sizes are likely biased towards larger particle sizes due to the poor electron-density contrast between the nanoparticles and the underlying titania support. Nevertheless, the Pd nanoparticles agglomerate less than the corresponding Au nanoparticles after removal of the dendrimer (4.4 ± 0.8 and 3.0 ± 0.6 nm, respectively).

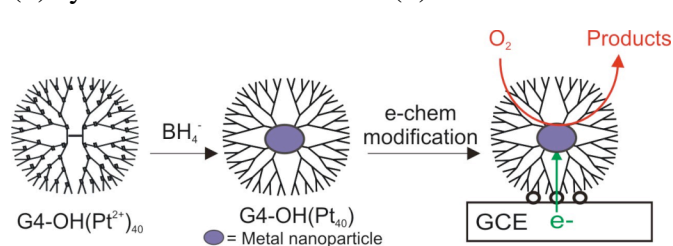
Supported PdAu bimetallic catalysts were also prepared via this sol-gel route. Importantly, the compositional fidelity of the original bimetallic DENs, and to some extent their size, is retained in the supported catalyst even after calcining at 500 °C to remove the dendrimer. Additionally, the gas-phase catalytic activity for CO oxidation is higher for the bimetallic catalysts than that for the corresponding Pd-only and Au-only monometallics. Prior to incorporation into the titania matrix G4-NH₂(Pd_{27.5}Au_{27.5}) DENs had an average particle size of 1.8 ± 0.4 nm, which was in accord with our previous results. Following the sol-gel synthesis and calcination at 500 °C the average size increased to 3.2 ± 0.9 nm. Complete removal of the dendrimer was confirmed by thermogravimetric and elemental analysis. Large-area energy-dispersive spectroscopy (EDS) of the calcined catalyst indicated an average composition of $48 \pm 3\%$ Pd and $52 \pm 3\%$ Au, which is in agreement with the molar percentages of PdCl₄²⁻ and AuCl₄⁻ used in the original synthesis mixture (50% each). The composition of the individual nanoparticles in the catalyst can be controlled by varying the percentage of the two metal salts complexed within the dendrimer at the beginning of the synthesis. For example, quantitative standardless EDS analysis of 13 particles prepared from a G4-NH₂(Pd₁₄Au₄₁)/TiO₂ precursor resulted in average Pd and Au compositions of $19 \pm 2\%$ and $81 \pm 2\%$ respectively. These values are comparable to the molar percentages of PdCl₄²⁻ and AuCl₄⁻ originally complexed within the dendrimers (25 and 75% respectively). Catalysis studies of CO oxidation revealed a ligand effect when the TiO₂-supported bimetallic nanoparticles were employed. The temperature for the onset of catalytic activity (1% CO conversion) for the PdAu catalyst was 150 °C, while the Pd and Au catalysts were inactive at this temperature. Complete (100%) CO conversion occurred at 250 °C and 285 °C for PdAu and Pd DENs, respectively. Interestingly, the Au-only supported catalysts exhibited no activity toward CO oxidation at temperatures <300 °C. Lifetime measurements of the PdAu catalysts indicated that 100% CO oxidation activity was retained for 24 h, but after this time there was a loss in activity of 60-80% over a period of two days, possibly due to coking.

(B) Electrocatalytic O₂ Reduction using Pt and PtPd DENs.

Monometallic and bimetallic dendrimer-encapsulated nanoparticles (DENs) have been used as catalysts for homogeneous hydrogenation and carbon-carbon coupling reactions as well as for

heterogeneous catalytic reactions. In this section, we are particularly interested in the application of DENs as electrocatalysts for oxygen reduction reaction (ORR). For this application, it is necessary to immobilize DENs on electrode surfaces and ensure good stability. We prepared Pt DEN films on glassy carbon electrodes (GCEs) using an electrochemical immobilization strategy and showed that they are electrocatalytically active for the ORR. This result is significant because there are few alternative methods for immobilizing highly uniform nanoparticle catalysts on electrode surfaces.

Scheme 3 shows the general synthetic approach for the preparation of Pt DEN films on GCEs, and their application to electrocatalytic O_2 reduction. This approach consists of two parts: (1) synthesis of Pt DENs and (2) immobilization of the Pt DENs onto GCEs. In the first step, Pt DENs were prepared by mixing 40 mol



equiv. of an aqueous K_2PtCl_4 solution and aqueous hydroxyl-terminated PAMAM dendrimer (G4-OH) solution, followed by chemical reduction using an aqueous $NaBH_4$ solution. Transmission electron microscopy of these Pt DENs (G4-OH(Pt_{40})) gave an average particle size of 1.4 ± 0.3 nm. In the second step, these

DENs were immobilized on GCEs using an electrooxidative coupling method. Briefly, a freshly polished GCE was placed in an aqueous $20 \mu M$ G4-OH(Pt_{40}) containing $0.1 M LiClO_4$, and scanned three times between $0 V$ and $1.0 V$ (vs. $Ag/AgCl$, $3 M NaCl$). This electrochemical process resulted in robust immobilization of the Pt DENs.

