

# **SANDIA REPORT**

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## **DOE/BES/NSET Annual Report on Growth of Metal and Semiconductor Nanostructures Using Localized Photocatalysts**

John A. Shelnett, Yujiang Song, Yi Yang, Craig J. Medforth, Eulalia Pereira, Anup K. Singl, Huifang Xu, Yingbing Jiang, C. Jeffrey Brinker, Frank van Swol, Zhongchun Wang, Yan Qiu, Sivakumar R. Challa, Raid E. Haddad, Richard K. Watt, and Eric Nuttall

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### **Abstract**

Our overall goal is to understand and develop a novel light-driven approach to the controlled growth of unique metal and semiconductor nanostructures and nanomaterials. In this photochemical process, bio-inspired porphyrin-based photocatalysts reduce metal salts in aqueous solutions at ambient temperatures to provide metal nucleation and growth centers. Photocatalyst molecules are pre-positioned at the nanoscale to control the location and morphology of the metal nanostructures grown. Self-assembly, chemical confinement, and molecular templating are some of the methods used for nanoscale positioning of the photocatalyst molecules. When exposed to light, the photocatalyst molecule repeatedly reduces metal ions from solution, leading to deposition and the synthesis of the new nanostructures and nanostructured materials. Studies of the photocatalytic growth process and the resulting

nanostructures address a number of fundamental biological, chemical, and environmental issues and draw on the combined nanoscience characterization and multi-scale simulation capabilities of the new DOE Center for Integrated Nanotechnologies, the University of New Mexico, and Sandia National Laboratories. Our main goals are to elucidate the processes involved in the photocatalytic growth of metal nanomaterials and provide the scientific basis for controlled synthesis. The nanomaterials resulting from these studies have applications in nanoelectronics, photonics, sensors, catalysis, and micromechanical systems. The proposed nanoscience concentrates on three thematic research areas: (1) the creation of nanoscale structures for realizing novel phenomena and quantum control, (2) understanding nanoscale processes in the environment, and (3) the development and use of multi-scale, multi-phenomena theory and simulation. Our goals for FY03 have been to understand the role of photocatalysis in the synthesis of dendritic platinum nanostructures grown from aqueous surfactant solutions under ambient conditions. The research is expected to lead to highly nanoengineered materials for catalysis mediated by platinum, palladium, and potentially other catalytically important metals. The nanostructures made also have potential applications in nanoelectronics, nanophotonics, and nanomagnetic systems. We also expect to develop a fundamental understanding of the uses and limitations of biomimetic photocatalysis as a means of producing metal and semiconductor nanostructures and nanomaterials. The work has already led to a relationship with InfraSUR LLC, a small business that is developing our photocatalytic metal reduction processes for environmental remediation. This work also contributes to science education at a predominantly Hispanic and Native American university.

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## **DOE/BES/NSET Annual Report on Growth of Metal and Semiconductor Nanostructures Using Localized Photocatalysts**

### **Introduction**

The focus of these studies is a novel light-driven catalytic approach to the controlled growth of new metal and semiconductor nanostructures and nanomaterials. The pre-positioned photocatalysts create new and controlled metal nanostructures when exposed to light by continuously reducing metal ions in their vicinity. Self-assembly, chemical confinement, and molecular templating are some of the methods for nanoscale positioning the photocatalyst molecules. Under controlled exposures to light, these photocatalysts continuously reduce metal ions in the vicinity of the molecule, leading to the controlled synthesis of new nanostructures and nanostructured materials.

To realize these goals, fundamental biological, chemical, and environmental issues must be addressed successfully. Toward these ends, we have coupled the vast nanoscience characterization capabilities of the University of New Mexico and Sandia National Laboratories together with strong emphasis on multi-scale modeling and simulations processes at the nanoscale to advance the knowledge base in this new area of nanoscience. The research is also associated with the new Sandia/Los Alamos Center for Integrated Nanotechnology (CINT) and the researchers have access to these new nanoscience facilities. Together, these experimental and theoretical studies are elucidating the processes involved in the photocatalytic growth of metal nanomaterials and are providing the scientific basis for controlling these processes. The resulting nanomaterials from these studies will likely have applications in catalysis, nanoelectronics, and photonics.

The studies have concentrated on three thematic nanoscience research areas, including (1) the creation of nanoscale structures for realizing novel phenomena and quantum control, (2) understanding nanoscale processes in the environment, and (3) the development and use of multi-scale, multi-phenomena theory, modeling, and simulation at the nanoscale. The research is expected to significantly impact both nanotechnology and environmental technologies. The studies could lead to nanoscale devices, manufacturing processes, and biosystems.

