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Metal-Lipid Nanocomposites from Reconfigurable Bicellar Structures

John A. Shelnutt
Sandia National Laboratories
Molecular Nanocomposites Project

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Team: Yujiang Song; Darryl Y. Sasaki; Frank van Swol; Sivakumar Challa; Rachel Dorin; Robert Garcia

Motivation – Our goal is to develop nano-to-microscale structures that allow structural and functional manipulation, interrogation, and fabrication of new bio/nano composites and interfaces. The ability to *in situ* reconfigure or adapt structure and thereby control function is important for developing new classes of bioinspired nanomaterials and functional behaviors. The overall objective is the development of new methods for materials design, development of new building blocks, and organization of the building blocks by self-assembly, directed assembly, templating, and non-covalent interactions. Ultimately these new functional nanocomposites will be integrated into platforms allowing their structural and functional characterization, establishment of structure-property relationships, and incorporation in bio/nano devices for diverse applications. One aspect of our research involves reconfigurable and adaptible lipid assemblies, which respond to differing solution condititions by altering the structure of the lipid assembly or by forming hierarchical superstructures. These reconfigurable assemblies can then be used as templates for the growth of metal nanostructures and metal-lipid nanocomposites. Liposomes and bicelles are lipid structures that can be altered by changes in solution conditions, relative lipid concentrations, presence or absence of metal ions, temperature, and other factors. In addition, they can serve as templates for metal growth to produce metal structures that reflect the present morphology of the lipid assemblies. Our current efforts are directed toward establishing control over these reconfigurable lipid structures and utilizing them to template the growth of catalytic metal nanomaterials and nanocomposites.

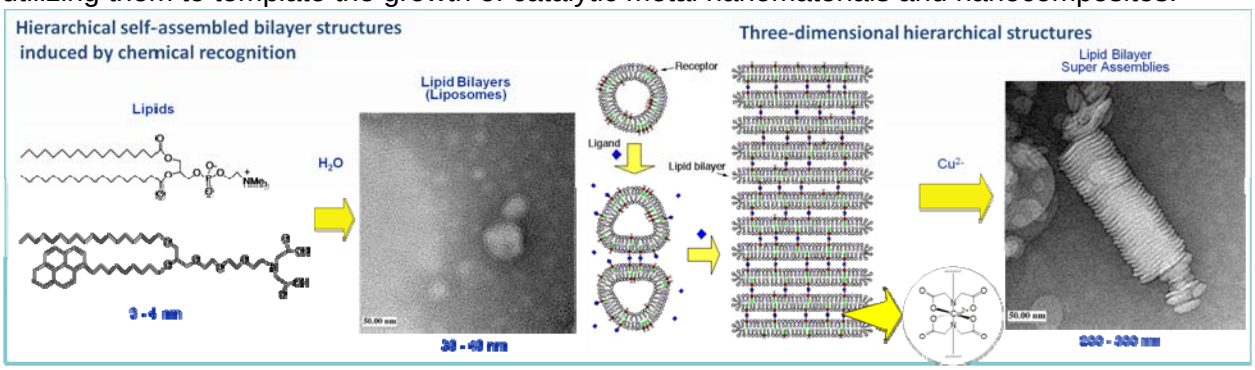

Fig. 1. Lipids used to form metal-sensitive liposomes and their conversion to stacks of lipid bicelles.

Background – Our use of reconfigurable lipid assemblies as templates for directed synthesis of metal nanomaterials is an outgrowth of our prior work in two area—the dendritic growth and photocatalytic control of metal nanostructres [1-5] and the structural control of liposomes and bicelles [6,7]. Fig. 1. illustrates the use of lipids that bind metal ions to control the interconversion of liposomes into bicelles and their hierarchical self-organization in to bicellar stacks. Metal ion binding can also cause the differential aggregation of metal-bound and unbound lipid molecules in the liposomes, which can be used as a sensing mechanism and as a means of controling the morphology of the lipid structures. Fig. 2. illustrates our use of various lipid assemblies as templates to control the dendritic growth of platinum metal to produce a wide variety of metal nanostructures, including globular Pt nanodendrites, flat dendritic nanosheets, foam-like nanospheres, nanocages, and nanowire networks.

