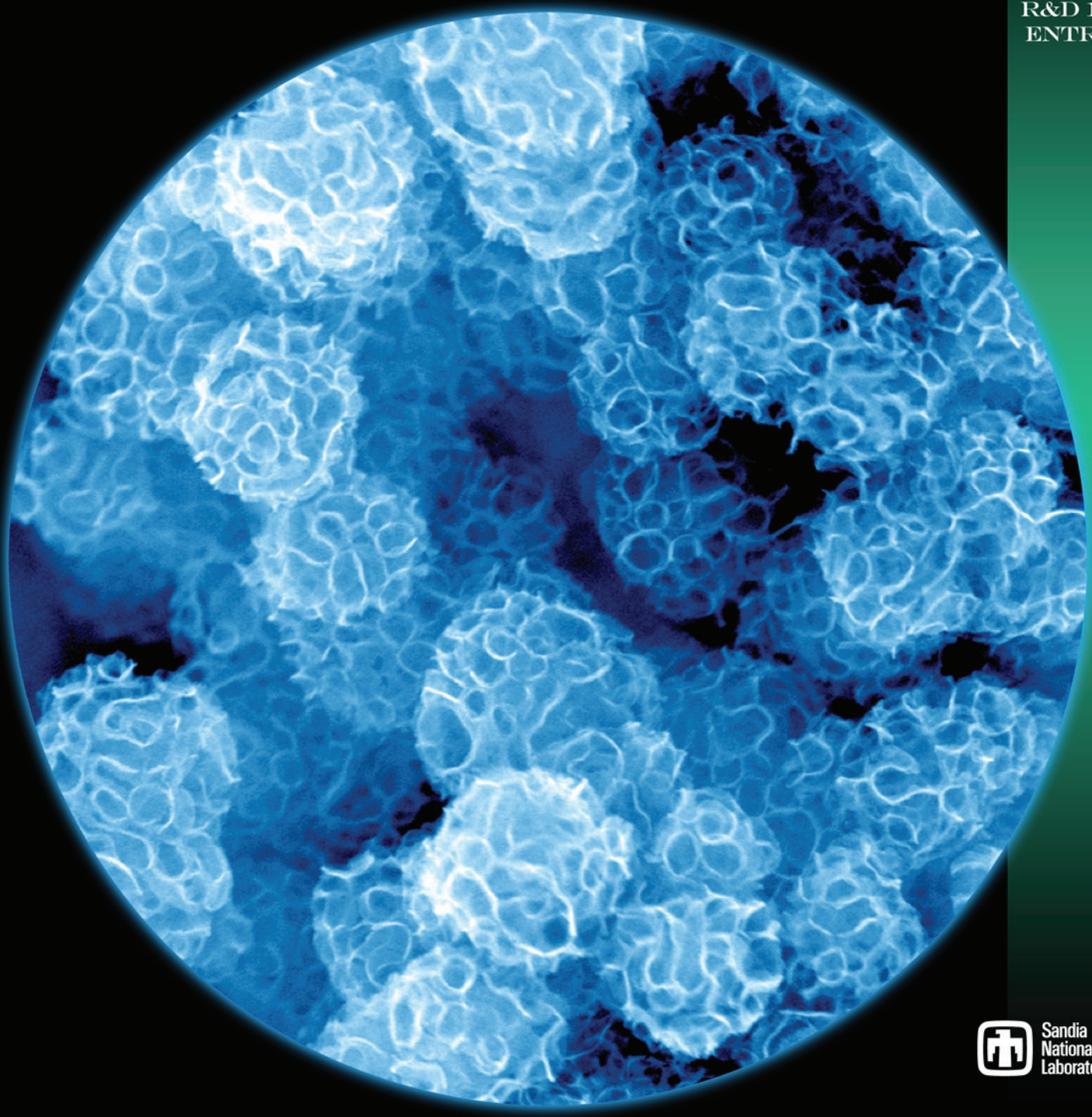


NANOCORAL™

Dendritic platinum nanostructures for renewable energy applications



R&D 100
ENTRY

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PRODUCT NAME

NanoCoral™ Dendritic platinum nanostructures for renewable energy applications

BRIEF DESCRIPTION

This Sandia National Laboratories technology produces novel size- and shape-controlled platinum nanostructures with applications in many areas; the first available product is an electrocatalyst for fuel cells.

PRODUCT FIRST MARKETED OR AVAILABLE FOR ORDER

Licensed July 2, 2008; first product (NanoCoral™) available on July 21, 2008

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PRODUCT PRICE

NanoCoral™ will cost approximately 4x platinum (Pt) spot price.

PATENTS OR PATENTS PENDING

Patents Issued:

1. US 7,374,599, B1, May 20, 2008, DENDRITIC METAL NANOSTRUCTURES, Shelnut, Medforth, Song (UNM), Pereira.
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Patent Applications:

3. US Patent Application #12/107,803, April 23, 2008, SINTERING RESISTANT NANOSCALE NOBLE METAL MORPHOLOGIES, van Swol, Shelnut, Song, Miller, Challa (UNM).
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5. US Patent Application #12/147,059, June 26, 2008, HIGHLY UNIFORM POROUS METALLIC NANOSHELLS, Shelnut, Song, Wang, Medforth (UNM).
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9. US Patent Application #11/995,954, Nov. 13, 2007, METALLIC NANOWIRE NETWORKS (filed), Shelnut, Song.
10. US Patent Application #2006/0,251,953 A1, Nov. 9, 2006, PHOTOCATALYTIC METHODS FOR PREPARATION OF ELECTROCATALYST MATERIALS, (Toyota, PCT published) Shelnut, Miller, Song, Takahashi (Toyota), Muldoon (Toyota), Kawamura (Toyota), Nagami (Toyota), Li (Toyota).

PRODUCT'S PRIMARY FUNCTION

We have developed an innovative nanotechnology for producing platinum catalysts that offers unique control over the shape, size, porosity, composition, stability, and other functional properties of platinum nanostructures compared with those achieved by existing methodologies. Novel catalysts and electrocatalysts produced by the Sandia National Laboratories (Sandia) approach are expected to reduce significantly the platinum metal usage and thus the cost of

Novel catalysts and electrocatalysts produced by the Sandia National Laboratories (Sandia) approach are expected to reduce significantly the platinum metal usage and thus the cost of platinum catalysts for use in fuel cells, solar cells, and other applications in the renewable energy sector.

platinum catalysts for use in fuel cells, solar cells, and other applications in the renewable energy sector.

Some of the platinum nanostructures also exhibit enhanced structural durability to ripening, a process by which small structural features become larger during fuel cell operation resulting in decreased active surface area. These ripening-resistant platinum nanostructures, such as those composed of holey nanosheets, preserve the high surface area and activity of these nanocatalysts in a wide variety of technologically and industrially important processes.

These platinum nanomaterials are produced by controlling the dendritic metal growth that occurs during the chemical reduction of aqueous platinum complexes, which was first reported by our group at Sandia. The **dendritic** growth produces branching metal arms that are approximately 3 nanometers (nm) in width with spaces between the branches of approximately 1 nm. Researchers attained control over the structure of these dendritic platinum materials through a combination of a photocatalytic seeding method pioneered at Sandia, and **templated dendritic growth** in or on soft or hard nanostructures, another technology developed at Sandia. The templating nanostructures include surfactant assemblies (liposomes, vesicles, bicelles, micelles, worm-like micellar networks, etc.), inorganic or organic microspheres and other structures, droplets in emulsions, and other microscale and nanoscale structures.