The resulting Pt DEN films are electrocatalytically active for O_2 reduction. Figure 1 shows cyclic voltammograms (CVs) for the O_2 reduction at three different types of electrodes: a naked GCE, a GCE modified with Pt-free G4-OH dendrimers, and a GCE modified with G4-OH(Pt_{40}) DENs. Pt DEN films exhibit an onset current of about $0.5 V$ and a well-defined peak at $0.22 V$ for O_2 reduction in O_2 -saturated $0.5 M H_2SO_4$ solution while the films without Pt

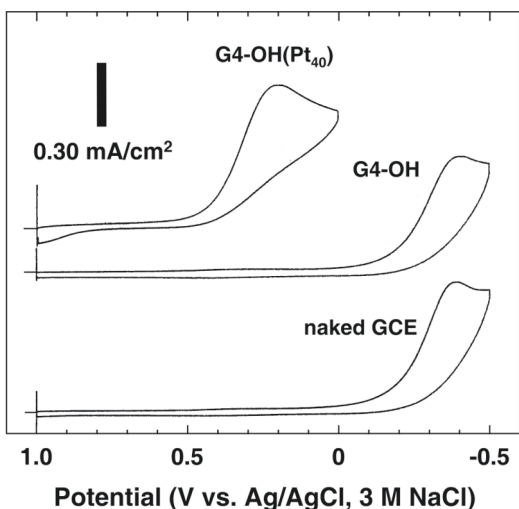


Figure 1. CVs for the reduction of O_2 using (top to bottom) a GCE modified with G4-OH(Pt_{40}) DENs, a GCE modified with Pt-free G4-OH dendrimers, and a naked GCE.

nanoparticles show a rising current with an onset of $-0.1 V$ with a well-defined peak at $-0.39 V$ for the ORR. The $610 mV$ positive shift in the O_2 reduction peak for Pt DENs indicates a significant electrocatalytic effect. The resulting films are also quite stable, and retain their electrocatalytic properties, even after 50 consecutive scans for O_2 reduction in $0.5 M H_2SO_4$ solution and after 10 min of sonication in $0.5 M H_2SO_4$ solution.

To verify that the Pt nanoparticles remain within the dendrimers during the electrochemical immobilization procedure, a selective Pt DEN poisoning experiment was performed using 1-dodecanethiol ($C_{12}SH$) dissolved in either ethanol or CH_2Cl_2 . The top CV in Figure 2 corresponds to O_2 reduction after exposing the Pt DEN-modified electrode to a solution of CH_2Cl_2 containing $3 mM C_{12}SH$. We hypothesized that the dendrimer would

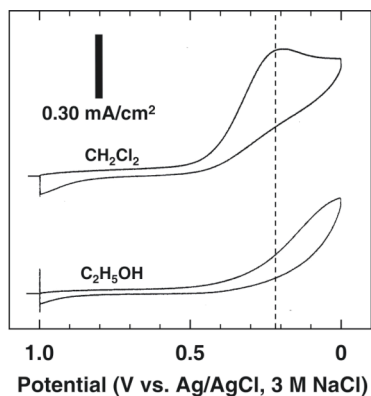


Figure 2. CVs of the reduction of O_2 after thiol poisoning experiments.

and subsequent electrocatalytic reduction of O_2 .

In addition to Pt DENs, we have also recently undertaken a study of the electrocatalytic properties of bimetallic PtPd DENs. The results show that certain PtPd alloys have almost the same catalytic activity for the ORR as Pt-only DENs.

collapse around the nanoparticle in a poor solvent such as CH_2Cl_2 , and that this would protect the nanoparticle surface from the thiol poison. A comparison of the top CV in Figure 2 with the top CV in Figure 3 confirms this hypothesis. In contrast, when the same experiment was carried out using ethanol, which is a good solvent for the dendrimer, the bottom CV in Figure 2 showed some loss of catalytic activity of the Pt DEN-modified electrode. In this case, the dendrimer does not collapse, and the thiol is able to penetrate to the Pt catalyst surface and poison it. If the Pt nanoparticles were not associated with the dendrimers, then they would become poisoned by the thiol regardless of the nature of the solvent. We conclude, therefore, that the nanoparticles remain within the dendrimers even after immobilization on the GCE surface