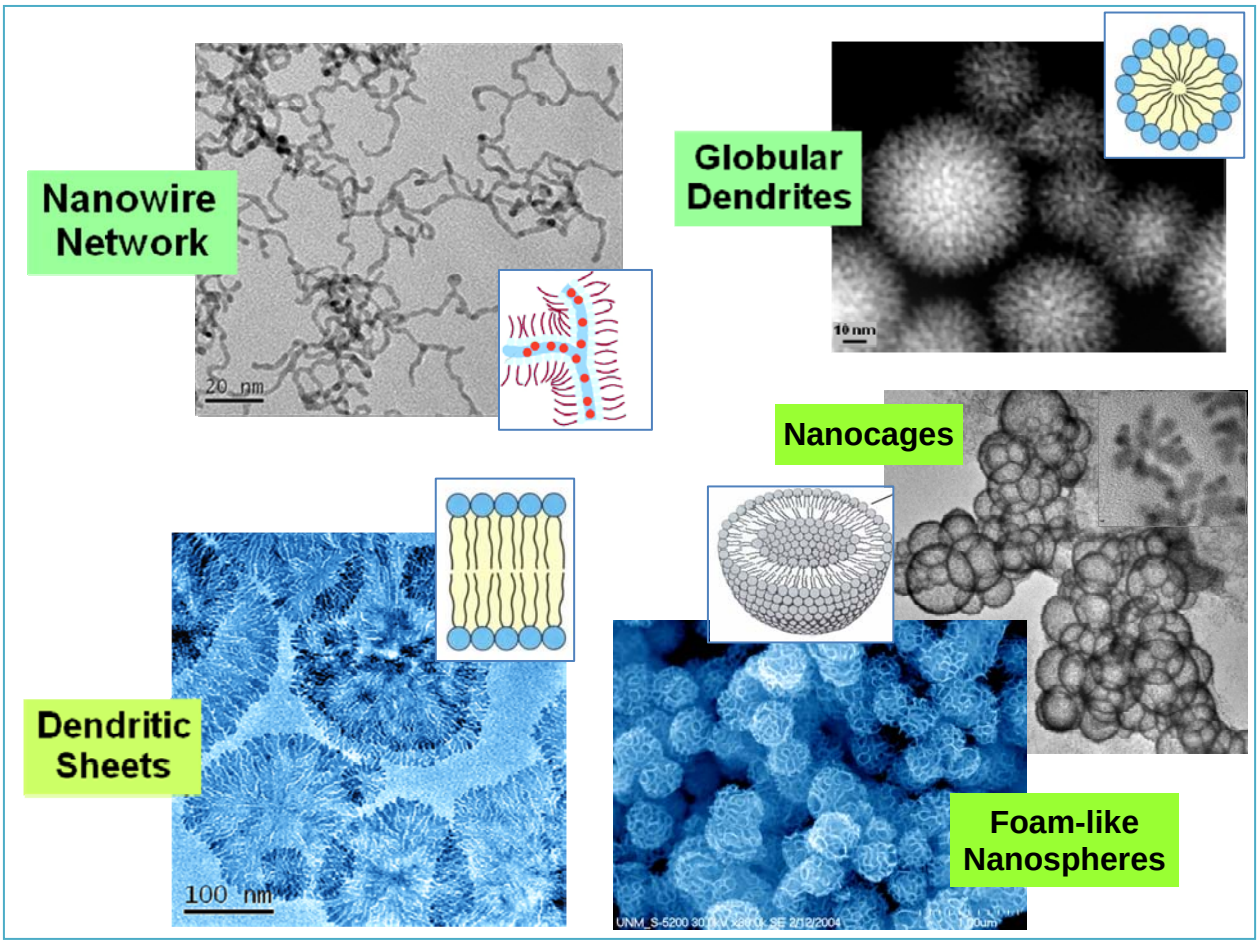

Fig. 2. Platinum nanomaterials produced with various templates obtained from lipid assemblies: (a) worm-like micellar networks, (b) micelles, (c) large liposomes or vesicles, and (d) unilamilar liposomes.