Researchers accomplished photocatalytic seeding and growth using various photoactive porphyrins, localized on or in the templating structure. Upon irradiation with light of visible wavelengths, the photocatalyst molecule absorbs a photon and subsequently is reduced by a sacrificial electron donor. The reduced porphyrin molecule, usually a Sn(IV) porphyrin, is a long-lived radical species that can reduce metal ions in solution to the zero valent metal. Under appropriate conditions, the metal deposits in the vicinity of the porphyrin molecule. A nanoparticle seed is produced as the photocatalytic reduction by the molecule and deposition of metal continues. When the seed grows large enough, it becomes catalytic for the oxidation of ascorbic acid and reduction of metal ions, resulting in the rapid autocatalytic dendritic growth of metal nanostructures. Typically ascorbic acid is used as the electron donor for its environmentally sensitive – green – attributes and participation in the dendritic growth process.

Figure 1 below shows scanning electron microscope (SEM) (figures 1 A, B, D) and transmission electron microscope (TEM) (figure 1C) images of several of the platinum nanostructures made by using the Sandia technology. The technology enables the size and shape of platinum structures to be deftly manipulated at the nanoscale. Of particular note are structures composed of dendritic nanosheets, such as the 3-dimensional globular dendrites (NanoCoral™) shown in figure 1B. Remarkably, these nanosheets can be transformed into “holey sheets” that exhibit enhanced structural durability under thermal, catalytic, and electrocatalytic reaction conditions. Monte Carlo computer simulations of the sintering processes show that the ripening-resistance of the holey nanosheets arises from a unique mechanism resulting from their negative curvature surfaces.

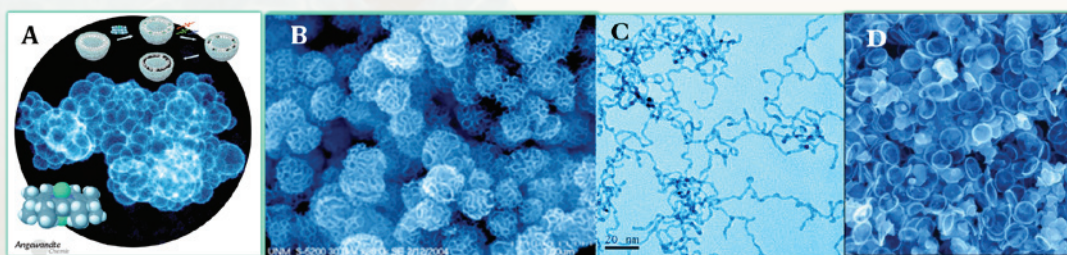


Figure 1. Some of the complex platinum nanostructures that can be produced, offering a wide range of potential applications in addition to hydrogen fuel cells; (A) platinum nanocage spheres templated by surfactant liposomes; (B) nanospheres composed of convoluted dendritic nanosheets templated by liposomal aggregates; (C) 2 nm diameter nanowire networks templated by worm-like micellar networks; and (D) platinum nanowheels templated by surfactant bicellar disks. (Images © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim)

PRODUCT'S COMPETITORS

The Pt (platinum) products offered by major suppliers are mainly preparations of Pt black (solid spherical Pt nanoparticles of different sizes and size distributions) together with Pt black supported on substrates (usually carbon). Some of the commercially available products are listed below. No competitors produce the unique shaped Pt nanostructures developed at Sandia, such as the nanowire networks or the Pt NanoCoral™.

Sigma Aldrich Chemical Company

- » Product #520780: fuel cell grade Pt black, 99.9+ %

Strem Chemicals

- » Product #78-0007: Platinum, 97% (2-5 nanometers)
- » Product #78-0009: Platinum, min. 90% (5-13 nanometers)
- » Product #78-1600: Platinum, 5% on activated carbon

BASF Corporation

- » Product #43838: Platinum black, high surface area

COMPARISON MATRIX

Pt Product	High Specific Activity	Long-range Conductivity	Enhanced Durability	Sintering Resistance	Surface Area (m ² /gm)
NanoCoral™	x4	Yes	Yes	Yes	30
Nanowire Networks	Not Measured	Yes	No	No	50-80
Pt black (BASF Corp.)	x1	No	No	No	30

The products offered by the competitors are primarily different preparations of platinum black, which are platinum nanoparticles of differing sizes and size distribution, and platinum black supported on substrates. None of our competitors produce platinum nanowire networks.

HOW PRODUCT IMPROVES UPON COMPETITION

There is a pressing need for new ways to optimize the efficiency of platinum usage in fuel cells. Existing commercially available materials are based on solid platinum nanospheres, either as Pt black (a powder of solid platinum nanospheres) or Pt black supported on carbon (solid platinum nanospheres dispersed on conducting carbon substrates). Shaped Pt nanostructures provide a novel strategy for improving the cost and efficiency of fuel cells by optimizing the design at the nanoscale. The methods developed at Sandia allow Pt catalysts to be designed with features optimized for fuel cell usage. For example, compared to Pt black the NanoCoral™ offers enhanced sintering resistance related to its structural durability. In addition, the nanosheets in NanoCoral™ have been found to offer increased specific activity compared to Pt black. The shaped materials also have potential advantages in the materials processing and fabrication of fuel cell electrodes. For example, many of the platinum nanostructures (e.g., nanowire networks, holey nanosheets, and dendritic nanosheets) possess long-range conductivity because of their extended crystalline metal structures.

PRODUCT'S PRINCIPAL APPLICATIONS

Renewable energy technologies are of great interest today because of the increasing costs and negative environmental impact associated with continued fossil fuel use. Hydrogen-powered fuel cell automobiles offer an attractive and

... durable, efficient, and inexpensive fuel cell electrocatalysts are required before fuel cells can be a practical and cost-effective solution to the growing energy crisis.

appealing energy alternative to current technologies; however, more durable, efficient, and inexpensive fuel cell electrocatalysts are required before fuel cells can be a practical and cost-effective solution to the growing energy crisis. The Sandia-developed nanotechnology offers one promising method for developing relatively

inexpensive platinum catalysts for hydrogen fuel cells using a green synthetic process.

The Sandia technology is described and documented in ten patents and patent applications that have recently been licensed by Sandia to Compass Metals, Inc. for commercialization in the area of fuel cells (see Appendix C). The platinum nanomaterials offer advantages in terms of enhanced activity per unit surface area, through-platinum electrical conductivity, novel fuel cell membrane electrode fabrication, and enhanced durability.

The holey nanosheets have unique sintering-resistance properties that result from their shape. The remarkable properties of holey sheets have just recently been recognized as one outcome of the metals nanostructuring research. Platinum holey-sheet nanostructures are now being evaluated by fuel cell companies as ripening-resistant electrocatalysts for fuel cells.

OTHER APPLICATIONS

Thus far, the Sandia technology has only been licensed for fuel cell applications, but the technology offers similar potential advantages in other catalytic and electrocatalytic areas, such as direct hydrogen-generating solar cells and electrolysis. Other anticipated areas of application are sensors, organic solar cells, nanotagging, imaging, and electronics.



SUMMARY

Dendritic and ripening-resistant holey-sheet nanocatalyst technology enables the size and shape of platinum structures to be manipulated at the nanoscale to produce novel platinum catalysts and electrocatalysts and other nanomaterials. In particular, the technology produces platinum nanomaterials that promise to dramatically reduce costs and improve the efficiency and durability of hydrogen fuel cells and other renewable energy technologies.

The metals nanostructuring technology is based on two novel platform technologies—templated dendritic nanostructure growth and photocatalytic seeding and growth. Both platform technologies were conceived, pioneered, and developed exclusively by Sandia. The metals nanostructuring technology is applicable to a wide range of metals, templating structures, and applications beyond those currently licensed. The benefits of the metal nanomaterials are just now beginning to be realized, and new opportunities are presenting themselves in solar cells, sensors, electronics, and catalysis.