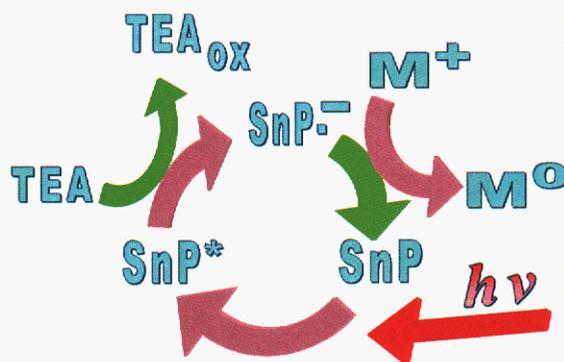
*Background.* In large part, the proposed work stems from an effort by Professors Werner Lutze, Eric Nuttall, and John Shelnett to improve on the ability of bacteria naturally resident in

soil to reduce heavy-metal wastes to nanometer-size precipitates by using specific enzymes from the bacteria instead of the bacteria themselves. The iron-porphyrin-containing enzymes (e.g., cytochromes  $c_3$ ) of these bacteria catalyze the *in situ* chemical reduction of soluble metal ions to insoluble metals, metal alloys, or compounds. The enzymatic reactions were found to mostly produce nanoscale metal particles, although self-assembly of  $\text{Se}^0$  nanowires was found for selenate.

Subsequently, it was found that some porphyrin-based photocatalysts worked just as well as the enzymes. These biomimetic photocatalysts do not require the addition of a strong inorganic chemical reductant because light energy is used to generate a strongly reducing porphyrin radical anion that can reduce the metal ions. (See Scheme 1.) Only a weak electron donor such as a tertiary amine is needed. More to the point, photocatalysts differ from simple chemical reductants for creating metal nanostructures in that they act like a molecular ‘metal pump’, continuously producing zero-valent metal atoms at the site of the molecule as illustrated in Scheme 1. Each photocatalyst molecule can potentially grow a nanowire or other nanoscale metal structure as zero-valent metal is generated.

The photocatalytic growth mechanism is somewhat similar to the catalytic growth of carbon nanotubes. In the carbon nanotube case, a metal nanoparticle (e.g., Ni, Co) catalyzes the growth of the nanotube from carbon in the vapor phase. The nature of the catalytic particle, the details of the local environment, and the graphitic axis at initiation of growth are some of the factors determining the structure and electronic properties

of the resultant carbon nanotube. In a similar way, the photocatalyst molecule (upon irradiation with visible light) can grow a metal nanostructure. The nanostructural properties are determined by the photocatalyst molecule, its interactions with metal atoms and ions, the properties of metal itself, the solution conditions, the light intensity and duration of exposure, and in some cases the presence of confined space surrounding the photocatalytic reaction.



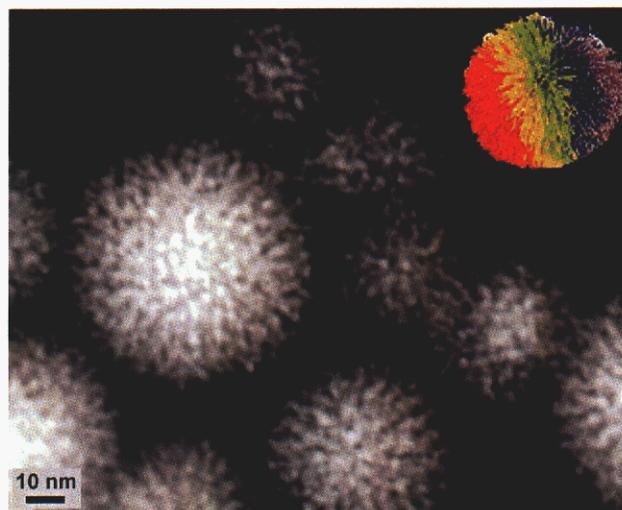
**Scheme 1.** Reductive photocycle used to reduce metal ions to zero-valent metals. SnP: tin(IV) porphyrin, TEA: triethanolamine; M: metal. Quantum efficiency is approximately 0.5.

## Detailed Description of Results

Metal nanostructures are of considerable interest because of their importance in catalysis, photochemistry, sensors, tagging, and optical, electronic, and magnetic devices. Metal nanostructures have been synthesized in many forms, ranging from conventional metal colloids to modern near-monodispersed nanoclusters, shape-controlled nanocrystals, and other nanostructures such as wires and sheets. Nanostructured platinum is of particular interest for many applications, including catalysis, sensors and other devices. While a few platinum nanostructures have been reported, including nanoparticles, nanowires, nanosheets, and others, the synthesis of additional types of nanostructures is highly desirable and potentially technologically important.

