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Nanostructured Platinum for Fuel Cells

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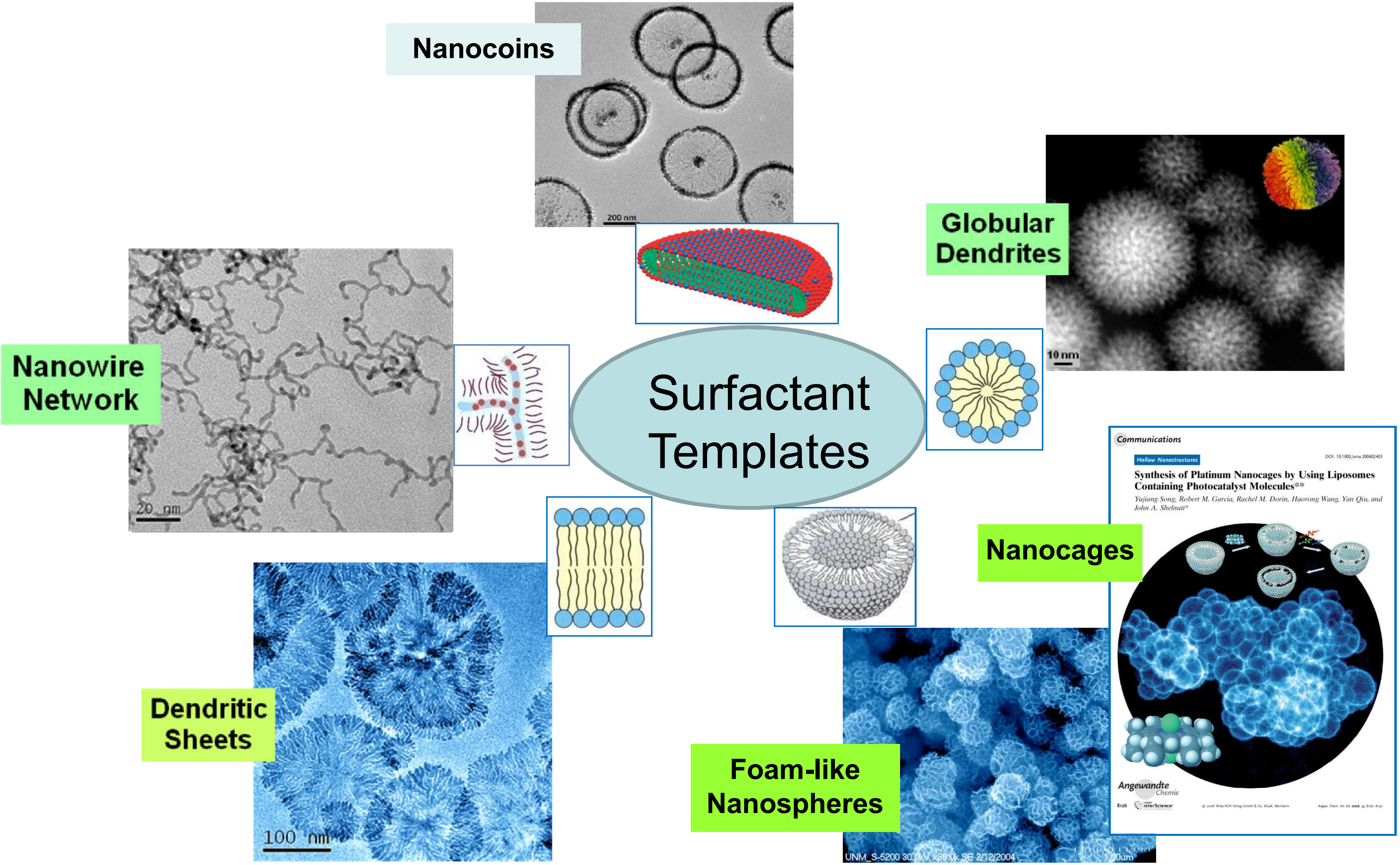
Dendritic Platinum Nanomaterials