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APPENDICES ITEMS

Appendix A

Articles about Nanostructured Platinum Catalysts: Dendritic and Ripening-resistant Hole-Sheet Nanocatalysts

Appendix B

References using this Technology

Appendix C

Patents

Appendix D

Letter of Support



APPENDIX ITEM A

Articles about Nanostructured Platinum Catalysts: Dendritic and Ripening-resistant Holey-Sheet Nanocatalysts

Synthesis of Platinum Nanocages Using Liposomes Containing Photocatalyst Molecules, Song, Y.; Garcia, R. M.; Dorin, R. M.; Wang, H.; Qiu, Y.; Shelnutt, J. A., *Angew. Chem., Int. Ed.* **2006**, 45, 8126-8130.

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Synthesis of Platinum Nanowire Networks Using a Soft Template, Song, Y.; Garcia, R. M.; Dorin, R. M.; Wang, H.; Qiu, Y.; Coker, E. N.; Miller, J. E.; Shelnutt, J. A., *Nano Lett.* **2007**, 7, 3650-3655.

Synthesis of Platinum Nanocages Using Liposomes
Containing Photocatalyst Molecules
Journal Cover

2009

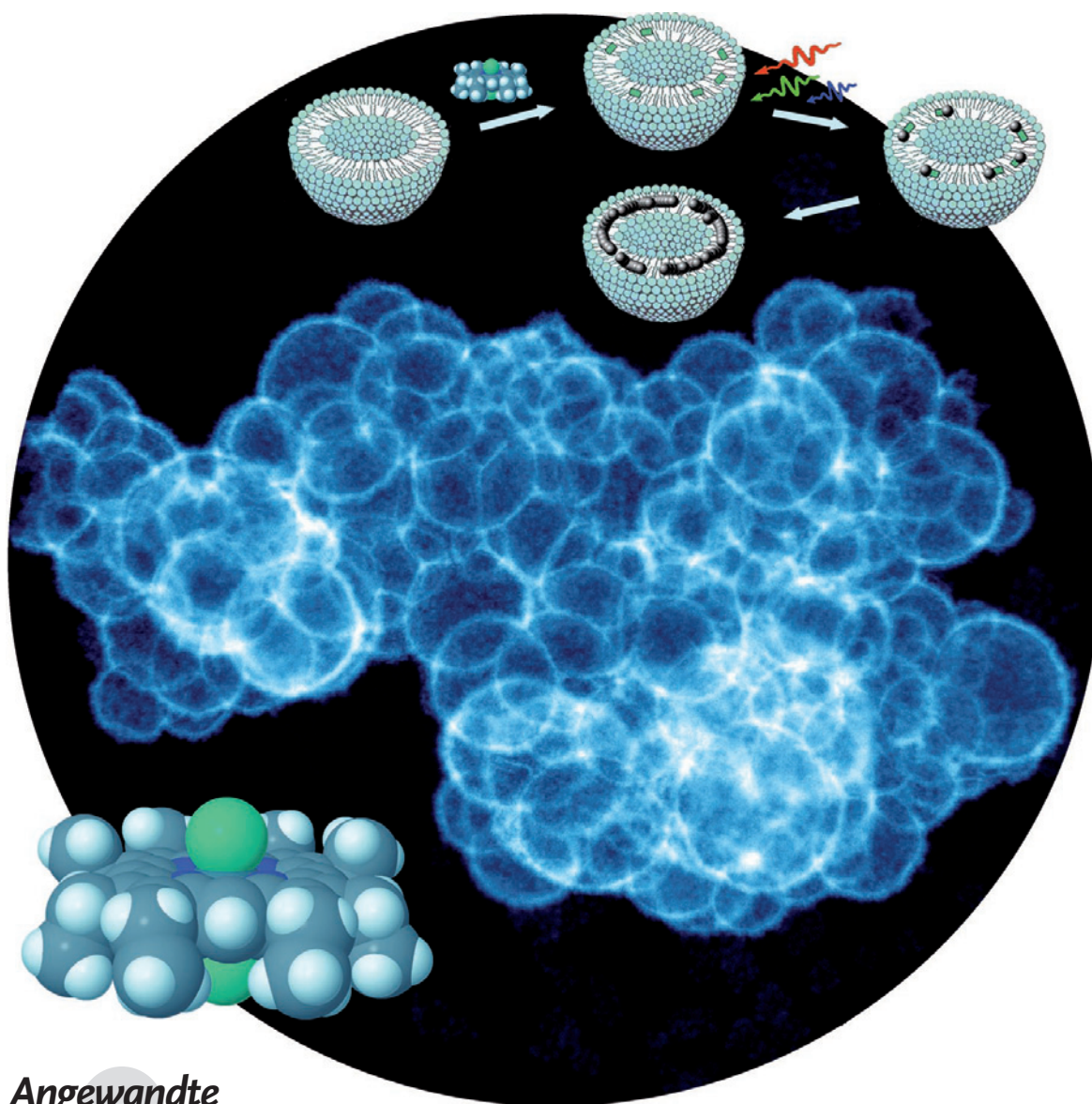
Communications

Hollow Nanostructures

DOI: 10.1002/anie.200602403

Synthesis of Platinum Nanocages by Using Liposomes Containing Photocatalyst Molecules**

Yujiang Song, Robert M. Garcia, Rachel M. Dorin, Haorong Wang, Yan Qiu, and
John A. Shelnett*



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Chemie

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Angew. Chem. Int. Ed. 2006, 45, 8126–8130

Self-Metallization of Photocatalytic Porphyrin Nanotubes

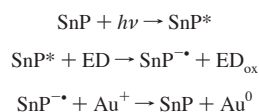
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Functional self-assembled nanostructures with well-defined shapes and dimensions are of great current interest^{1–3} for applications in electronics, photonics, light-energy conversion, and catalysis. Porphyrins are attractive building blocks for these nanostructures because of their electronic, optical, and catalytic properties. Recently, we showed that porphyrin nanotubes can be prepared by ionic self-assembly of two oppositely charged porphyrins in aqueous solution.⁴ These sturdy nanotubes represent a new class of porphyrin nanostructures for which the molecular building blocks can be altered to control their structural and functional properties. Here, we show that the nanotubes containing a Sn porphyrin are photocatalytic and can reduce metal ions from aqueous solution. The metal is selectively deposited onto the tube surfaces, producing novel composite metal nanostructures (Figures 1 and 2). These composites are themselves photocatalytically active and have potential applications as nanodevices.

Sn porphyrins are known to be good photocatalysts in homogeneous solutions,^{5,6} so we investigated whether the Sn porphyrins in the nanotubes make the tubes photocatalytic. To demonstrate photocatalytic activity of the tubes, we examined the reduction of aqueous metal complexes, for example, Au(I) and Pt(II) complexes. The photocatalytic reduction reaction mediated by Sn(IV) porphyrins in homogeneous solutions is described for reduction of a Au(I) complex by the following simplified cyclic reactions:



Au(I)-thiourea or -thiosulfate complexes were used with ascorbic acid as the electron donor (ED). These reductions are predominately photocatalytic, unlike those for many other gold complexes that may also involve chemical and photochemical reduction. The photochemical reduction is prevented by the higher stability of the Au(I) complexes relative to Au(III) complexes and their transparency to visible light. Autocatalytic growth of gold was found to be negligible.