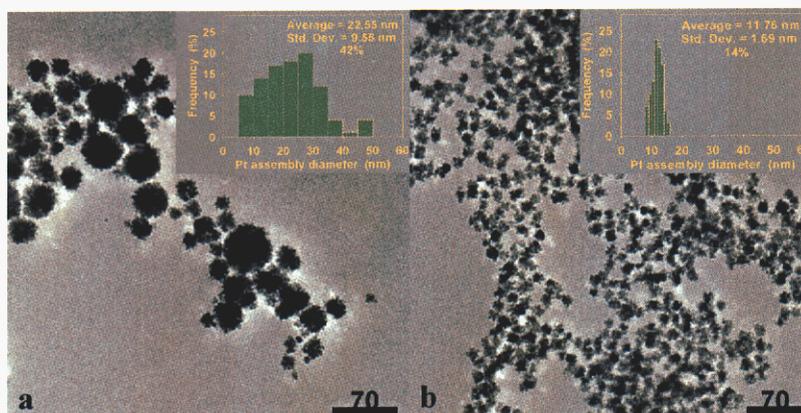
New methods for the synthesis of metal nanostructures are needed for providing the desired reproducibility and control over properties required for advanced technological applications. A recognized goal of these new synthetic approaches is control over the composition, size, surface species, solubility, stability, isolability, and other functional properties of the nanostructures. For example, shape-controlled platinum nanocrystals have been synthesized by El-Sayed and coworkers using a capping polymer material, giving mixtures of tetrahedral, cubic, irregular-prismatic, icosahedral, and cubo-octahedral nanoparticles. The shapes produced are determined by interfacially directed control over the relative growth rates of different crystalline faces. As another example, nanosheets have been produced by reduction of platinum-chloride intercalation compounds confined between graphite layers.

With similar goals of synthetic control in mind, we have discovered and elucidated a method of synthesis that leads to novel types of fractal-shaped platinum nanostructures of controlled sizes. This synthetic method is based on a seeding and fast autocatalytic growth approach in which an aqueous solution of platinum salts is reduced by ascorbic acid in the presence of



**Figure 1.** HAADF scanning TEM image of the three-dimensional platinum dendrites grown in the presence of Brij-35 micelles and in the absence of photocatalyst. Inset: a Koosh<sup>®</sup> ball.

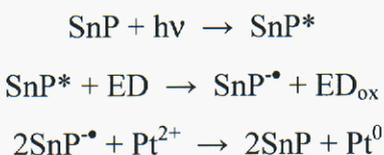
surfactant. The seeding/autocatalytic growth approach employed by us produces nanodendrites like those shown in Figure 1, which grow by interfacially directed autocatalytic reduction of platinum onto Pt nanoparticle seeds in an aqueous surfactant solution. To our knowledge, such metallic platinum nanodendrites have not been



**Figure 2.** TEM images of platinum nanostructures produced in the presence of SDS without (a) and with (b) photocatalyst and their respective size distributions (Insets). Average diameters were measured for 100 nanostructures and their frequencies are plotted in the inset graphs. The average size and the standard deviations are given in the plots, along with the percentage ratio of the standard deviation to average size.

observed previously. Our main goal for the first year has been to fully understand the chemical and photochemical processes involved in the formation of these platinum nanodendrites and similarly synthesized nanofoams. Most importantly, we have clarified the use of porphyrin photocatalysis to control the size and uniformity of these nanostructures.

The photocatalytic reduction of platinum salts by the SnP is accomplished in the presence of visible light and an electron donor (ED), ascorbic acid in this case. The SnP photoreaction is a reductive photocatalytic cycle, which has been used previously in the photosynthesis of reduced methylviologen and to evolve  $H_2$  in the presence of colloidal Pt. In the present photoreaction,  $Pt^{2+}$  is reduced according to the following simplified equations:



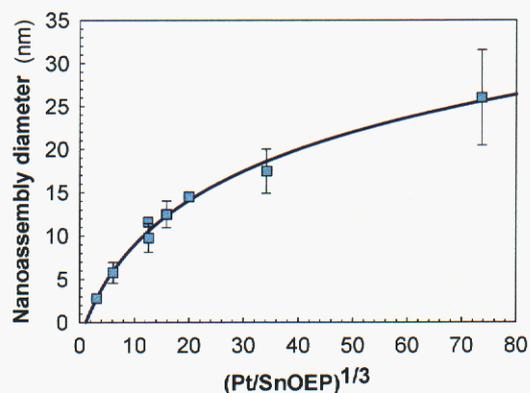
Absorption of visible or UV light by the SnP yields the long-lived excited triplet  $\pi-\pi^*$  state,  $\text{SnP}^*$ , which is rapidly reduced ( $\text{SnP}^*/\text{SnP}^{\bullet-}$ , +1.1 V) by an ED. The product is a long-lived (~10 seconds) radical anion,  $\text{SnP}^{\bullet-}$ , which is a strong reductant ( $\text{SnP}/\text{SnP}^{\bullet-}$ , -0.66 V) capable of efficiently reducing a variety of metal ions including Ag, Au, Hg, Pb, Cu, and Pt to the zero-

valent metals. Reduction of the metal regenerates neutral SnP, which again becomes available to absorb light and initiate a successive photochemical cycle.

In the case of micellar surfactant solutions, slow reduction of Pt(II) by ascorbic acid yields seed nanoparticles that autocatalyze the reduction reaction. The fast autocatalytic growth from the seeds produces three-dimensional platinum nanodendrites of diameters ranging from 6 to 200 nm as shown in the scanning TEM image of Figure 1. Nanodendrites of uncontrolled size are produced by slow reduction of Pt(II) by ascorbic acid to produce small seed particles, which then grow rapidly by autocatalytic reduction of Pt(II) into the dendrites. The surfactant micelles themselves can have negatively charged head groups (sodium dodecylsulfate, SDS) or polar headgroups (Brij-35), but surfactant must be present to obtain the nanodendrites. These nanostructures were not initially recognized as dendrites, but thought to be nanoparticle clusters and were modeled by DFT methods as Pt particles on a micelle. However, the true dendritic nature was only fully realized after 2-dimensional dendrites were discovered.