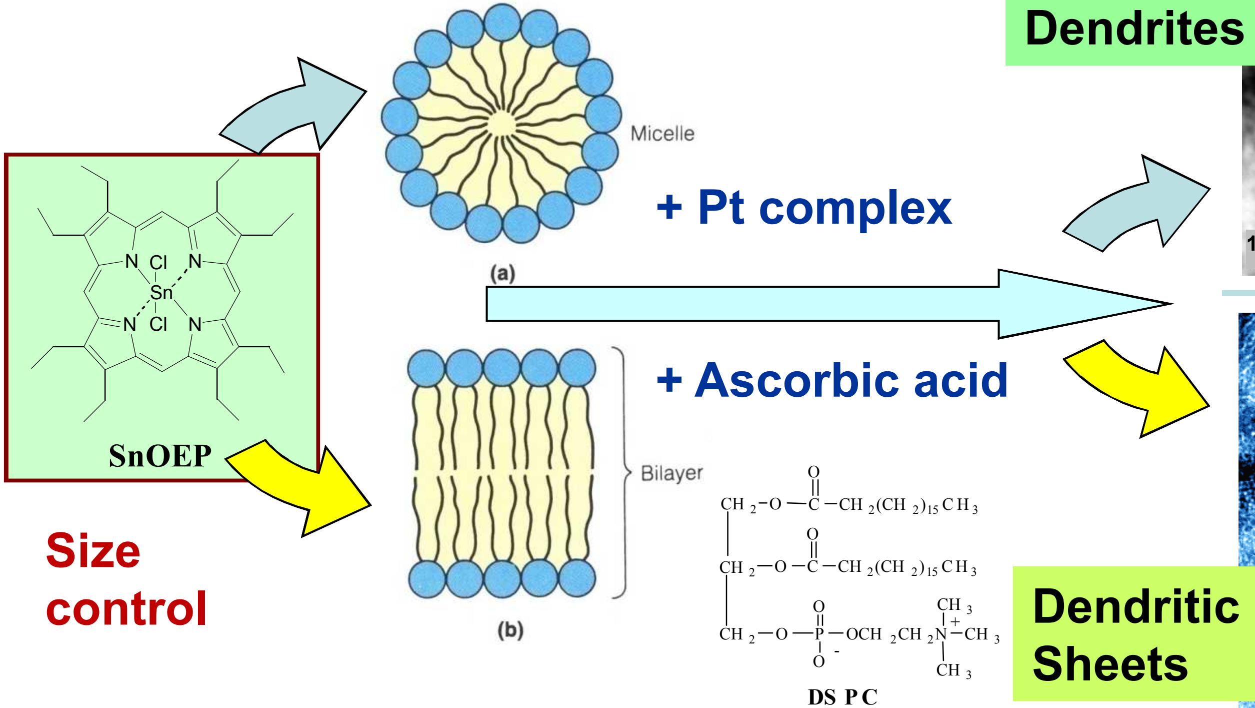


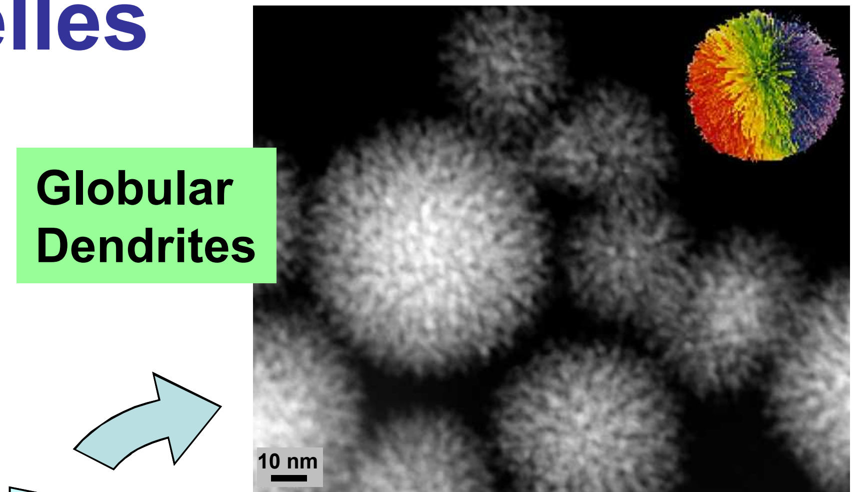
• **Combination of templating on surfactant assemblies, dendritic metal growth, and photocatalytic seeding, gives nanostructured metals for applications in fuel cells and other energy technologies.**

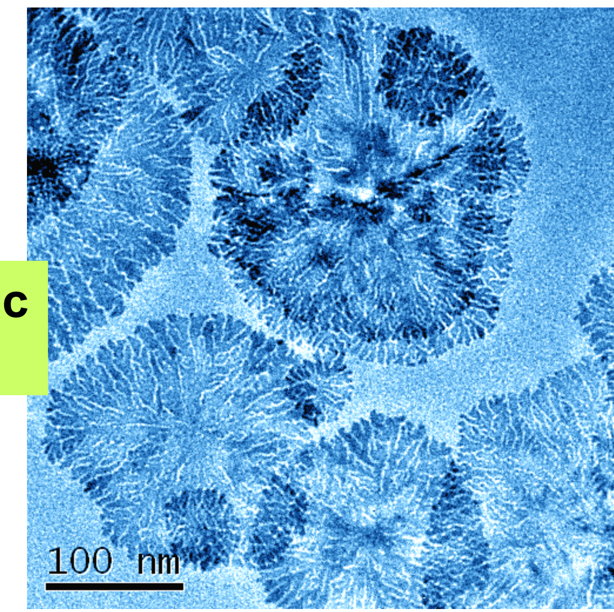
Pt Nanospheres

- Composed of 2-nm thick dendritic platinum nanosheets.