Peer-Reviewed Scientific Publications Citing this Project

1. H. Ye; R. M. Crooks "Effect of Elemental Composition of PtPd Bimetallic Nanoparticles Containing an Average of 180 Atoms on the Kinetics of the Electrochemical Oxygen Reduction Reaction" *J. Am. Chem. Soc.* **2007**, *129*, 3627-3633.
2. O. M. Wilson; M. R. Knecht; J. C. Garcia-Martinez; R. M. Crooks "The Effect of Pd Nanoparticle Size on the Catalytic Hydrogenation of Allyl Alcohol" *J. Am. Chem. Soc.* **2006**, *128*, 4510-4511.
3. H. Ye; R. M. Crooks "Electrocatalytic O_2 Reduction at Glassy Carbon Electrodes Modified with Dendrimer-Encapsulated Pt Nanoparticles" *J. Am. Chem. Soc.* **2005**, *127*, 4930-4934.
4. R. W. J. Scott; C. Sivadinarayana; O. M. Wilson; Z. Yan; D. W. Goodman; R. M. Crooks "Titania-Supported PdAu Bimetallic Catalysts Prepared from Dendrimer-Encapsulated Nanoparticle Precursors" *J. Am. Chem. Soc.* **2005**, *127*, 1380-1381.
5. O. M. Wilson; R. W. J. Scott; J. C. Garcia-Martinez; R. M. Crooks "Synthesis, Characterization, and Structure-Selective Extraction of 1-3 nm-Diameter AuAg Dendrimer-Encapsulated Bimetallic Nanoparticles" *J. Am. Chem. Soc.* **2005**, *127*, 1015-1024.
6. R. W. J. Scott; O. M. Wilson; R. M. Crooks "Synthesis, Characterization, and Applications of Dendrimer-Encapsulated Nanoparticles" *J. Phys. Chem. B* **2005**, *109*, 692-704. (Feature Article).
7. R. W. J. Scott; O. M. Wilson; R. M. Crooks "Titania-Supported Au and Pd Composites Synthesized from Dendrimer-Encapsulated Metal Nanoparticle Precursors" *Chem. Mater.* **2004**, *16*, 5682-5688.
8. R. W. J. Scott; O. M. Wilson; S.-K. Oh; E. A. Kenik; R. M. Crooks "Bimetallic Palladium-Gold Dendrimer-Encapsulated Catalysts" *J. Am. Chem. Soc.* **2004**, *126*, 15583-15591.

9. O. M. Wilson; R. W. J. Scott; J. C. Garcia-Martinez; R. M. Crooks "Separation of Dendrimer-Encapsulated Au and Ag Nanoparticles by Selective Extraction" *Chem. Mater.* **2004**, *16*, 4202-4204.

Invited Lectures

1. CNM Nanomaterials Conference (The University of Texas at Austin, Austin, TX, November, 2006) "Electrocatalytic Oxygen Reduction using Well-defined PtPd Bimetallic Nanoparticles"
2. Trinity University (San Antonio, TX, November, 2006) "Synthesis, Characterization, and Electrocatalytic Applications of Dendrimer-Encapsulated Nanoparticles"
3. Texas Section of the Electrochemical Society (Austin, TX, October, 2006). "Electrocatalytic Oxygen Reduction using Well-defined PtPd Bimetallic Nanoparticles"
4. American Chemical Society National Meeting (San Francisco, CA, September, 2006). "Electrocatalytic O₂ Reduction at Glassy Carbon Electrodes Modified with Well-defined Dendrimer-encapsulated PtPd Alloy Nanoparticles"
5. Workshop on Surface Reactivity and Nanocatalysis (Ebeltoft, Denmark, June, 2006) "Solution Routes to Nanoparticle Synthesis"
6. Southern Illinois University (Carbondale, IL, April, 2006) "Synthesis, Characterization, and Electrocatalytic Applications of Dendrimer-Encapsulated Nanoparticles"
7. University of Wyoming (Laramie, WY, April, 2006) "Synthesis, Characterization, and Electrocatalytic Applications of Dendrimer-Encapsulated Nanoparticles"
8. Colorado State University (Ft. Collins, CO, April, 2006) "Synthesis, Characterization, and Electrocatalytic Applications of Dendrimer-Encapsulated Nanoparticles"
9. University of Southern Mississippi (Hattiesburg, MS, March, 2006) "Synthesis, Characterization, and Electrocatalytic Applications of Dendrimer-Encapsulated Nanoparticles"
10. Georgetown University (Washington, DC, March, 2006) "Synthesis, Characterization, and Electrocatalytic Applications of Dendrimer-Encapsulated Nanoparticles"
11. Simon Fraser University (Victoria, BC, Canada, March, 2006) "Synthesis, Characterization, and Electrocatalytic Applications of Dendrimer-Encapsulated Nanoparticles"
12. University of British Columbia (Vancouver, BC, Canada, March, 2006) "Synthesis, Characterization, and Electrocatalytic Applications of Dendrimer-Encapsulated Nanoparticles"
13. University of Victoria (Victoria, BC, Canada, March, 2006) "Synthesis, Characterization, and Electrocatalytic Applications of Dendrimer-Encapsulated Nanoparticles"
14. University of California, Davis (Davis, CA, February, 2006) "Synthesis, Characterization, and Catalytic Applications of 1-3 nm-Diameter Dendrimer-Encapsulated Nanoparticles"
15. University of California, Riverside (Riverside, CA, January, 2006) "Synthesis, Characterization, and Catalytic Applications of 1-3 nm-Diameter Dendrimer-Encapsulated Nanoparticles"