When photocatalyst and light are present, the size of the nanodendrites is smaller and more uniform as shown in Figure 2. Control over the size of these dendritic nano-structures is conveniently realized by using a tin-porphyrin photocatalyst to rapidly generate an initial population of growth centers. These seed particles then grow by the rapid autocatalytic reduction of Pt(II) into the dendrites, limited only by the amount of Pt(II) present in solution. The size can be controlled either by varying the concentration of the porphyrin photocatalyst under constant Pt(II) concentration and illumination conditions, by varying the light exposure at constant Pt(II) and porphyrin concentrations, or by varying the Pt(II) concentration at constant light and porphyrin concentration. The effect of varying the photocatalyst concentration on the size of the nanodendrites is illustrated in Figure 3.

In the case of the three-dimensional nanodendrites, this photocatalytic seeding approach can be used to produce nanodendrites with average sizes in the range of 10 to 50 nm and narrow size distributions. Under the highest photocatalyst concentration conditions, size can be reduced to the point where only ~3-nm diameter Pt particles are formed. The effects of light



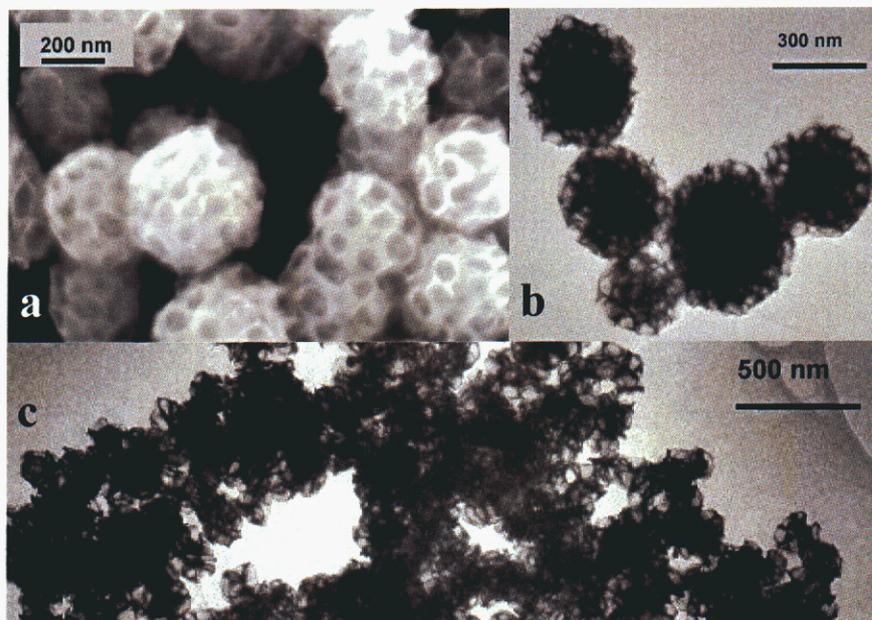
**Figure 3.** Nanostructure diameter versus the cube root of the Pt-to-porphyrin molar ratio (a measure of the nanostructure volume per growth center).

exposure and porphyrin concentration on the size of the nanodendrites were also evaluated in detail as describe in a full article submitted to the *Journal of the American Chemical Society*.

Besides demonstrating the ability to control size, these studies also verify the proposed

seeding/autocatalytic growth mechanism.

When large liposomes are used as a template, dendritic disk-like sheets



**Figure 4.** Foam-like balls composed of platinum nanosheets grown at the interfaces between aggregated DSPC liposomes. The balls have a uniform size because the porphyrin photocatalyst initiates growth within the liposomal aggregates, and growth occurs along the interfaces between the liposomes in a spherically symmetric manner until the Pt(II) is exhausted. (a) SEM image of the platinum foam balls. (b) TEM image of the foam balls. (c) Under certain condition the foams the growth centers are close enough so that growth leads to a continuous phase, which retains the nanoscale pore size dictated by the liposomal template.