Platinum has technological applications in sensors, biosensors and other devices, and as catalysts and electrocatalysts for reduction of tailpipe emissions, polymer electrolyte membrane (PEM) fuel cells, and solar water-splitting devices. Because of the limited supply and high cost of platinum, researchers are developing methods for reducing the precious metal content in these applications. One way to minimize Pt usage is to increase catalytic efficiency by nanostructuring high-surface-area morphologies that are resistant to sintering/ripening processes. Our recent studies of bicelles and bicelle stacks aid in understanding the interactions of various lipid assemblies as well as their metal-templating properties that lead to formation of some extraordinary metal nanostructures using these bio-inspired templates.

New Insights and Directions – During the past year we have extended and combined our original work in these two research areas of reconfigurable lipid assemblies and templated growth of dendritic metal nanostructures. In the area of reconfigurable and responsive lipid assemblies, we have investigated the multi-component system involving two lipids, one of which binds metal ions, by varying the concentrations of lipids and metal ions to determine the amounts of each component necessary to induce stacking as shown on the right in Fig. 1. In the TEM study of the resultant lipid assembles, we also discovered a liposomal folding mechanism by which the stacks of bicelles may form, which might also play a role in biology.

Remarkable new platinum nanomaterials have resulted from the combined use of bicelles and