16. University of California, Irvine (Irvine, CA, January, 2006) "Synthesis, Characterization, and Catalytic Applications of 1-3 nm-Diameter Dendrimer-Encapsulated Nanoparticles"
17. Université de Montréal (Montreal, December, 2005) "Synthesis, Characterization, and Catalytic Applications of 1-3 nm-Diameter Dendrimer-Encapsulated Nanoparticles"
18. McGill University (Montreal, December, 2005) "Synthesis, Characterization, and Catalytic Applications of 1-3 nm-Diameter Dendrimer-Encapsulated Nanoparticles"
19. Université du Québec à Montréal (Montreal, December, 2005) "Synthesis, Characterization, and Catalytic Applications of 1-3 nm-Diameter Dendrimer-Encapsulated Nanoparticles"
20. Society for Analytical Chemists of Pittsburgh (Pittsburgh, PA, September, 2005) "Synthesis, Characterization, and Electrocatalysis using Dendrimer-Encapsulated Catalysts"
21. The 8th SPSJ International Polymer Conference (Fukuoka, Japan, July, 2005) "Dendrimer-Encapsulated Nanoparticles: Application to the Oxygen Reduction Reaction"
22. DuPont (Wilmington, DE, April, 2005) "Synthesis, Characterization, and Catalytic Applications of 1-3 nm-Diameter Dendrimer-Encapsulated Nanoparticles"
23. University of Louisville (Louisville, KY, April, 2005) "Synthesis, Characterization, and Catalytic Applications of 1-3 nm-Diameter Dendrimer-Encapsulated Nanoparticles"
24. Leopoldina Meeting (Heidelberg, Germany, March, 2005) "Dendrimer-Encapsulated Bimetallic Nanoparticles: Synthesis, Characterization, and Applications to Catalysis"
25. Materials Research Society (San Francisco, CA, March, 2005) "Synthesis, Characterization, and Catalytic Applications of 1-3 nm-Diameter Dendrimer-Encapsulated Nanoparticles"
26. University of Florida (Gainesville, FL, December, 2004) "Dendrimer-Encapsulated Metal Nanoparticles: Synthesis, Characterization, and Catalysis"
27. University of Maryland (College Park, MD, March, 2004) "Dendrimer-Encapsulated Metal Nanoparticles: Synthesis, Characterization, and Catalysis"
28. Gordon Research Conference on Facilitated Chemical Synthesis (Ventura, CA, March, 2004) "Dendrimer-Encapsulated Metal Nanoparticles: Synthesis, Characterization, and Catalysis"
29. Vanderbilt University (Nashville, TN, March, 2004) "Dendrimer-Encapsulated Metal Nanoparticles: Synthesis, Characterization, and Catalysis"
30. Kyoto University (Kyoto, Japan, February, 2004) "Dendrimer-Encapsulated Metal Nanoparticles: Synthesis, Characterization, and Catalysis"
31. University of Texas-Austin (Austin, TX, January, 2004) "Dendrimer-Encapsulated Metal Nanoparticles: Synthesis, Characterization, and Catalysis"
32. University of Delaware (Newark, DE, December, 2003) "Dendrimer-Encapsulated Metal Nanoparticles: Synthesis, Characterization, and Catalysis"

Special Recognition of Project Scientists

1. Ms. Orla Wilson was selected for an ACS Division of Analytical Chemistry summer fellowship in 2005 and graduated with a doctoral degree in December, 2005. She is presently employed as the manager of the Texas A&M Materials Characterization Facility.
2. Mr. Heechang Ye was awarded a travel grant from Chemistry Department, Texas A&M University. These funds were used to attend the Gordon Research Conference on

Electrochemistry in 2005. He has since graduated with a doctoral degree and is presently employed as a postdoctoral fellow at The University of Texas at Austin.

3. Dr. Robert Scott finished his postdoctoral appointment in 2004 and is presently assistant professor of chemistry at the University of Saskatchewan (Canada).
4. Prof. Crooks was chairman of the Gordon Research Conference on Analytical Chemistry and the inaugural Gordon/Kenan Graduate Research Seminar on Analytical Chemistry.
5. Prof. Crooks was appointed a senior editor of the ACS journal Langmuir in December, 2003.