The Sn-porphyrin-containing nanotubes used in the metallization reactions were prepared in aqueous solutions by ionic self-assembly of *meso*-tetrakis(4-sulfonatophenyl)porphyrin diacid ($\text{H}_4\text{TPPS}_4^{2-}$) and Sn(OH)(H₂O/OH) tetrakis(4-pyridinium)porphyrin ($\text{SnTPyP}^{5+/4+}$) as described previously.⁴ A transmission electron microscope (TEM) image of the porphyrin nanotubes before metal deposition is shown in Figure 1a. The tubes can be micrometers in length and have diameters typically in the range of 50–70 nm with approximately 20-nm thick walls. Images of the nanotubes caught in vertical

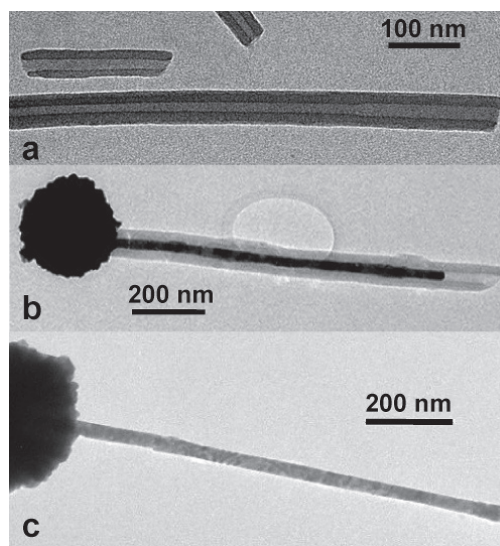


Figure 1. Transmission electron microscopy images of (a) the porphyrin nanotubes, (b) a gilded nanotube obtained using the Au(I)-thiourea complex, and (c) a gold wire obtained after the porphyrin tube has been dissolved away at pH 10 by adding 0.05 M NaOH. The latter demonstrates the structural integrity of the free-standing nanowires. Concentrations of the Au(I) complex and ascorbic acid were 1 and 10 mM, respectively; the light exposure time was 8 min at 800 nmol cm² s⁻¹.

orientations confirm a hollow tubular structure with open ends rather than a solid cylindrically symmetric structure.

When the nanotubes are used to photoreduce the positively charged Au(I)-thiourea complex, the metal is deposited exclusively within the hollow interior of the nanotubes, forming a continuous polycrystalline gold nanowire that is of the same diameter as the tube core (Figure 1b). For those tubes that contain nanowires, only continuous gold wires are found, that is, multiple short segments of wire are not observed in the same nanotube. In addition, the nanowires are typically terminated at one end of the nanotube with a gold ball of larger diameter than the tube. When the porphyrin nanotubes are dissolved by raising the pH, the gold wire and ball remain intact, as shown in Figure 1c. In contrast with the thiourea complex, reduction of the negatively charged Au(I)-thiosulfate complex produces gold particles mainly on the outer surfaces of the tubes (data not shown). These results suggest that the electrostatic and other interactions between the complex and the tube surfaces determine where the metal is deposited for the two oppositely charged complexes. Directional electron/energy transport within the tube walls might also play a role. (Experimental details

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Light-driven synthesis of hollow platinum nanospheres

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Hollow platinum nanospheres that are porous and have uniform shell thickness are prepared by templating platinum growth on polystyrene beads with an adsorbed porphyrin photocatalyst irradiated by visible light.

Hollow nanospheres possess tunable structural features such as shell thickness, interior cavity size, and chemical composition, leading to relatively high surface area, low density, material economy, and reduced cost compared with their solid counterparts.¹ Metallic hollow nanospheres are of special interest and importance due to various applications in biomedical,^{1–3} catalytic,⁴ and optical sciences.⁵ Previously, nanoscale metal shells have been prepared by metal deposition onto a central core followed by core removal,^{6–10} and co-assembly of metal nanoparticles with organic molecules.¹¹ Using unilamellar liposomes to confine the growth of metallic nanosheets within a liposomal bilayer, we recently used a tin(IV) porphyrin photocatalyst to control the sheet size to prepare spherical nanocages.¹² We now report a new method of preparing Pt nanospheres that utilizes polystyrene beads covered with a porphyrin photocatalyst to grow uniform and porous platinum nanoshells. Subsequent removal of the polystyrene core with an organic solvent results in hollow platinum nanospheres. Synthetic control over the nanoshell is realized by simply varying the concentration of platinum precursor at fixed light exposure.

Fig. 1 illustrates the synthetic scheme for the preparation of platinum hollow spheres, including evaporation induced self-assembly of hydrophobic tin(IV) octaethylporphyrin (SnOEP, Frontier Scientific) on hydrophobic polystyrene beads (Bangs Laboratories), irradiation with visible light to promote photocatalytic seeding, autocatalytic growth of seeds to form a platinum shell, and dissolution of the beads and SnOEP. The key to the synthesis is the generation of a large number of initial platinum seeds in the vicinity of the SnOEP molecules on each bead. When the seeds reach a critical size (about 2 nm), they become catalytic and autocatalyze the further reduction of platinum complex and growth of the seeds into dendrites until the Pt complex is completely consumed.^{13,14}

Consequently, many neighbouring small dendrites join to evenly cover the beads and form the spherical platinum nanoshells.

In a typical synthesis, 1 mL aqueous suspension of beads with an average diameter of 99 nm (10.2 wt% solid content) is mixed with 9 mL of ethanol containing 17.6 mg SnOEP in a round-bottom flask. Subsequently, ethanol and water in the mixture are removed by rotary evaporation resulting in pink flakes that peel off the glass wall. The flakes of polystyrene beads with adsorbed SnOEP are collected and further dried overnight in a desiccator under vacuum. Because SnOEP molecules are hydrophobic, they are expected to adsorb onto the hydrophobic surface of the beads. 1.76 mL of 20 mM aged K₂PtCl₄ aqueous solution and 0.24 mL water from a Barnstead Nanopure system (Chesterland, OH) are mixed with 2 mg of the dried beads coated with SnOEP. The mixture is sonicated for an hour in a water-bath cleaner to well suspend the beads. Next, 2 mL of 150 mM ascorbic acid (AA) aqueous solution is added to the above mixture. A representative UV–visible spectrum (Fig. 2, spectrum a) of the initial reaction system ([K₂PtCl₄] = 8.8 mM, [AA] = 75 mM, ~6.2 × 10¹² beads mL⁻¹, [SnOEP] = ~10.4 μM) shows a characteristic absorption peak at 402 nm for SnOEP molecules. The high sloping baseline reflects light scattering caused by the presence of the colloidal beads. The weaker absorption features of the Pt complex in spectrum a can be identified with the aid of the spectrum b (Fig. 2) of the pure aqueous Pt complex (8.8 mM).

The reaction system reacts under stirring and irradiation by two incandescent light sources (800 nmol cm⁻² s⁻¹) for 30 minutes. After discontinuation of the stirring, a colourless supernatant with a black precipitate at the bottom is observed, suggesting that the reduction reaction has gone to completion and the beads have settled out. The UV–visible

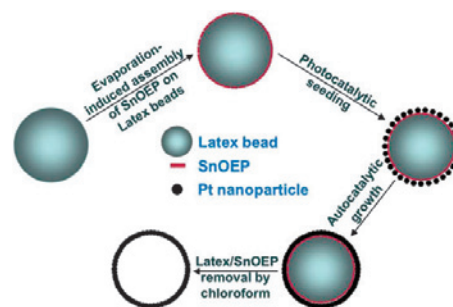


Fig. 1 Diagram of steps for the synthesis of hollow platinum nanospheres.

