# Monitoring the Synthesis and Composition Analysis of Microsilica Encapsulated Acetylacetonatocarbonyl Triphenylphosphinerhodium Catalyst by Inductively Coupled Plasma (ICP) Techniques

Qing Dai, David Menzies, Qiang Wang, Agnes E. Ostafin, Seth N. Brown, Dan Meisel, and Edward J. Maginn

***Abstract*—A novel technique to monitor the synthesis process of encapsulated acetylacetonatocarbonyl triphenylphosphinerhodium within a microsilica nanoshell has been studied using inductively coupled plasma (ICP) techniques. Nanospheres sized around 50-100 nm were obtained and ICP was used to quantify the exact composition of rhodium, phosphorous, and silicon with differing digestion solvents. In addition, ICP was used to detect rhodium and phosphorous in the nano core-shell catalysts as a quality control procedure.**

***Index Terms*—Encapsulation, inductively coupled plasma (ICP), nanotechnology, Rh catalyst, silica nanoshell.**

## I. Introduction

HETEROGENEOUS catalysts are preferred in many industrial applications because the catalyst is usually more stable compared to those in solution, and much easier to recover. Inorganic supports are usually preferred because they are less susceptible to microbial attack, and can survive high temperature and pressures without change in architecture. A material such as silica is particularly suited as a heterogeneous catalyst support because of its high physical strength and chemical inertness. Moreover, $SiO_2$ is transparent to UV and visible light, allowing *in situ* optical monitoring of reactions [1]–[3]

Compared to heterogeneous catalysts, reactions with the homogeneous catalyst are carried out much more efficiently. By encapsulating the catalyst in a hollow silica nanoshell with controlled void sizes, porosity, and thickness, it is possible to combine the favorable properties of the homogeneous and heterogenous catalysts and also to minimize the leaching of the catalyst, which is usually a major disadvantage of supported catalysts. Overall, development of such products has not only potential to improve performance properties of catalyst but also will have a positive effect on economy and also to solve environmental problems.

A current problem in the development of nanoshell-based catalytic materials is the lack of accompanying characterization methods in which material composition and quality can be measured. The techniques for elemental analysis such as atomic absorption spectrometry (AAS) and instrumental neutron activation analysis (INAA) have been commonly used in the field of advanced materials research. While INAA requires access to a reactor, AAS suffers from the limitation of higher detection limits. In addition, AAS analyzes one element at a time and is time consuming when dealing with a multielement analysis. The analytical techniques based on inductively coupled plasmas (ICPs) are relatively new and are suitable for elemental analysis of a wide variety of catalysts. These techniques link together two established tools: the plasma torch as an efficient source of energy for excitation/ionization of atoms and the spectrophotometer for their detection. Two types of instruments—namely, ICP-mass spectrometer (ICP-MS) and ICP-optical emission spectrometer (ICP-OES)—are commercially available. In general the high-speed multielement analysis capabilities of ICP techniques are opening up whole new areas to make them suitable tools for research in the field of material sciences. While ICP-OES measures the elements on the basis of their wavelengths, ICP-MS characterizes elements on the basis of their mass to charge ratios. Moreover, the detection limits of ICP-OES are in the range of ng/g (PPB), and ICP-MS has an order of magnitude lower detection limits. The wide dynamic range of these techniques has the advantage of analyzing trace and major elements together. However, like other analytical techniques, ICP-MS and ICP-OES techniques are not devoid of problems. These techniques are sensitive to the total amount of dissolved solids and the samples must be diluted to <0.2%

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Q. Dai is with the School of Chemistry and School of Materials Engineering, Monash University, Melbourne 3800, Vic., Australia. She is also with The Center for Molecularly Engineered Materials, University of Notre Dame, Notre Dame, IN 46556, USA (e-mail: qing.dai@monash.edu.au).

D. Menzies is with the School of Chemistry and School of Materials Engineering, Monash University, Melbourne 3800, Vic., Australia.

Q. Wang, A. E. Ostafin, S. N. Brown, D. Meisel, and E. J. Maginn are with The Center for Molecularly Engineered Materials, University of Notre Dame, Notre Dame, IN 46556 USA (e-mail: aostafin@nd.edu).

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prior to analysis. The details [4] of the techniques have been described in numerous papers and review chapters.