Growth of Platinum in the Bilayers of Liposomes and in Micelles



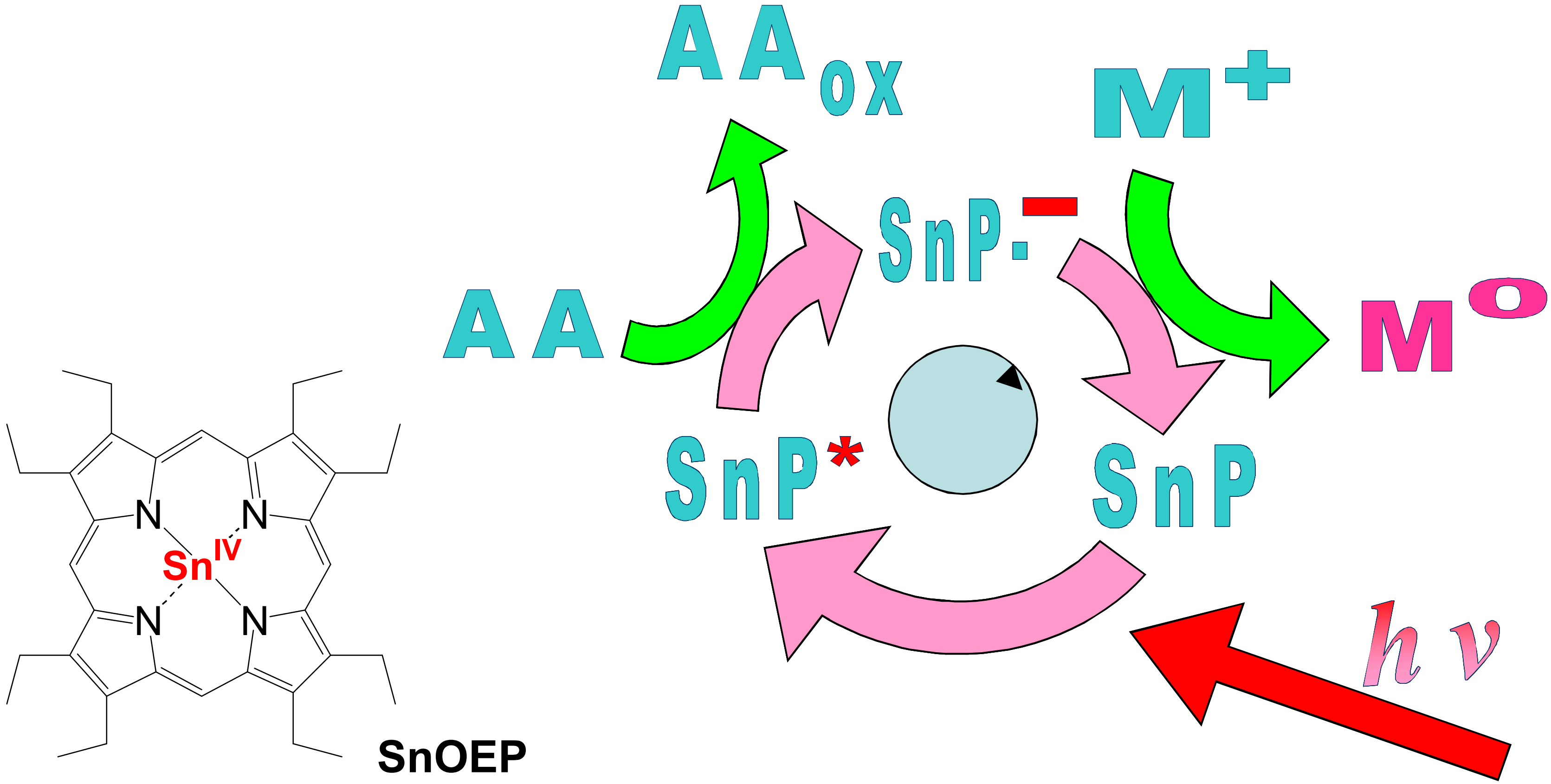




- **Growth of Pt on liposomes gives 2-nm thick dendritic sheets.**