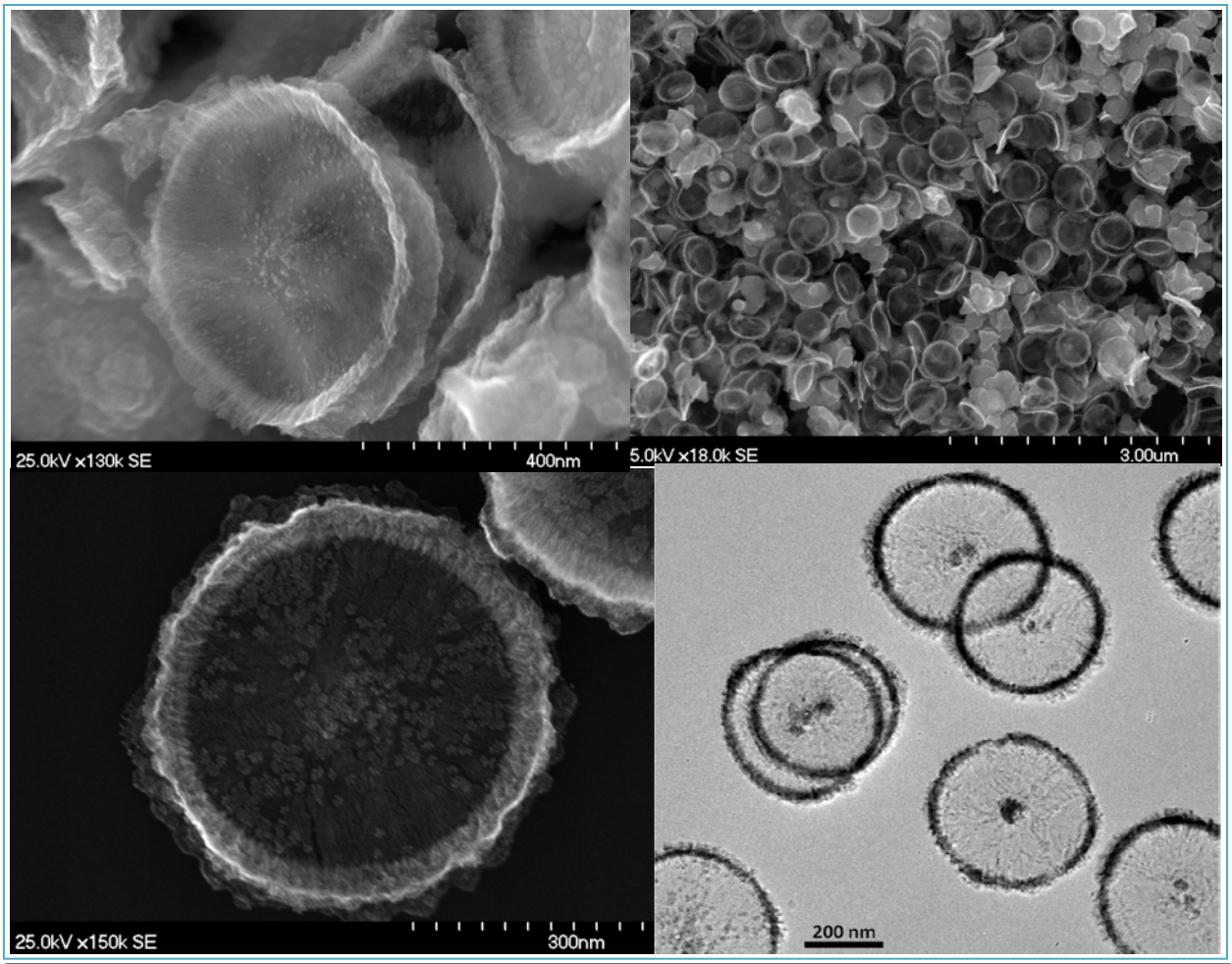

Fig 3. SEM images of platinum nano-coins produced by dendritic growth of metal with lipid bicelles composed of the two surfactants shown in Fig. 4.

dendritic metal growth in these lipid assemblies. Using lipid bicelles as templates for dendritic platinum growth, we produced the wheel-shaped nano-coins shown in the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of Fig. 3. The lipids and reactants used to synthesize the Pt nano-coins are illustrated in Fig. 4.

The stacking of bicelle disks was also investigated by Monte Carlo simulation of hard circular cylinders. Simulations at various packing fractions (not shown), demonstrate the oriented ordering characteristic of hard coins. Hard coins do not overlap and have no short-range and no long-range interactions. The simulations provide an understanding of the super-stacks of Pt coins and bicelles and verify that interaction between bicelles must play a role in their stacking.

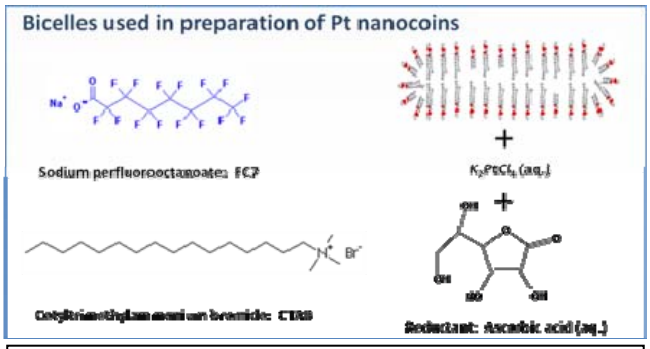

Fig 4. Surfactants and reactants used in producing the platinum nano-coins by dendritic growth of metal with lipid bicelles composed of the two surfactants shown.

TEM studies and Monte Carlo simulations of

the sintering process of platinum dendritic nanosheets demonstrate the formation of persistent nanopores during sintering and the formation of sintering-resistent holey sheets (Fig. 5). This study illustrates one of the unique properties of these new bionanomaterials, which is of particular importance for catalysis. The nanopores form quickly and their diameters is close to a critical value related to the sheet thickness at which they persist for long times during sintering. In the present case, the persistent pores also form in the thinnest possible Pt sheet (2-3 nm) to give the highest surface area possible in a sintering-resistant holey sheet morphology.