While significant improvements in ICP-OES and ICP-MS make these techniques valuable for the development of materials in general, their application in the field of nanoshell-based catalyst development is impeded by problems associated with sample preparation. The main problem is that the nanoshell catalyst is a complex material with elements whose solubilities vary greatly in different solvents. Therefore, incomplete recovery of analytes limits the accuracy of the method, and prevents knowing the true composition of active catalyst the material.

In this paper we have developed a systematic method based on ICP techniques to analyze the composition of a phosphine-modified rhodium commercial hydroformylation catalyst, acetylacetonatocarbonyl triphenylphosphinerhodium [5], encapsulated within silica nanoshells. Using the ICP-based method, the incorporation of the catalyst into the silicate nanoshell platform and the structural integrity of the catalyst were evaluated.

## II. Materials and Methods

### A. Materials

Acetylacetonatocarbonyl triphenylphosphinerhodium [Rh-$(C_5H_7O_2)(CO)(PPh_3)$ or (acac)Rh(CO)- $(PPh_3)$] was obtained from Alfa Aesar. Tetramethylorthosilicate (TMOS) and octyltrimethoxysilane were obtained from Sigma. Reagent grade ammonium hydroxide, HPLC grade toluene, and E-pure water (18 Ω) were used in all preparations. All other chemicals were analytical grade and used without further purification. Anodisc membrane filters (pore size: 25 nm) for ultrafiltration were obtained from Whatmann

### B. Synthesis of Encapsulated Catalyst in Silica Nanoshells

Octyltrimethoxysilane is a well-known surfactant, with a C8 alkyl tail and a trimethoxysilane headgroup. In the presence of toluene and water it forms surfactant stabilized oil-in-water microemulsion in the aqueous phase, and water-in-oil microemulsions in the oil phase. The trimethoxy silane head group at pH values below 11 hydrolyzes in water, leaving a charged silane head group that is able to polymerize with other head groups as well as with activated silicate monomer added subsequently to the stirring mixture. As a result of the crosslinking between adjacent surfactant headgroups and additional silica, a shell of silicate can be formed which enclosed the oil microemulsion as well as its solubilized contents, in this case the rhodium catalyst. It should be noted that the formation of nanoshells of this type competes with the formation of solid silicate which does not solubilize the catalyst at all since the amorphous silicate that forms in the aqueous phase is hydrophilic.

In a typical experiment, 11.8 mg of (acac)Rh(CO)$(PPh_3)$ was dissolved in 1380 μL toluene. This solution was mixed with 26 μL of octyltrimethoxysilane diluted in 620 μL methanol. To this reaction mixture, 20 ml of deionized water was added dropwise with stirring. The oil/water microemulsion was kept stirring for another 30 min. The pH was then adjusted between 8–9. One milliliter of 1.34 mM TMOS in $CH_3OH$ was added to the above reaction mixture under mild agitation to induce the formation of silica nanoshells. The reaction mixture was aged with continuous stirring for 24 h. The solution was concentrated, washed with water and methanol several times, respectively, by using ultrafiltration apparatus, and then dried at room temperature.

To ensure complete removal of the unencapsulated catalyst from outside the nanoshells, the as-synthesized sample was soaked in toluene several times until no Rh could be detected by the ICP-MS technique. During this period, the toluene was then filtered by Anodisc membrane each time. Then the filter cake was dried overnight under a vacuum oven at 50 °C.

### C. Sample Preparation

To avoid loss of any necessary information for the ICP-based measurements, different digestion methods from the same sample were tried. The details are as follows.

1) Lithium metaborate fusion (two methods): Approximately 10 mg of the powdered silicate nanoshell catalyst sample was mixed with 0.5 g of lithium metaborate (Baker analyzed reagent) in a weighing boat. The mixture was transferred to a clean graphite crucible and fused in a muffle furnace at 1000 °C for 30 min. The crucible was removed from the furnace and the molten mass was poured directly into a clean Teflon beaker containing 50 ml of 5% $HNO_3$ or HCl. The contents of the beaker were transferred to a 125-ml screw-capped polypropylene bottle and diluted up to 100 ml by addition of 5% nitric acid or HCl. The bottle containing the suspension was placed in a sonic bath until all solids dissolved. A procedural blank was also prepared and analyzed with the samples
2) Acid digestion (three methods): Three aliquots, approximately 10 mg each of the nanoshell sample was weighed into a precleaned screw-capped Teflon vessel to which was added 2 ml of concentrated nitric acid or HF solution. The sample was left at room temperature for 2 h and then 1 ml of concentrated hydrochloric acid was added and the beaker was placed on a hot plate set at 100 °C overnight. The sample was evaporated to dryness and the residue taken into solution in 2.5 ml of concentrated $HNO_3$, capped and kept on a hot plate at 100 °C overnight. The sample was cooled and transferred to a polypropylene bottle and diluted with deionized water to 50 ml.
3) Sodium hydroxide dissolution (two methods): Two aliquots, approximately 10 mg each, of the silicate nanoshell catalyst sample were weighed and mixed with 10 ml of 0.1 M NaOH and left at room temperature overnight. One aliquot was diluted by deionized water to 25 ml. The other aliquot was dried on a hot plate set at 100 °C. To the dried mass 2 ml of aquaregia ($HNO_3$ : HCl, 1 : 3) was added and the residue was dissolved at 100 °C overnight. The sample was redried and finally dissolved in 25 ml of 5% aquaregia.