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**Foamlike Nanostructures Created from Dendritic
Platinum Sheets of Liposomes**
Excerpt

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**Foamlike Nanostructures Created from Dendritic Platinum Sheets
on Liposomes**

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The synthesis of novel dendritic platinum sheets of 2-nm thickness by the reduction of an aqueous metal complex with ascorbic acid in the presence of liposomes is reported. Variation of the reaction conditions, including incorporation of a tin porphyrin photocatalyst within the liposomal bilayer to initiate seed-particle growth, allows access to a diverse range of platinum nanostructures, including dendritic nanosheets of uniform diameters and convoluted foamlike structures composed of interwoven dendritic nanosheets. The mechanism of formation of these nanomaterials is investigated with regard to the photocatalytic generation of platinum nanoparticle seeds, the autocatalytic dendritic growth, and the templating on liposomes. The discrete nanospheres of foamlike platinum are of particular interest, as they may have advantages over conventional platinum black in some applications. For example, they will likely exhibit improved electrical connectivity and mass-transport properties in electrocatalytic applications. Electrochemical CO-stripping measurements and N₂ adsorption experiments show that the nanospheres of foamlike platinum possess high surface areas. In addition, these platinum foam nanospheres are as active as commercial platinum black in catalyzing the four-electron oxygen reduction reaction.

Introduction

Platinum has many technological applications^{1–3} such as in sensors,^{4–6} biosensors,⁷ and other devices,^{8–10} as a catalyst for reduction of tailpipe emissions, as an electrocatalyst in polymer electrolyte membrane (PEM) fuel cells,^{11,12} and as a catalyst in solar water-splitting devices.^{13,14} Because of the limited supply and high cost of Pt, researchers are developing

methods for eliminating or reducing the precious metal content of these catalysts. One way to minimize Pt usage is to increase catalytic efficiency by nanostructuring the platinum metal. As catalytic or device efficiency may depend on both the size and the shape of the platinum material,^{15–18} the preparation of nanostructured platinum with specific structural features is an area of considerable interest.

Nanostructured platinum has been prepared using a range of techniques. Nanotubes¹⁹ and mesoporous platinum films^{20,21} have been obtained by chemical and electrochemical reduction of platinum salts confined within the aqueous environment of the lyotropic liquid crystalline phases of surfactants. The templating channels²² of porous materials have also been used to produce nanoparticles,^{23–25} nanowires,^{26–28} or nano-

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Controlled Synthesis of 2-D and 3-D Dendritic
Platinum Nanostructures

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Controlled Synthesis of 2-D and 3-D Dendritic Platinum
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Abstract: Seeding and autocatalytic reduction of platinum salts in aqueous surfactant solution using ascorbic acid as the reductant leads to remarkable dendritic metal nanostructures. In micellar surfactant solutions, spherical dendritic metal nanostructures are obtained, and the smallest of these nanodendrites resemble assemblies of joined nanoparticles and the nanodendrites are single crystals. With liposomes as the template, dendritic platinum sheets in the form of thin circular disks or solid foamlike nanomaterials can be made. Synthetic control over the morphology of these nanodendrites, nanosheets, and nanostructured foams is realized by using a tin-porphyrin photocatalyst to conveniently and effectively produce a large initial population of catalytic growth centers. The concentration of seed particles determines the ultimate average size and uniformity of these novel two- and three-dimensional platinum nanostructures.

Introduction

Metal nanostructures are of considerable interest because of their importance in catalysis,¹ photochemistry,² sensors,³ tagging,⁴ and optical,⁵ electronic,⁵ and magnetic devices.^{3,6} Metal nanostructures have been synthesized in many forms, ranging from conventional metal colloids^{3,5} to modern near-monodispersed nanoclusters,^{7–16} shape-controlled nanocrystals,^{17–21} and

other nanostructures such as wires^{22,23} and sheets.²⁴ Nanostructured platinum is of particular interest for many applications, including catalysis,^{2,17,25} sensors,²⁶ and other devices.^{25,27–29} While a few platinum nanostructures have been reported, including nanoparticles,^{17,18} nanowires,^{22,23} nanosheets,²⁴ and others,^{30–33} the synthesis of additional types of nanostructures is highly desirable and potentially technologically important.

New methods for the synthesis of metal nanostructures are important for providing the reproducibility and control over

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Synthesis of Platinum Nanowire Networks
Using a Soft Template
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Synthesis of Platinum Nanowire Networks Using a Soft Template

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ABSTRACT

Platinum nanowire networks have been synthesized by chemical reduction of a platinum complex using sodium borohydride in the presence of a soft template formed by cetyltrimethylammonium bromide in a two-phase water-chloroform system. The interconnected polycrystalline nanowires possess the highest surface area ($53 \pm 1 \text{ m}^2/\text{g}$) and electroactive surface area ($32.4 \pm 3.6 \text{ m}^2/\text{g}$) reported for unsupported platinum nanomaterials; the high surface area results from the small average diameter of the nanowires (2.2 nm) and the 2–10 nm pores determined by nitrogen adsorption measurements. Synthetic control over the network was achieved simply by varying the stirring rate and reagent concentrations, in some cases leading to other types of nanostructures including wormlike platinum nanoparticles. Similarly, substitution of a palladium complex for platinum gives palladium nanowire networks. A mechanism of formation of the metal nanowire networks is proposed based on confined metal growth within a soft template consisting of a network of swollen inverse wormlike micelles.

Nanostructured platinum is important in many technical applications, including as an electrocatalyst in proton exchange membrane fuel cells^{1,2} and as catalysts in many reactions including solar water-splitting devices.^{3,4} However, the high cost and limited supply of platinum in these applications remain a challenge that demands its efficient commercial usage. The manipulation of the size and shape of platinum materials at the nanoscale can contribute to lowering Pt usage and achieving the necessary cost reduction.^{5–8} Previous efforts to produce platinum in various shapes have produced Pt nanowires,^{9,10} tetrahedra, and octahedra¹¹ using the polyol method. Cubic, cuboctahedral, and porous Pt nanoparticles have been synthesized using a capping polymer combined with differing reduction conditions.^{12–14} Pt nanotubes¹⁵ and mesoporous Pt films^{16,17} were obtained by chemical and electrochemical reduction of Pt salts confined within the aqueous environment of the lyotropic liquid crystalline phases of surfactants. In addition, Pt multipods have been synthesized by an induced anisotropic growth in organic solvents,¹⁸ and very recently monodispersed Pt nanocubes have been obtained by decomposing a Pt precursor with pressurized hydrogen.¹⁹ Finally, using

templating assemblies such as peptide tubes, surfactant micelles, multilamellar vesicles, unilamellar liposomes, and liposomal aggregates, with/without incorporated molecular photocatalysts, our group has successfully synthesized a series of platinum nanostructures with shape control, which include peptide-nanotube/nanoparticle composites,²⁰ globular nanodendrites,^{21,22} flat dendritic nanosheets,^{22,23} foamlike nanospheres composed of convoluted dendritic sheets,^{22,23} and porous nanocages.²⁴

Herein, we report the synthesis of platinum nanowire networks based on a modified phase-transfer method, similar to that originally developed by Brust et al. in the 1990s.^{25–27} Our approach is simple, environmentally friendly, and can be scaled up readily. Shape selectivity in this case relies on the formation of a network of wormlike micelles within an organic solvent phase that acts as a soft template for metal growth. On the basis of a templateless method, Ramanath and his co-workers^{28,29} have prepared Ag and Au nanowire networks via assembly of nanoparticles at water/toluene interface. However, this templateless strategy has not been shown to be capable of producing metallic nanowire networks other than Ag and Au. Using hard templates like the interconnected channels of mesoporous silica, similar platinum nanowire networks have been prepared by chemical³⁰ and electrochemical deposition^{31,32} of platinum followed by the removal of the silica framework. However, these methods generally produce poor networks because of the

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Synthesis of Platinum Nanowheels Using a Bicellar Template

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Synthesis of Platinum Nanowheels Using a Bicellar Template

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Disc-like micelles called bicelles are a rare class of microstructures composed of mixed lipid and detergent molecules.¹ Bicelles have also been obtained by self-assembly of two oppositely charged single-chain surfactants or by using a block copolymer.^{2–5} Investigations of bicelles have mainly focused on their alignment and their use as biomimetic membrane models especially for reconstitution of membrane proteins.^{6–10} However, bicelles also provide a unique inhomogeneous reaction environment possessing both low curvature and high curvature regions within a bilayer disk. Although the utilization of bicelles as soft templates for the synthesis of nanomaterials has been suggested,^{2,4} no examples of their successful use for this purpose have been reported. Herein, we show that bicellar templates can be used to control the growth of platinum, producing metal nanodisks and nanowheels.