In conclusion, lipid bicelles have successfully used as soft-templates for the first time for the growth of dendritic platinum nano-coins. The lipid stacks of bicelles were prepared via chemical recognition and these will be platinized to form nanoscale Pt nano-coin stacks. Monte Carlo simulations aid in understanding for the assembly and organization of both the Pt coins and the lipid stacks. In addition, *in situ* TEM studies and Monte Carlos simulations of the dendritic Pt nanosheets show that they for holely nanosheets that are resistant to further sintering, indicating that the Pt nano-coins may also have similar sintering-resistant properties due to their similar dendritic and sheet-like structural features.

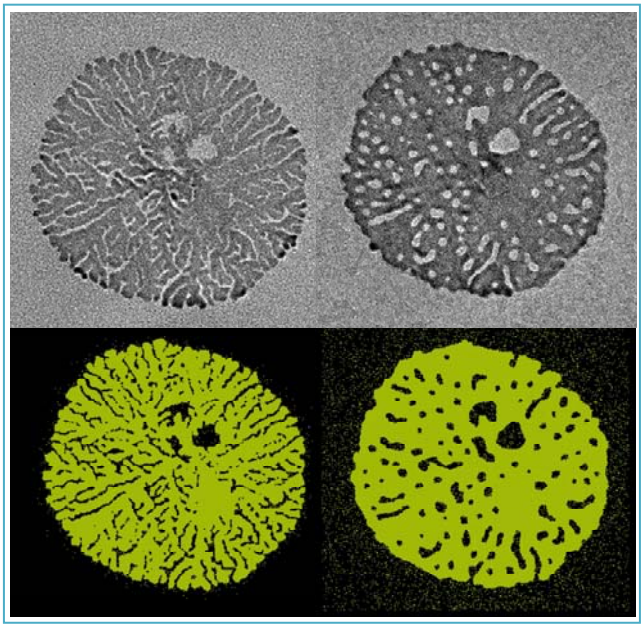

Fig 5. Sintering of Pt dendritic sheets like that forming the 'spokes'of the platinum nano-coins in the electron beam for 0 and 40 minutes (top) and Monte Carlo simulations of the sintering process showing the conversion of the dendrites to the sintering-resistant holey nanosheet.

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Soft-Template Synthesis of Platinum Nano-Coins Using Bicelles

Yujiang Song,[1] Rachel M. Dorin,[2] Robert M. Garcia,[2] Darryl Y. Sasaki,[1] Sivakumar R. Challa,[2] Frank van Swol,[1,2] John A. Shelnutt[1,3]

[1]*Nanomaterials Sciences and Biomolecular Interfaces & Synthesis Departments, Sandia National Laboratories, Albuquerque, NM 87185, USA.*

[2]*Departments of Chemistry and Chemical & Nuclear Engineering, University of New Mexico, Albuquerque, NM 87131, USA.*

[3]*Department of Chemistry, University of Georgia, Athens, GA 30602-2556, USA; E-mail: jasheln@unm.edu*