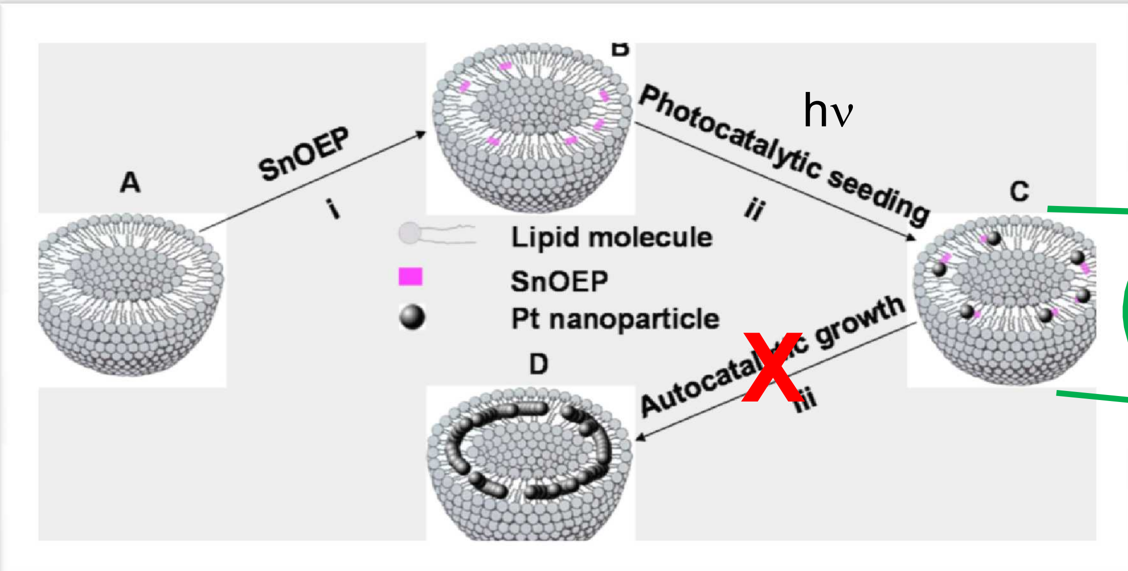
Song, Y.; Yang, Y.; Medforth, C. J.; Pereira, E.; Singh, A. K.; Xu, H.; Jiang, Y.; Brinker, C. J.; van Swol, F.; Shelnutt, J. A., *J. Am. Chem. Soc.* **2004**, *126*, 625-635.