Bicelles like that illustrated in Figure 1a can be assembled from the surfactants cetyltrimethylammonium bromide (CTAB) and sodium perfluorooctanoate (FC7).^{4,11} Jung and Zasadzinski reported the presence of a small percentage of bicelles mixed with dominant spherical vesicles and cylinders at a CTAB/FC7 molar ratio of 25:75 and 2 wt% total surfactant.⁴ The CTAB/FC7 molar ratio of 50:50 used in this work gives a higher yield of bicelles. For metal growth, platinum was chosen for its dendritic growth characteristics,^{12–14} and catalytic activity.^{15,16} Following our previous syntheses of Pt metal nanostructures using lipid vesicles,^{12–14} a typical Pt reduction reaction employed 264 mg of ascorbic acid (AA) as a reducing agent and 10 mL of 20 mM aqueous K₂PtCl₄ added to 10 mL of CTAB (1 mM) and FC7 (1 mM) (0.08 wt% total surfactant); these were allowed to react for at least 1 h at 25 °C to give a black precipitate. A transparent and colorless supernatant was obtained after reduction, suggesting that the reaction was complete. This was confirmed by the absence of UV–visible bands of the Pt(II) complex in the supernatant (Figure S1). Additional details of the synthesis are given in the Supporting Information.

Scanning electron microscopy (SEM) reveals that the black precipitate consists largely of circular platinum nanostructures, along with a small percentage of Pt metal without a defined morphology (Figures 1b, S2). The average diameter of the Pt nanostructures is uniform, 496 ± 55 nm, as determined by the measurement of 100 randomly selected nanostructures (Figure S3). The random packing of the structures results in their being tilted at different angles thus revealing their morphological details. In particular, the tilted circular structure shown in Figure 1c shows the flaring at the edge that produces the wheel-like morphology as well as the thin inner portion of the disk. In Figure 1d,e for a platinum nanowheel lying flat on the supporting substrate, the dendritic sheet features of the inner

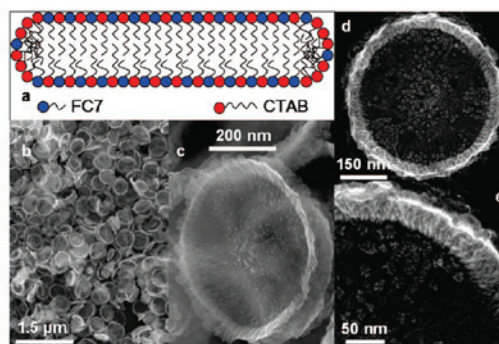


Figure 1. (a) Illustration of the cross-sectional view of a bicelle composed of two different surfactants, CTAB and FC7 in the present system. (b–e) SEM images of platinum nanowheels at different magnifications

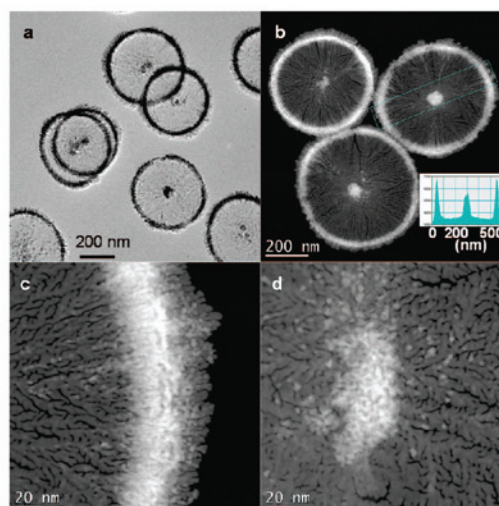


Figure 2. TEM (a) and HAADF STEM (b–d) image of platinum nanowheels (Inset: platinum density profile crossing selected region of a wheel in (b)).

disk are discernible. In these SEM images, very small globular dendrites¹⁴ are also seen growing outward from the dendritic sheet.

The transmission electron microscopy (TEM) images shown in Figure 2 further elucidate the morphology and growth pattern. In particular, the images reveal that the centers of the platinum nanowheels

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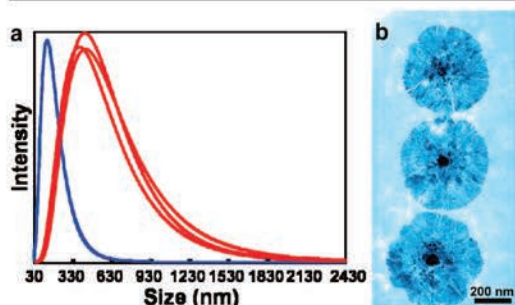


Figure 3. (a) DLS size distributions of bicelles in stock suspension containing 1 mM of CTAB and FC7 (blue), and three repetitions for the reaction system containing bicelles, Pt(II) salt, and AA (0.5 mM CTAB and FC7, 10 mM K_2PtCl_4 , and 150 mM AA (red)). (b) TEM image of platinum nanodisks.

are thickened (Figure 2a). The central thickening is possibly due to the fact that dendritic growth is initiated at a centrally located seed nanoparticle. Slow growth normal to the surface of the sheet occurs throughout the reduction reaction and is thus most extensive near the center of the sheet where growth occurs for the longest time. The reason that the seed particles locate at the center of the bicelle may be due to electrostatic forces caused by the high positive charge density⁴ at the edge of the bicelles. A radial mechanical stress also likely exists in the bicelle because the layers are bound together more tightly at the highly curved edge than at the loose central region, which can thus more easily accommodate the Pt seed particle.

The high-angle annular dark-field scanning TEM (HAADF-STEM) images (Figure 2b), for which the brightness is related to the Pt density, confirm that the rim and the center are much more dense than the intermediate region. Additionally, the Pt density profile (Figure 2, inset) indicates that the disk-like part between the center and the edge is roughly uniform in thickness. Consistent with other dendritic Pt sheets formed in lipid bilayers, the thickness is estimated to be about 2 nm.¹³ This can be seen by comparing the size of dendritic tips and the width of bright lines originating from the approximately vertically aligned dendritic branches in the edge region (see Figure S4). In high-magnification images (Figure 2c,d), the dendritic nature of the Pt nanowheels is obvious; the branches are 2–8 nm in width with 1–4 nm spaces between them. The X-ray diffraction pattern of the Pt nanowheels in Figure S5 exhibits characteristic reflection peaks of face-centered cubic Pt, and the peak broadenings are consistent with the nanoscale features seen in the TEM images.