Sandia National Laboratories — A Department of Energy National Laboratory

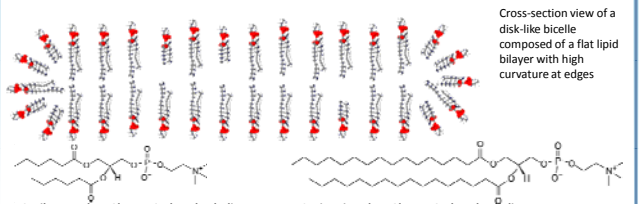
The University of New Mexico

The University of Georgia

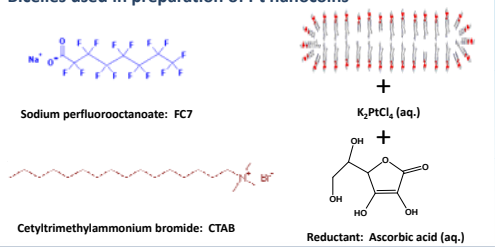
Abstract

Platinum has technological applications in sensors, biosensors, and other devices, and as catalysts and electrocatalysts for reduction of tailpipe emissions, in polymer electrolyte membrane (PEM) fuel cells, and in solar water-splitting devices. Because of the limited supply and high cost of Pt, researchers are developing methods for reducing the precious metal content in these applications. One way to minimize Pt usage is to increase catalytic efficiency by nanostructuring high-surface-area morphologies that are resistant to sintering processes. Herein, we report the synthesis of remarkable platinum nanocoins by using soft surfactant assemblies called bicelles, as templates. Monte Carlo simulations have been performed to provide understanding of the stacking and packing properties of the templating bicelles and of the resulting platinum 'nanocoins'. Monte Carlo simulations of the sintering of dendritic platinum sheets suggests that they form holey sheets, which are resistant to further sintering and thus preserve active surface area. The studies of bicelles and bicelle stacks also aid in understanding the interactions of various lipids that lead to formation of these extraordinary assemblies.

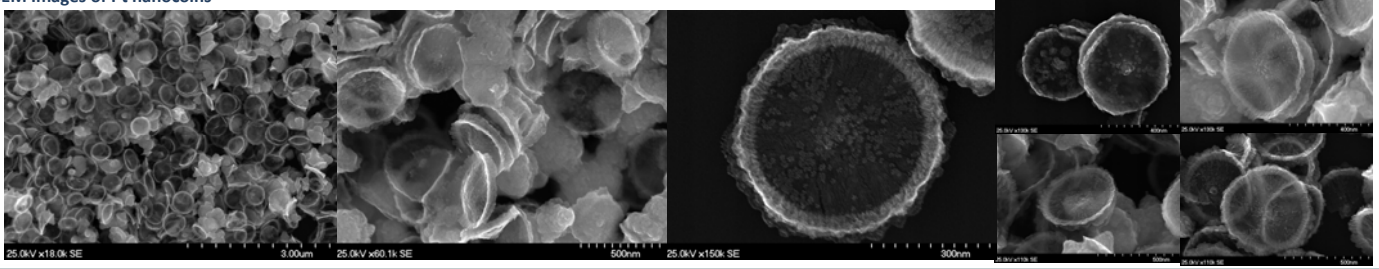
A typical bicelle: Co-assembly of short- (DHPC) and long-chain (DMPC) lipids



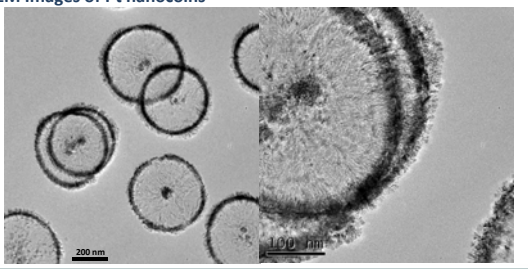
Bicelles used in preparation of Pt nanocoins