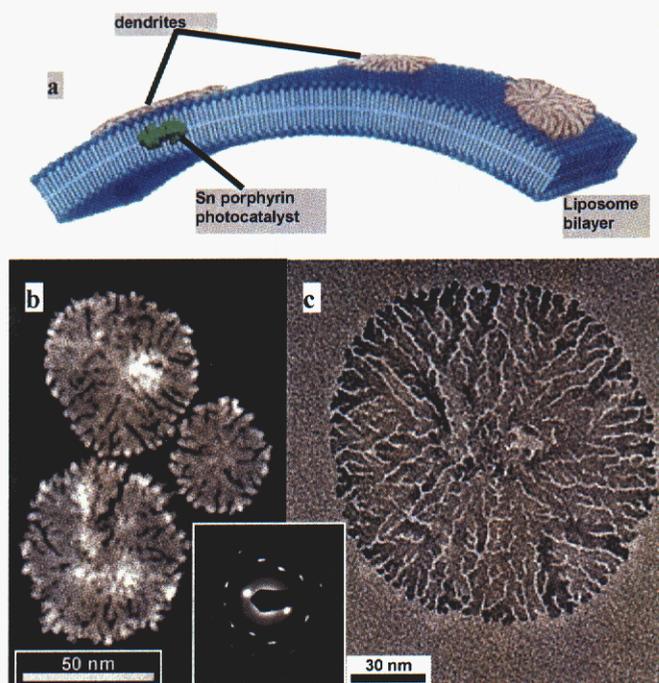
(nano-caps) or solid foam-like nanomaterials are produced at the liposome surface. Some of the nanostructured Pt materials produced are shown in Figure 4. The particular nanostructure obtained depends on the solution conditions and size of the liposomes. Some control over the morphology is provided by the diameter of the templating unilamellar DSPC liposomes. The large cavities in the foams are determined by the liposomes size; when 65-nm liposomes are used in the reaction, the cavities in the foams have this average size, and similarly when 120-nm or 165-nm liposomes are used instead, the cavities in the nanofoams reflect the larger liposomal size.

We have achieved additional control using a porphyrin photocatalyst. When the porphyrin photocatalyst is incorporated into the liposomes, exposure of the reaction solution to incandescent light produces smaller balls of the foam and a more uniform ball size distribution. Varying the light exposure and porphyrin loading at constant platinum salt concentration determines the size of the foam balls and even gives continuous foam phases under certain conditions.

The platinum metal foams are also porous at a smaller scale than the diameter of the liposomes. The arms of the 2-dimensional Pt sheets ( $\sim 2$  nm thick) on the liposomal surface are separated by  $\sim 1$ - $2$ -nm spaces, providing small crevices through which small chemical species have access to the lipid bilayer (Figures 5(b) and 5(c)). This porosity is particularly evident in the isolated nanosheets or nano-caps that can be grown on the liposomes under certain conditions. The nanocap growth is illustrated in Figure 5(a), and the TEM images of the nanocaps clearly show the dendritic nature of these 2-dimensional nanostructures.

The platinum metal foams have potential applications in catalysis because of their high surface area, the ability to control their porosity on different length scales, and the possibility of tailoring their structural stability. Fuel cells may be one commercial area in which the platinum nanofoams may have advantages.

For the small three-dimensional platinum nanodendrites in Figure 2(b), we have demonstrated that they are functional catalytic/photocatalytic units capable of  $H_2$  evolution from water. The photocatalytically active porphyrin molecule likely remains associated with surfactant in the nanostructure that it nucleated and it can act as a photosynthetic system. Since colloidal platinum is a well-known catalyst for  $H_2$  evolution from water in artificial photosynthesis systems, the Pt nanostructure and the associated porphyrin photocatalyst should therefore be able to generate  $H_2$  in the presence of light and an electron donor. This  $H_2$  photosynthetic chemistry is similar to the reaction mechanism described above for Pt(II) reduction, except that SnP $^{\bullet}$  provides electrons to  $H^+$  at the Pt metal surface to produce hydrogen. To see if hydrogen evolution was occurring, the reaction mixture containing the (12-nm) three-dimensional platinum



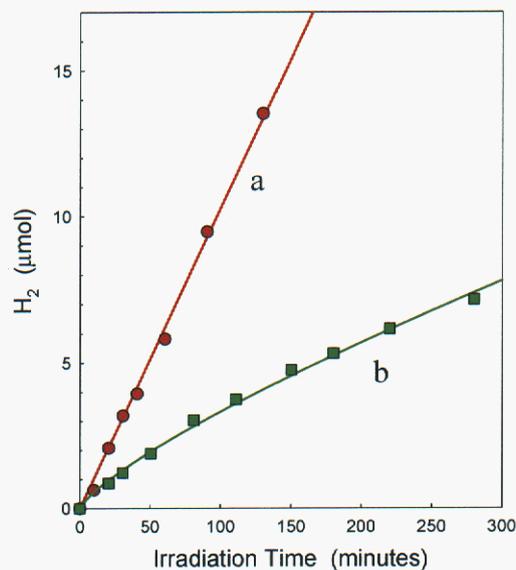
**Figure 5.** Dendritic platinum nanocaps templated by liposomes. (a) Illustration of the growth of Pt nanocaps on the liposomal surface; other possible growth mechanisms are discussed in the text. (b) HAADF scanning TEM image of three platinum nanocaps grown on 160-nm diameter DSPC liposomes. (c) TEM image of a large dendritic Pt nanocap made using DSPC liposomes and (Inset) its electron diffraction pattern. The surfactant assemblies cannot be seen in the TEM images because of the lack of contrast with the much denser Pt and the interference from the carbon film of the TEM grid.

dendrites and associated porphyrin photocatalyst was irradiated with room light in the presence of ascorbic acid. After two months, the head-space of the sealed reaction vessel was analyzed by gas chromatography, and the presence of hydrogen was confirmed (~30% by volume). Two interesting aspects of this catalytic reaction are that H<sub>2</sub> evolution is observed even in the presence of the surfactant coating on the nanodendrites, and that the porphyrin delivers its strongly reducing electrons directly to protons at the Pt surface without the aid of a relay molecule such as methylviologen, as has been used in some previous studies.