It is likely that flaring occurs when the growing sheet reaches the edge of the templating bicelle. First, confined growth of Pt within the hydrophobic region of the bicellar bilayer¹⁷ gives the same dendritic sheet growth pattern observed previously for liposomal and vesicular bilayers.^{12,13} Second, close examination shows that branching of the inner dendritic sheet occurs from the center outward toward the rim. Moreover, it is likely that crowding occurs and simple sheet growth can no longer be supported when the growing sheet reaches the highly curved edge of the bicelle, leading to the flared edge. So, the diameter of the nanowheel would be determined by the size of the bicelle.

Dynamic light scattering (DLS) results for the stock CTAB/FC7 suspension (pH 6.7) given in Figure 3 (blue line) show that the hydrodynamic size of the bicelles is 144 ± 67 nm. Moreover, the DLS results for the reaction mixture obtained before significant Pt(II) reduction (Figure 3, red line) give a hydrodynamic diameter of 453 ± 216 nm as might be expected for the radically altered

solution conditions of this complex mixture of diluted bicellar solution, Pt salt and aqueous AA, and the different pH (2.7).^{2,18,19} In this mixture, the hydrodynamic size could also be increased by bicellar aggregation and the presence of other mesophases. Nevertheless, a bicellar diameter of 602 nm calculated from the hydrodynamic diameter (details given in the Supporting Information) is compatible with the diameter of the Pt nanowheels obtained from electron microscopy (496 nm), especially given that Pt sheet growth might shrink the bicelles.

To conclusively demonstrate that the flaring at the edge of the Pt nanowheels is a consequence of nanosheet growth reaching the edge of the bicelle, we lowered the Pt(II) concentration from 10 to 5 mM while holding the other parameters constant. For this case, circular dendritic nanodisks with thickened centers are observed, but without the flaring (Figures 3b and S6a). This was expected because the Pt complex is consumed before the sheet reaches the edge of the bicelle. This also provides further proof that the nanowheel grows outward from a central nucleation site.

Finally, when the original synthesis was conducted at 30 and 20 °C, nanowheels with small and large flarings at the edges (Figure S6b,c) were observed, respectively. This is consistent with the production of fewer bicelles containing seed particles at low temperature, leaving more Pt complex per seed and thus more extensive growth for the fewer seeded bicelles. Variation of total surfactant concentration provides additional opportunities to direct the growth of Pt to produce complex nanostructures. The metal growth methods described here might also be used as a means of imaging and discovering structural features of other types of surfactant assemblies and other templating materials.

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Supporting Information Available: Experimental details; UV–vis spectrum; SEM, TEM, and STEM images; size analysis plot; and XRD pattern. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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APPENDIX ITEM B

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APPENDIX ITEM C

Patents Issued:

1. US 7,374,599, B1, May 20, 2008, DENDRITIC METAL NANOSTRUCTURES, Shelnutt, Medforth, Song (UNM), Pereira.
2. US 6,627,048, Sept. 30, 2003, REDUCTIVE PRECIPITATION OF METALS PHOTSENSITIZED BY TIN AND ANTIMONY PORPHYRINS, Shelnutt, Abdesselam (UNM), Gong (UNM), Lutze (UNM).

US 7,374,599, May 20, 2008, DENDRITIC METAL
NANOSTRUCTURES:

2009



US007374599B1

(12) **United States Patent**
Shelnutt et al.

(10) **Patent No.:** **US 7,374,599 B1**
(45) **Date of Patent:** **May 20, 2008**

(54) **DENDRITIC METAL NANOSTRUCTURES**

6,660,058 B1 12/2003 Oh et al.

(75) Inventors: **John A. Shelnutt**, Tijeras, NM (US);
Yujiang Song, Albuquerque, NM (US);
Eulalia F. Pereira, Vila Nova de Gaia
(PT); **Craig J. Medforth**, Winters, CA
(US)

(73) Assignee: **Sandia Corporation**, Albuquerque, NM
(US)

(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 561 days.

(21) Appl. No.: **10/887,535**

(22) Filed: **Jul. 8, 2004**

(51) **Int. Cl.**
C22B 5/20 (2006.01)

(52) **U.S. Cl.** **75/370; 148/430; 419/23**

(58) **Field of Classification Search** **75/255,**
75/351, 743

See application file for complete search history.

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Primary Examiner—Roy King

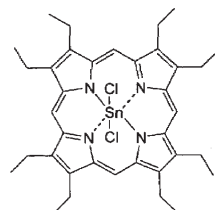
Assistant Examiner—Weiping Zhu

(74) *Attorney, Agent, or Firm*—Carol I Ashby

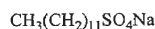
(57) **ABSTRACT**

A method for making dendritic metal nanostructures using a
surfactant structure template, a metal salt, and electron
donor species.

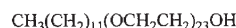
18 Claims, 10 Drawing Sheets



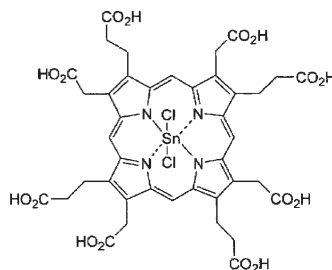
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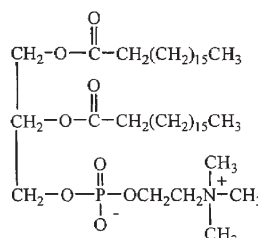
SDS



Brij-35



SnUroP



DSPC

US 6,627,048, Sept. 30, 2003, REDUCTIVE PRECIPITATION OF METALS PHOTOSENSITIZED BY TIN AND ANTIMONY PORPHYRINS.

2009



(12) **United States Patent**
Shelnutt et al.

(10) **Patent No.:** US 6,627,048 B1
(45) **Date of Patent:** Sep. 30, 2003

(54) **REDUCTIVE PRECIPITATION OF METALS PHOTOSENSITIZED BY TIN AND ANTIMONY PORPHYRINS**

(75) **Inventors:** John A. Shelnutt, Tijeras, NM (US); Weiliang Gong, Albuquerque, NM (US); Abdesselam Abdelouas, Nantes (FR); Werner Lutze, Albuquerque, NM (US)

(73) **Assignee:** Sandia Corporation, Albuquerque, NM (US)

(*) **Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 179 days.

(21) **Appl. No.:** 09/846,593

(22) **Filed:** Apr. 30, 2001

(51) **Int. Cl.⁷** C07C 1/00

(52) **U.S. Cl.** 204/157.75; 204/157.4

(58) **Field of Search** 204/157.4, 157.75

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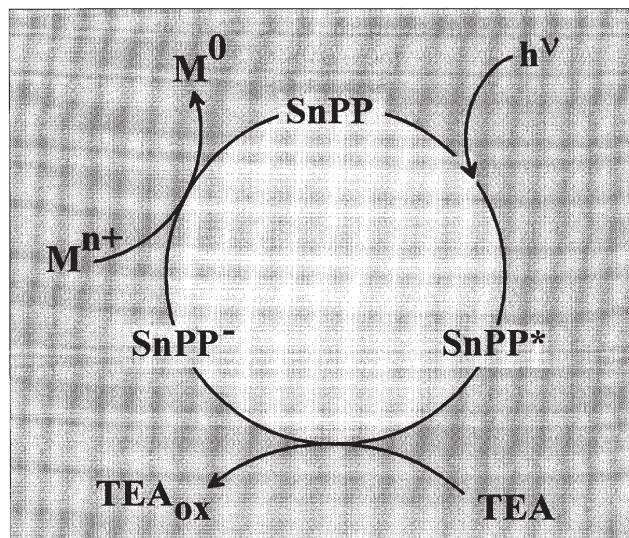
Primary Examiner—Edna Wong

(74) *Attorney, Agent, or Firm*—Elmer A. Klavetter

(57) **ABSTRACT**

A method for reducing metals using a tin or antimony porphyrin by forming an aqueous solution of a tin or antimony porphyrin, an electron donor, such as ethylenediaminetetraacetic acid, triethylamine, triethanolamine, and sodium nitrite, and at least one metal compound selected from a uranium-containing compound, a mercury-containing compound, a copper-containing compound, a lead-containing compound, a gold-containing compound, a silver-containing compound, and a platinum-containing compound through irradiating the aqueous solution with light.