Growth of Metal Nanostructures by Photocatalytic Reduction of Aqueous Metal Ions

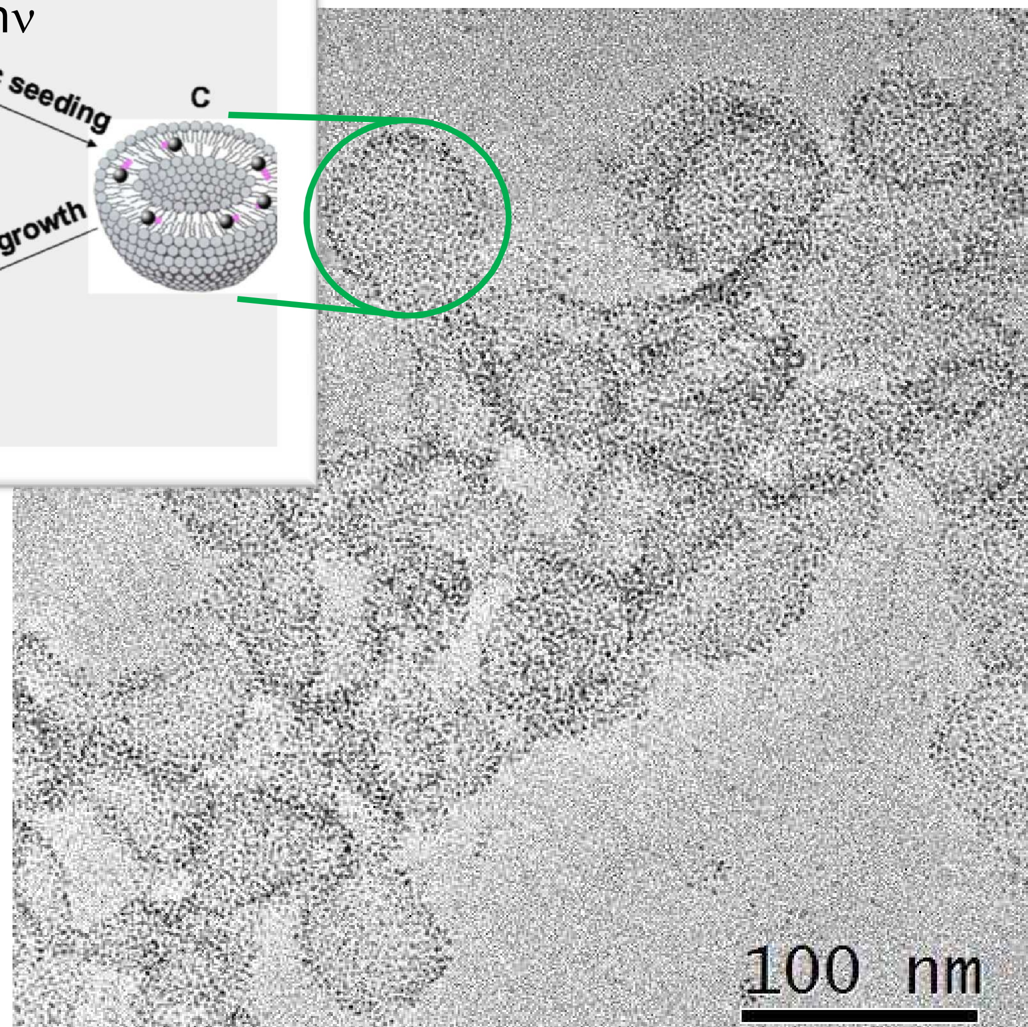


- Metal ions are continually reduced to metal and deposited near the tin-porphyrin molecule.