The nanodendrite-surfactant assemblies probably suffer from poor light-harvesting ability because of the low concentration of the light-absorbing porphyrin per nanodendrite and the opacity of the colloidal solution. To address these deficiencies, water-soluble Sn uroporphyrin was added to an ascorbic acid solution containing only a small amount of the nanodendrite mixture. In this case, H<sub>2</sub> evolution is greatly accelerated, consistent with increased light flux and the additional light harvesting provided by

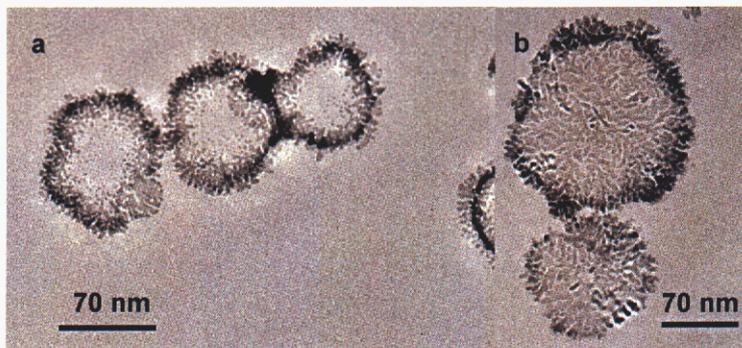
the added tin porphyrin. As shown in Figure 6, hydrogen evolution increases linearly for hours with turnover rates as high as 390 h<sup>-1</sup> (mole H<sub>2</sub>/mole atomic Pt). Given these findings, nanodendrites can be viewed as functional nanocomposites consisting of the platinum dendrite, the adsorbed surfactant and possibly ascorbic acid, and the associated active photocatalyst.

We have made some progress on the use of photocatalytic metal reduction as a means for removing heavy metals from water. The work has focused on two areas—identifying an electron donor compatible with environmental uses and determining which metals may be removed and to what level. A small business (InfraSUR LLC) is developing this method of waste remediation



**Figure 6.** Photocatalytic reduction of water to hydrogen by the platinum nanostructures, composed of the platinum nanodendrite, surfactant, and SnOEP, with added SnUroP (80 μM). The Pt nanostructures are diluted into an ascorbic acid (ED) solution containing the Sn uroporphyrin for the measurement. Water is reduced at rates as high as 6 μmol-hr<sup>-1</sup> (H<sub>2</sub> turnover rate of 33 hr<sup>-1</sup> in terms of SnUroP) by electrons from the Sn uroporphyrin anions supplied to the surface of the Pt catalyst. Incandescent white light intensity is 800 nmol-cm<sup>-2</sup>-s<sup>-1</sup>, but mostly light with wavelengths in the region of the Soret band of the porphyrin is absorbed. Reaction conditions are: (a) low Pt (6.5 μM) and high ascorbic acid concentration (200 mM) and (b) high Pt concentration (65 μM) with low ascorbic acid concentration (60 mM). H<sub>2</sub> turnover rates in terms of atomic Pt are (a) 390 hr<sup>-1</sup> and (b) 14 hr<sup>-1</sup>.

under the name NanoMOR with the intention of commercializing a reactor based on the process. The efforts this year have focused on using benign electron donors like ethanol, which is already used for purification of municipal water supplies, and on removing Cr(VI), which is removed by the process to undetectable levels.



**Figure 7.** (a) *Platinized liposomes?* (b) *Liposomes coated with nanometer-thick palladium dendritic sheets.*

### Description of Objectives

Now that we have obtained a full understanding of the role of photocatalysis in the platinum reduction reaction and characterized many of the Pt nanostructure that result, we are in a better position to exploit this new understanding to tailor desired nanostructures and nanomaterials. Several new opportunities for creating new functional nanostructures are evident and will be pursued in the next year.

One intriguing possibility that has arisen from our work this year is the chance that we can make individual liposomes coated with nanometer-thickness platinum sheeting. TEM images suggest that this possibility is realistic as shown in Figure 7. Although the platinized liposomes (Figure 7(a)) appear to have collapsed when dried on the TEM grid, they may be structurally sound while wet, or in solution, or when more wholly formed under optimal synthesis conditions. In addition, palladium also seems to form sheets on the liposomes as shown in the TEM image in Figure 7(b).