## III. Instruction and Analysis

As-synthesized silica nanoshell catalyst samples were evaluated first by transmission electron microscopy (TEM), then by ICP-MS and ICP-OES methods. In TEM, a thin specimen

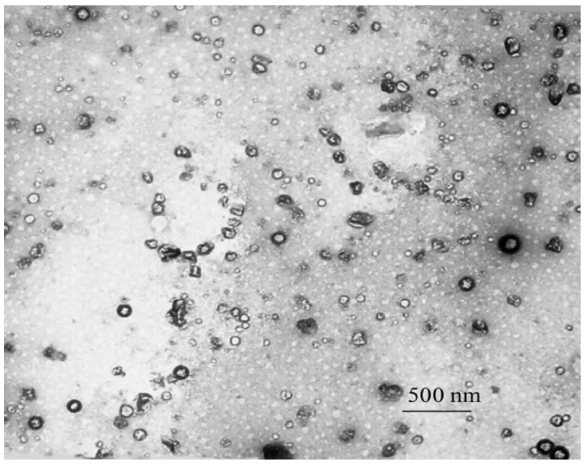


Fig. 1. TEM image of the sample before washing with toluene.

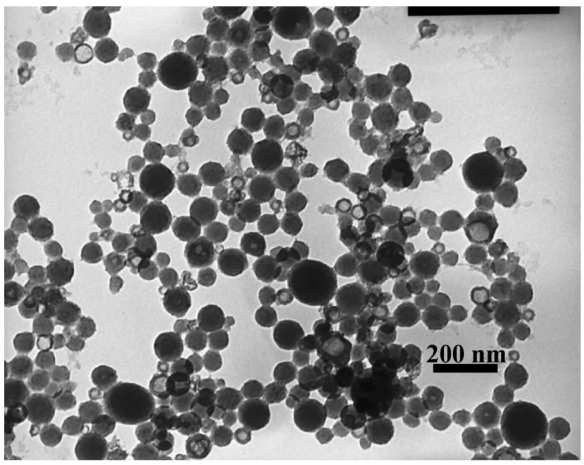


Fig. 2. TEM image of the sample after washing with toluene.

is irradiated with an electron beam of uniform current density. The electron intensity distribution behind the specimen was imaged with a three- or four-stage lens system, onto the fluorescent screen. TEM images were obtained using a JEOL 100SX electron microscope operating at between 60 and 160 kV with a 35-$\mu$m objective aperture. The samples were deposited on a thin amorphous carbon film supported by copper grids from ultrasonically processed ethanol suspension of the particles.

The samples were further analyzed using ICP-MS and ICP-OES techniques. In both cases the analysis was carried out using an external calibration procedure and internal standards were used to correct for instrumental drift and matrix effect. Samples were introduced into the instrument using a peristaltic pump at 1.0 ml/min and samples for analysis were collected using an autosampler. A Perkin-Elmer Optima 3300 XL (axial view) spectrometer was used for analysis of samples. Operating conditions followed were those described by Whitman *et al.* [4], [8]. The samples and calibration standards were spiked with 0.1 ppm Y, an internal standard. The calibration standard concentrations used were between 0.1 and 100 ppm. The following wavelengths were selected for each element: Rh (343.489 and 233.477 nm), P (213.617, 214.914, 178.221, and 177.434 nm), Si (251.611, 212.412, 288.158, 252.851, and 221.667 nm).