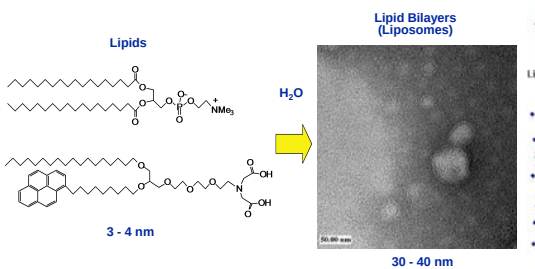
SEM Images of Pt nanocoins



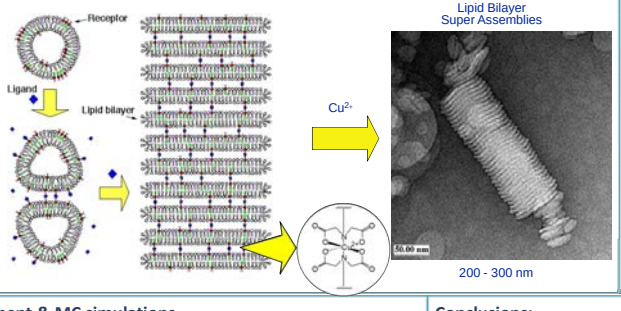
TEM Images of Pt nanocoins



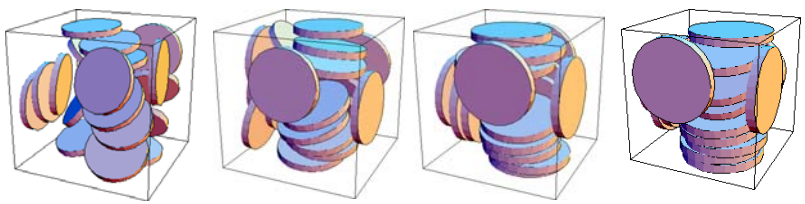
Hierarchical self-assembled bilayer structures induced by chemical recognition



Three-dimensional hierarchical structures

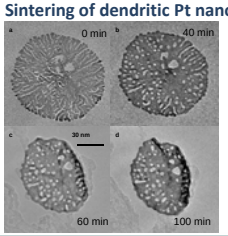


Monte Carlo Simulations



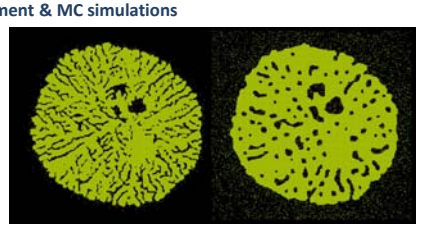
Monte Carlo simulations of hard circular cylinders (coins) at various packing fractions (0.15, 0.22, 0.3, and 0.43 volume fraction shown left to right), demonstrating the oriented ordering characteristic. Hard coin means no overlapping and no short-range and no long-range interactions. This is purely a geometrical effect, providing understanding of the Pt coins and the lipid super-stacks.

Sintering of dendritic Pt nanosheets to form holey sheets: experiment & MC simulations



Holey sheet formation is observed during the electron-beam heating of a 2-nm thick Pt dendritic sheet (at left) for different times.

Monte Carlo simulations of platinum dendritic nanosheets (at right) demonstrate the formation of nanopores during sintering. The nanopores form quickly and, if their diameter is close to a critical value related to the sheet thickness, then they persist for long times during sintering. Persistent pores in the thinnest possible sheet (2-3 nm) give the highest surface area possible in this sintering-resistant holey sheet morphology.



Conclusions:

Lipid bicelles are successfully used as soft-templates for the first time for the growth of dendritic platinum nanocoins. The lipid stacks similar to bicelles prepared via chemical recognition will be platinized to form nanoscale Pt coin stacks. Monte Carlo simulations provide some understanding for the assembly of both the Pt coins and the lipid stacks. In addition, TEM in-situ study and Monte Carlos simulations show the dendritic Pt nanosheet are resistant to sintering to some degree, indicating that the Pt nanocoins may also have similar sintering-resistant property due to their dendritic and sheet-like structural features.

Selected References:

1. Y. J. Song, R. M. Garcia, R. M. Dorin, H. R. Wang, Y. Qiu, J. A. Shelnutt, *Angew. Chem. Int. Ed.* **2006**, 45, 8126-8130.
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Contact:

John A Shelnutt
Sandia National Laboratories
Advanced Materials Laboratory
1001 University Blvd SE
Albuquerque, NM 87106 **Phone: 505-272-7160**
Email:jasheln@unm.edu **FAX: 505-272-7077**