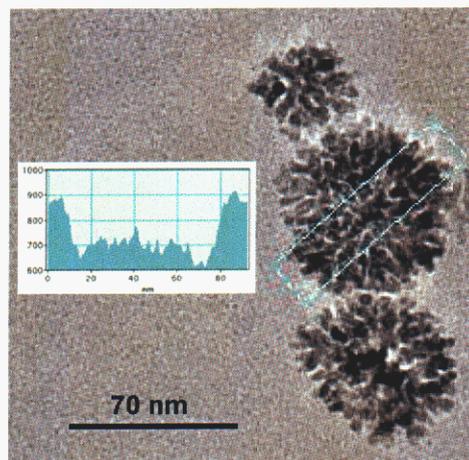
Very recently, we have observed another type of metallized liposome, which is shown in the TEM image in Figure 8. Based on density profiles of these nanostructures, the liposomes appear to have been coated with palladium grown in the form observed for the micelle-templated 3-dimensional dendrites instead of the nanometer-thick sheets, i.e, they have the appearance of the 3-dimensional nanodendrites but are hollow indicating an intact liposomal interior. These structures might serve as structural and functional units of nano-constructs such as a biomimetic chloroplast like that illustrated in Figure 9. We will explore the possibility of reliably

synthesizing such nanostructures and determine some of their physical and chemical properties.

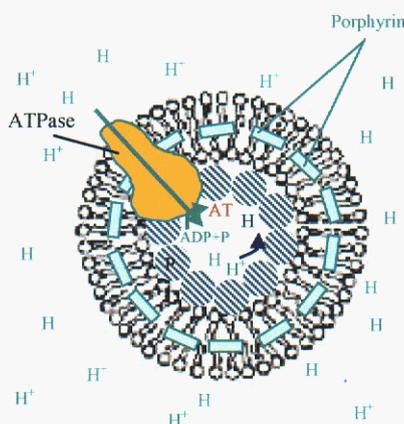
As just indicated, another opportunity that has arisen in the last few weeks is the possibility of making palladium nanostructures analogous to the platinum structures that we have studied extensively in the current year. Only a few experiments have been done with palladium, so we would like to further explore the differences and similarities of the synthesis using the photocatalytic/autocatalytic growth mechanism using these two metals and evaluate other possible metals for making such nanostructures.

Our original idea was to synthesize nanostructures purely photocatalytically, *i.e.*, without any autocatalytic reduction, which is inherently uncontrollable. This is possible with other metals, *e.g.*, silver. In the next year, we will turn our attention to silver and other metals in hopes of demonstrating our original idea of pre-positioning the porphyrin photocatalyst and then growing metal at the location of the photocatalyst molecules. In this regard, we have initiated studies of DNA-porphyrin complexes as templates for producing metal nanostructures such as nanowires.

Another approach is use the interface between an organic solvent and water to template formation of metal nanostructures. Since the tin-porphyrin photocatalyst is almost insoluble in water but readily soluble in organic

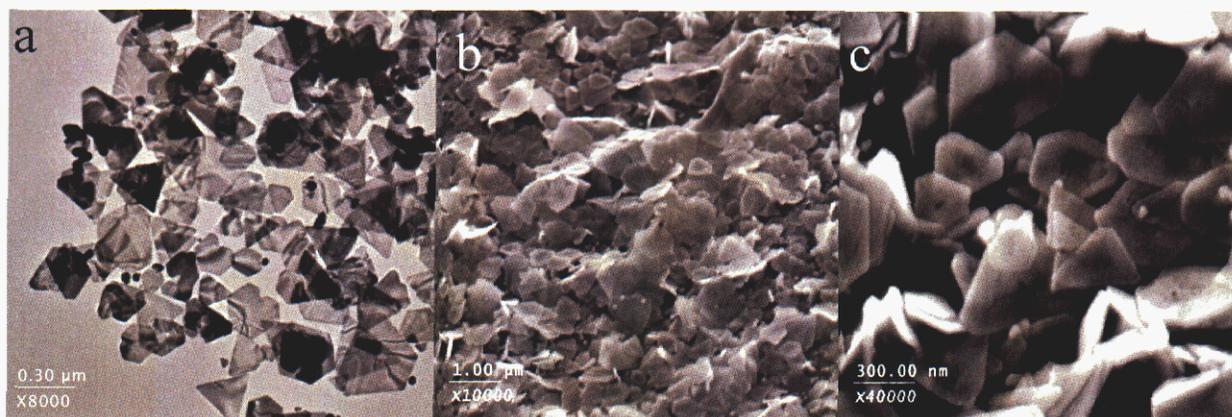


**Figure 8.** Palladium-coated liposomes. The Pd dendrites on the liposome surface are similar to those formed by Pt on micelles. The density profile (Inset) shows that these 3-D dendrites contain a liposome and thus appear 'hollow'.