In the case of ICP-MS analysis, a VG Elemental PlasmaQuad PQII instrument was used for data acquisition. The P analysis

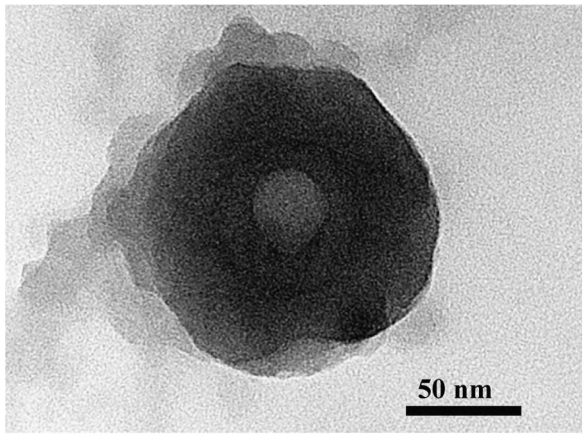


Fig. 3. TEM image of the washed nanoshell.

TABLE I
RECOVERY OF FINAL PRODUCTS FROM REACTION MIXTURE BY ICP-MS

| Samples | Rh, Weight % compared to the solid sample |
|---|---|
| Empty silica shells | 0.002 |
| Initial filtrate solution | 0.19 |
| Intermediate filtrate solution | 0.04 |
| Final filtrate solution | 0.002 |
| Intermediate filtered cake | 0.33 |
| Finished filtered cake | 0.24 |

TABLE II
Rh, P, Si CONTENTS OF THE SYNTHESIZED SILICATE NANOSHELL Rh CATALYST IN FOLLOWING DIFFERENT DIGESTIONS AS MEASURED BY ICP-MS

| The Type of Digestion | Rh | P | Si |
|---|---|---|---|
| Fusion/HCl | / | 0.09% | / |
| Fusion/HNO3 | / | / | 32% |
| HNO3/HCl | 0.24% | / | / |
| HF/HNO3/HCl | 0.24% | 0.08% | / |
| HF/HCl | 0.27% | / | 45.31% |
| Only NaOH | 0.25% | 0.08% | 44.41% |
| NaOH/HCl/HNO3* | 0.47% | 0.15% | / |

* Compared with the general procedures, double the amount of (acac)-Rh(CO)(PPh3) as starting material to synthesize the encapsulated sample.

was carried out on the original concentrations prepared in the material and methods section. However, in the case of Rh and Si, samples were diluted 20 times to bring the concentrations of elements within the instrument's dynamic range. The machine operating conditions followed were described in McGinnis *et al.* [6].

## IV. RESULTS AND DISCUSSION

The TEM micrographs in Figs. 1, 2, and 3 clearly show the samples were 50–100-nm spherical particles. Fig. 1 shows the typical TEM micrograph of the as-synthesized samples at low magnification. At this stage, the samples contain both encapsulated catalyst inside the silicate nanoshells, as well as unencapsulated catalyst in the solution. Fig. 2 shows the typical micrograph of the washed samples at higher concentration, and Fig. 3 shows a high magnification TEM image of one silica nanoshell. Comparing Fig. 2 with Fig. 1, it is clear that a mix of larger and smaller nanoshells are formed.

TABLE III
QUALITY CONTROL OF ANALYSIS BY ICP-MS

| Sample | Rh (Rel. Wt.) | | P (Rel. Wt.) | | Rh/Mr | P/Mr. | Measured Molar Ratio of Rh/P in the sample | Stoichiometric Ratio of Rh/P in the sample |
|---|---|---|---|---|---|---|---|---|
| | Add | Anal. | Add | Anal | | | | |
| (acac)Rh(CO)($PPh_3$) only | 411 | 379.8 | 124 | 127.7 | 3.7 | 4.12 | 0.90 | 1 |
| (acac)Rh(CO)($PPh_3$) only | 728 | 713.3 | 219 | 209.5 | 6.9 | 6.8 | 1.02 | 1 |
| (acac)Rh(CO)($PPh_3$) + 2 $PPh_3$ | 411 | 384.1 | 372 | 357.7 | 3.7 | 11.6 | 0.32 | 0.33 |
| 4$RhCl_3$ + $PPh_3$ | 2472 | 2470 | 186 | 193.4 | 24 | 6.2 | 3.90 | 4 |
| (acac)Rh(CO)($PPh_3$) + TMOS | 728 | 711.5 | 219 | 216.8 | 6.9 | 6.99 | 0.99 | 1 |
| (acac)Rh(CO)($PPh_3$) + TMOS | 146 | 137.6 | 44 | 43.9 | 1.33 | 1.41 | 0.95 | 1 |

Notes: "Rel. Wt. " (relative weight) means units which weren't used because of too small unit. "Add" means expected weigh while "Anal." means a measured weight. "Rh/Mr" or "P/Mr. means the measured weight is divided by its molecular weight.