Size Control by Variation of Photocatalyst Concentration – Seed Formation



TEM image

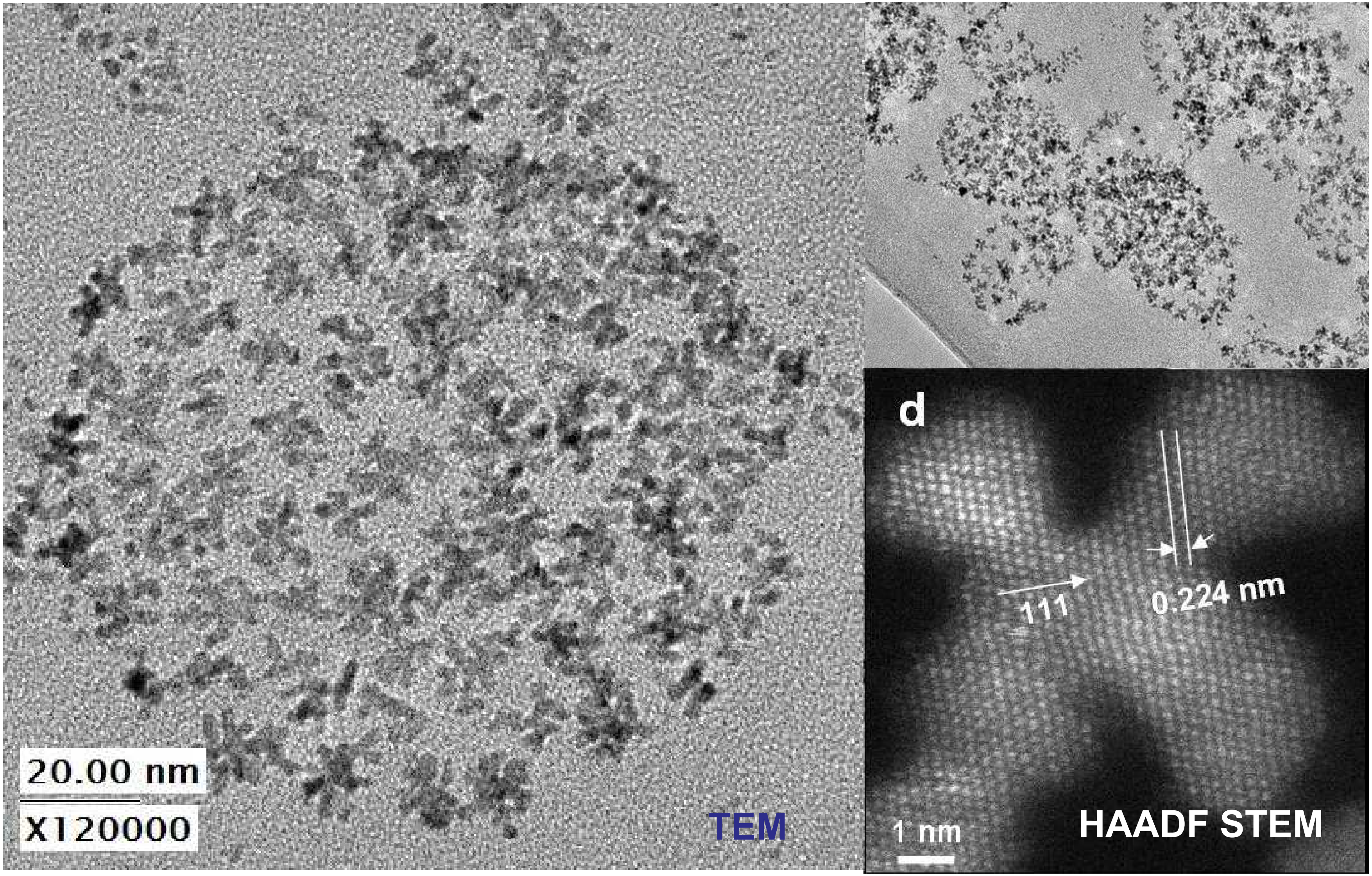


1 mM K_2PtCl_4

23.3 μM SnOEP

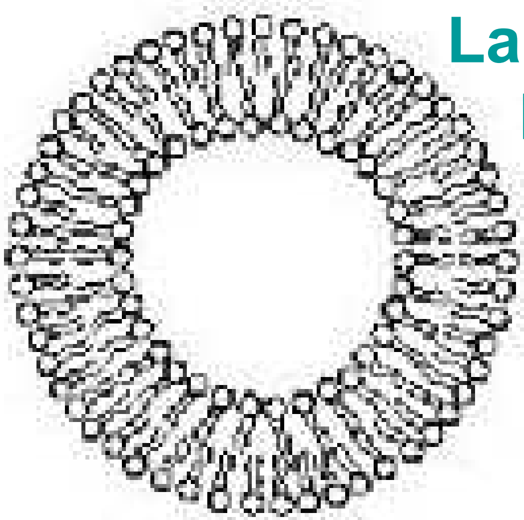
Song, Y.; Garcia, R. M.; Dorin, R. M.; Wang, H.; Qiu, Y.; Shelnutt, J. A., *Angew. Chem., Int. Ed.* **2006**, *45*, 8126-8130.