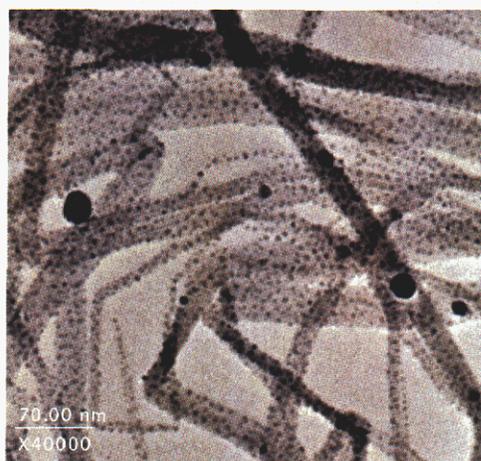
**Figure 9.** A biomimetic "chloroplast" based on platinized liposomes.

solvents and the metal precursor and the electron donor are highly soluble in water, the metal reduction must take place only at the organic/aqueous interface. In preliminary experiments, we found that metal reduction at the interface facilitates the growth of planar particles. In this way we have successfully made gold nano-plates of large aspect ratio. These gold nanoplates are illustrated in Figure 10, which shows large quantities of triangular nanoplates with edge lengths of 200-300 nm and thickness of 30 nm. The photocatalyst was dissolved



**Figure 10.** (a) TEM image of small Au nanoplates formed at the interface between organic and aqueous solution phases. (b), (c) SEM images of the Au nanoplates.

in benzene, while the gold precursor,  $\text{HAuClO}_4$ , and citric acid (ED) were dissolved in water. Figure 9(a) shows the TEM image of the Au nanoplates supported on carbon with a copper grid. SEM images of the nanoplates on ITO glass slides are shown in Figures 10(b) and 10(c). With higher acidity for the aqueous phase, triangular or hexagonal Au nanosheets with dimensions up to a few microns and thickness of  $\sim 30$  nm have been prepared. We will continue to explore this new approach to forming Au nanosheets in the next year. We expect that the Au nanoplates will have applications in single-molecule detection by surface enhanced Raman spectroscopy.



**Figure 11.** Porphyrin nanofibers with embedded silver nanoparticles formed by ascorbic acid reduction of silver cyanide.

Porphyrin nanofibers and rods are another templating material of interest to us for the photocatalytic synthesis of nanostructures. For example, preliminary results show that porphyrin nanofibers embedded with Ag nanoclusters are formed at the interface of the two-phase system composed of tin(IV) octaethylporphyrin in benzene,  $\text{K}[\text{Ag}(\text{CN})_2]$ , and ascorbic acid in water. As shown by the TEM images in Figure 11, the nanofibers are of a few microns in length and 20-50 nm in diameter, with embedded Ag nanoparticles of  $\sim 5$  nm in diameter. We will further investigate these nanofibers as well as several other methods of creating porphyrin nanofibers, which will serve as templates for photocatalytic reduction of metals and semiconductors in the next year.

## Current Publication References

### Journal articles:

1. "Controlled Synthesis of 2-D and 3-D Dendritic Platinum Nanostructures" Yujiang Song, Yi Yang, Craig J. Medforth, Eulalia Pereira, Anup K. Singh, Huifang Xu, Yingbing Jiang, C. Jeffrey Brinker, Frank van Swol, and John A. Shelnutt, submitted to *J. Am. Chem. Soc.* (July 2003).
2. "Photocatalytically Nanoengineered Foam-Like Platinum Materials Templated on Liposomes" Yujiang Song, Anup K. Singh, Zhongchun Wang, Yan Qiu, John A. Shelnutt, in preparation for *Angew. Chem., Int. Ed. Engl.* (Sept 2003).
3. "Synthesis and Molecular Simulation of the Formation of Di-Amino Acid Nanotubes and Pt-Nanoparticle-Nanotube Composites" Yujiang Song, Sivakumar R. Challa, Raid E. Haddad, Yan Qiu, Craig J. Medforth, Richard K. Watt, Frank van Swol, John A. Shelnutt, in preparation for *Chem. Commun.* (Sept 2003).

### Patents and patent disclosures:

1. "Photocatalytic control and autocatalytic growth of platinum nanostructures" John A. Shelnutt, Eulalia Pereira, Yujiang Song, Yi Yang, Frank van Swol, Craig J. Medforth.

### Conference Proceedings and Non-Reviewed Documents:

1. "Controlled Synthesis of 2-D and 3-D Platinum Dendrites Using Porphyrin Photocatalysts" Yujiang Song, Yi Yang, Craig J. Medforth, Eulalia Pereira, Anup K. Singh, Huifang Xu, Yingbing Jiang, C. Jeffrey Brinker, Frank van Swol, and John A. Shelnutt, American Chemical Society Annual Meeting, New York, NY, Sept 6-11, 2003.
2. "Synthesis and Control of Globular Platinum-Particle Nanoassemblies" Yujiang Song, Xiaolin Lu, Yi Yang, Craig J. Medforth, Frank van Swol, John A. Shelnutt, Materials Research Society, Spring Meeting, Apr 21-25, 2003
3. "Controlled Photocatalytic Growth of Platinized-Micelle Nanostructures" Yi Yang, Eulalia Pereira, Yujiang Song, Craig J. Medforth, Frank van Swol, C. Jeffrey Brinker, John A. Shelnutt, Materials Research Society Spring Meeting, Apr 21-25, 2003.

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