TABLE IV
Rh AND P MOLE RATIOS OF ENCAPSULATED CATALYSTS BY BOTH ICP-MS AND ICP-OES

| sample | ICP Techniques | Rh (Wt. %) | | P (Wt.%) | | Measured Molar Ratio of Rh/P in the sample | Stoichiometric Ratio of Rh/P in the sample |
|---|---|---|---|---|---|---|---|
| | | high Conc. | low Conc. | high Conc. | low Conc. | | |
| A [(acac)Rh(CO)($PPh_3$) in shells ] | MS | / | 0.25 | 0.08 | / | 0.90 | 1 |
| A [(acac)Rh(CO)($PPh_3$) in shells ] | OES | 0.24 | / | 0.07 | / | 1.00 | 1 |
| B [(acac)Rh(CO)($PPh_3$) in shells] | MS | / | 0.21 | 0.07 | / | 0.90 | 1 |
| B [(acac)Rh(CO)($PPh_3$) in shells] | OES | 0.21 | / | 0.06 | / | 1.10 | 1 |
| C [(acac)Rh(CO)($PPh_3$) in shells] | MS | / | 0.46 | 0.15 | / | 0.92 | 1 |
| C [(acac)Rh(CO)($PPh_3$) in shells] | OES | 0.47 | / | 0.15 | / | 0.94 | 1 |

Notes: Compared with the general experimental procedure, both sample A and sample B are using the same amount of (acac)Rh(CO)(PPh $)_3$but sample C using double amount of (acac)Rh(CO)(PPh $)_3$as starting material to synthesize the encapsulated catalysts and the only difference between Sample A and Sample B is the latter took 48h aging time. "Conc." means relative concentration of Rh or P in the samples. "Wt. %" means weights presented in wt%.

A well-defined washing protocol was developed to recover the unencapsulated catalyst from the nanoshell suspension, and the stability of the catalyst in the final washed product, and its leaching evaluated. The synthesized product was filtered and the resulting cake was washed repeatedly with toluene to extract unencapsulated catalyst.

Since the purpose of this paper is to demonstrate that both IC-MS and ICP-OES are suitable techniques for the analysis of the total amount of encapsulated catalyst, we do not provide information about the location of the catalyst in the material. They are amenable to automated survey of numerous catalyst specimens, unlike TEM, XPS, or SIMS which require one by one analyses with a live operator. The filtrate and wash solutions were analyzed for trace amounts of Rh by ICP-MS. Rhodium was chosen because it has better detection limits than phosphorus. The results presented in Table I indicate that at least five washes were needed to remove the unencapsulated catalyst contaminants from the cake. As the wash progressed, a reduction in Rh contents was seen in the solid material.

To confirm that some unleachable catalyst molecules remained in the nanoshells, the filtered cake was dried, powdered, and subjected to three different dissolution procedures. One aliquot was fused using lithium metaborate. The second was dissolved in the mixtures of 16-mol $L^{-1}$ $HNO_3$ and 12-mol $L^{-1}$ HCl with or without 20 mol $L^{-1}$ HF; a mixture of the 12-mol $L^{-1}$ HCl and 20 mol $L^{-1}$ HF, respectively. The third procedure involved dissolution in 0.1 M of NaOH solution with or without acid. The intended function of lithium metaborate was to avoid the effect from Rh element and others to try to get the full Rh information as well as P and Si. The solutions were then analyzed for Rh, P, and Si using both ICP-MS and ICP-OES techniques. The experimental data from ICP-MS with different digestions are shown in Table II. All dissolution yields were similar except for the last one, which was supposed to have twice as much material. Only the third digestion method using only NaOH treatment was found to be a suitable one to detect all three elements for the samples. The yield of encapsulation can be easily calculated from the results shown in Table II, i.e., about 22% of original catalyst was retained by the nanoshells after encapsulation.