16 Claims, 2 Drawing Sheets



APPENDIX ITEM D***Letter of Support******Notification of a 2009 Award of Excellence in Technology Transfer by the Federal Laboratory Consortium***

January 27, 2009

Dear Mr. Burdick:

It is our great pleasure to inform you that "Novel Dendritic Platinum Catalysts for Fuel Cells" has been selected as a winner of the 2009 Award for Excellence in Technology Transfer.

As you know, the Award for Excellence in Technology Transfer is presented annually by the Federal Laboratory Consortium for Technology Transfer (FLC). The award recognizes laboratory employees who have accomplished outstanding work in the process of transferring a technology developed by a federal laboratory to the commercial marketplace. This year your laboratory is one of a select number of recipients, an indication that your nomination was truly of the highest caliber.

A distinguished panel of technology transfer experts from industry, state and local government, academia, and the federal laboratory system evaluated the nominations. That yours was chosen as the cream of the crop by this broad cross-section of evaluators certainly enhances the award's value.

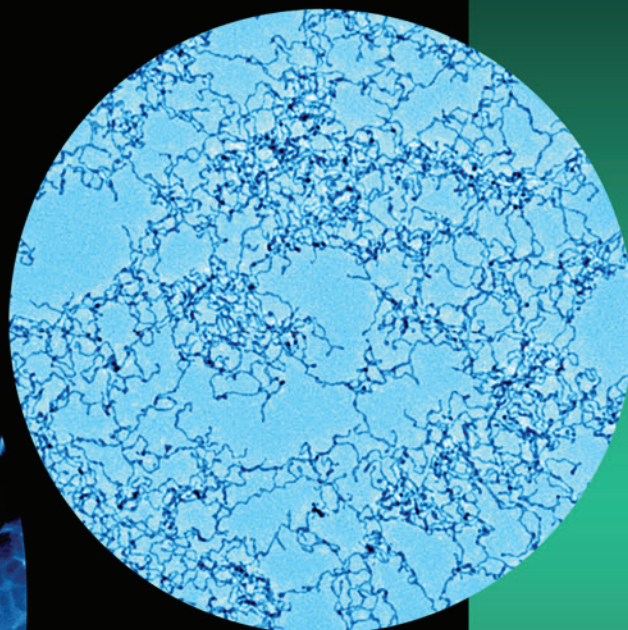
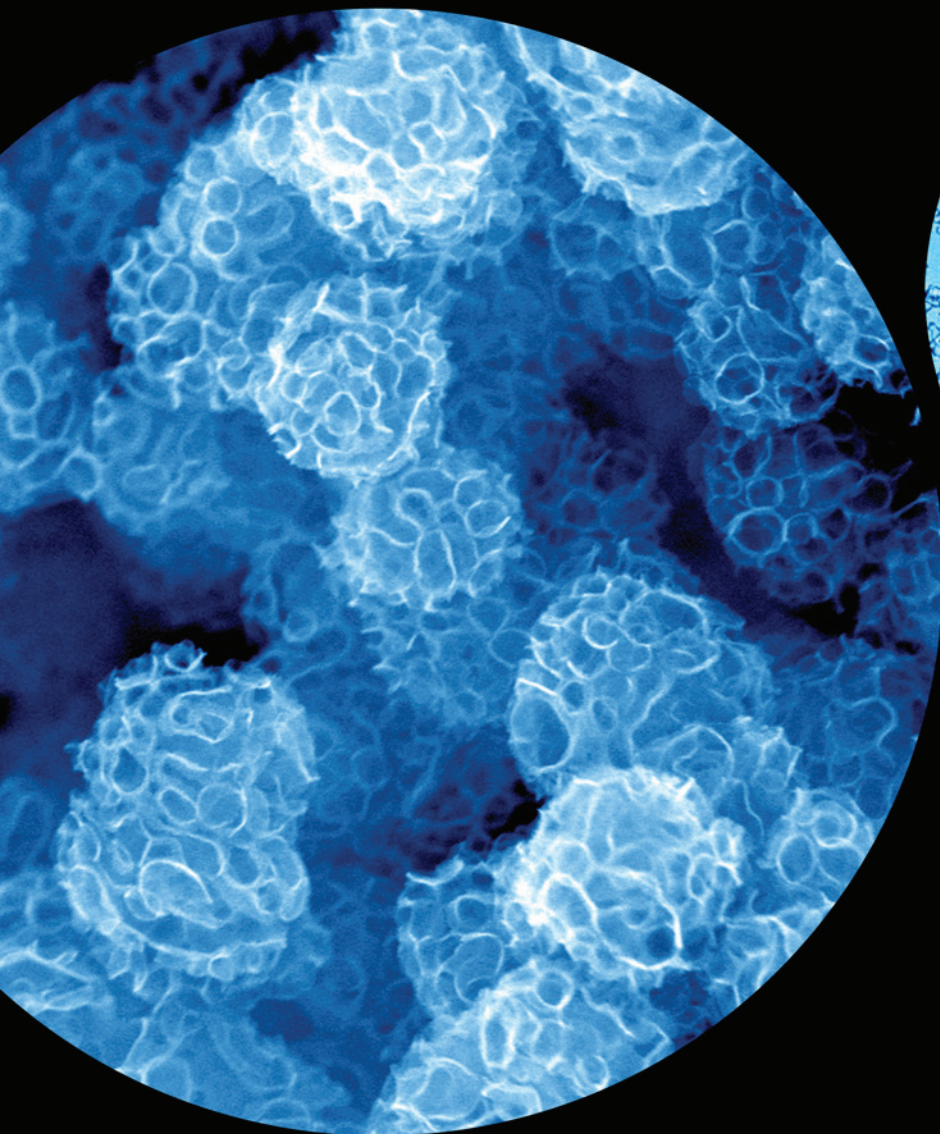
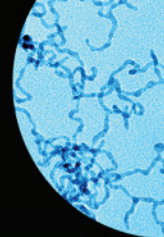
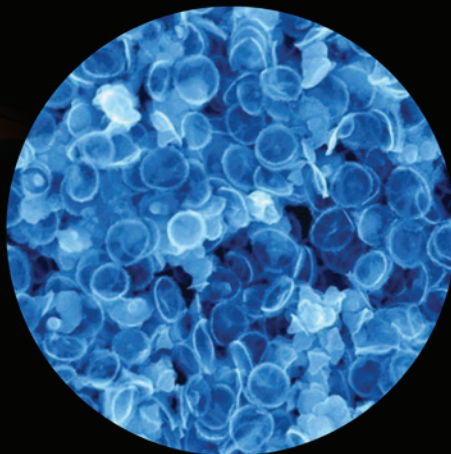
Your laboratory will be recognized at an award ceremony on Thursday, May 7, 2009 at the FLC National Meeting in Charlotte, North Carolina. We hope that you will be able to attend. Befitting such a prestigious honor, the FLC has invited to the National Meeting officials from the Department of Energy to recognize your accomplishments. A representative from the FLC Management Support Office will soon contact you to begin making the necessary arrangements to participate in the ceremony.

On behalf of the FLC, we extend our sincerest congratulations on a job well done.

Sincerely,

Dr. J. Scott Deiter
FLC Chair

Lorraine Flanders
FLC Awards Committee Chair
Michele D. Chambers
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