To prove whether the Rh catalyst was intact in the silica nanoshells, a series of quality control samples were selected and measured by both ICP-MS and ICP-OES using the above-described third digestion method using only NaOH dissolution. Both theoretical calculation and the experimental results are shown in Tables III and IV. The significance of Table III is that for all the control samples, which are not the silicate nanoshell Rh catalysts themselves, but simple Rh compounds, the sodium hydroxide digestion methods all gave expected results, including pure Rh catalyst and noncatalyst $RhCl_3$, mixed or not mixed with either pure phosphine or solubilized silica. The results indicate ICP-MS is very useful to quantify the exact composition of rhodium and phosphorous from their pure or mixture samples with or without silica content. Table IV shows results for silica nanoshell Rh catalyst samples measured by both ICP-MS and ICP-OES.

As we described the major differences between ICP-MS and ICP-OES in the introduction, the data in Table IV verify that, compared with ICP-OES, the samples for silicate nanoshell catalyst analyzed by ICP-MS can be more diluted suspensions because ICP-MS has lower detection limit, especially for the Rh element detection. However, for phosphorus detection, the diluted suspensions with higher concentration were needed by both ICP-based measurements. Both longer aging digestion and double the amount of the sample, resulted in more accurate the element detection. The results indicate, by choice of a proper sample preparation method, ICP-based techniques can monitor the encapsulation process of the silica nanoshell-encapsulated acetylacetonatocarbonyl triphenylphosphinerhodium.

The key difference between our synthesis and that of previously reported synthesis of silica encapsulated CdS nanoparticle [7], [8] which were found to leach catalyst is the use of the octyltrimethoxysilane surfactant which forms a stable crosslinked microemulsion containing the catalyst. Even if the silicate coating were imperfect, the crosslinked silicate head groups of the surfactant would still inhibit leaching of the catalyst on the basis of its size. Since the catalyst is poorly soluble, it would have difficulty making its way through the hydrophilic silicate layer as well. It should be noted that the described synthesis does not result in 100% encapsulation efficiency for the administered catalyst as the extensive washing steps demonstrate that some of the catalyst is in fact extractable. However, the synthesis does allow the retention of a significant amount of catalyst to remain entrapped in the particle, and the reported measurements of catalyst content were performed on the fully washed samples.

## V. Conclusion

Nanoencapsulation of acetylacetonatocarbonyl triphenylphosphine rhodium catalysts within silica nanoshells has been accomplished initially. This has been examined by TEM micrographs to produce 100-nm nanospheres. The ICP-based technique was proven to be an ideal technique to evaluate the quality of the catalyst through the synthesis. This should have an impact on the commercial market to ensure that the catalysts produced are of superior quality. Further optimization of the encapsulation yield and application in the reaction is under study.

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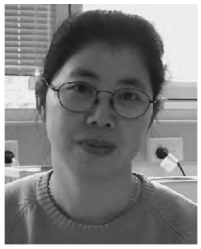

**Qing Dai** received the Ph.D. degree from Southeast University, China, in 1999.

She is currently an Australian Research Council Research Fellow at Monash University, Melbourne, Vic., Australia. She has published over 30 peer-reviewed papers in nanoscience and synthesis chemistry. Her research interests are in the area of nanomaterials, energy transfer, and functional materials synthesis, characterization, and application.

**David Menzies** received the Hon. degree from Monash University, Melbourne, Vic., Australia, in 2001. He is currently working toward the Ph.D. degree at Monash University.

His interests involve nanomaterials and their application in energy transfer.

**Qiang Wang** received the Ph.D. degree from University of Notre Dame, Notre Dame, IN, in 2004. His research interests involve the development of self-assembled nanomaterials.

**Agnes E. Ostafin** received the Ph.D. degree from the University of Minnesota, Twin Cities, in 1994.

She is currently Assistant Professor of Chemical and Biomolecular Engineering at the University of Notre Dame, Notre Dame, IN. Her research interests involve nanomaterial fabrication and functional characterization.

**Seth N. Brown** received the Ph.D. degree from the University of Washington, Seattle, in 1994.

He is currently Professor of Chemistry and Biochemistry at the University of Notre Dame, Notre Dame, IN. His research interests involve stereoelectronic effects in atom transfer reactions and catalytic oxygenation reactions.

**Dan Meisel** received the Ph.D. degree from the Hebrew University of Jerusalem in 1974.

He is currently Professor of Chemistry and Biochemistry at the University of Notre Dame, Notre Dame, IN. His research interests involve the radiation and photochemistry of nanoscale systems.

**Edward J. Maginn** received the Ph.D. degree from University of California, Berkeley, in 1995.

He is currently Professor of Chemical and Biomolecular Engineering at the University of Notre Dame, Notre Dame, IN. His research interests involve molecular simulations of fluid properties, ionic liquids, and nanomaterials.