Control of Pt Sheet Size by Pt Concentration



Song, Y.; Steen, W. A.; Peña, D.; Jiang, Y.-B.; Medforth, C. J.; Huo, Q.; Pincus, J. L.; Qiu,Y.; Sasaki, D. Y.; Miller, J. E.; Shelnutt, J. A., *Chem. Mater.* **2006**, *18*, 2335-2346.

Liposomes as templates for dendritic Pt nanosheets



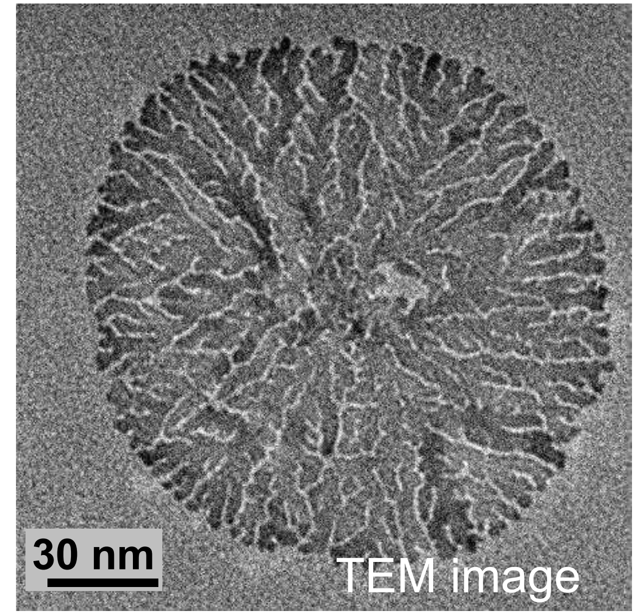
Large Liposome

Aggregated Liposomes

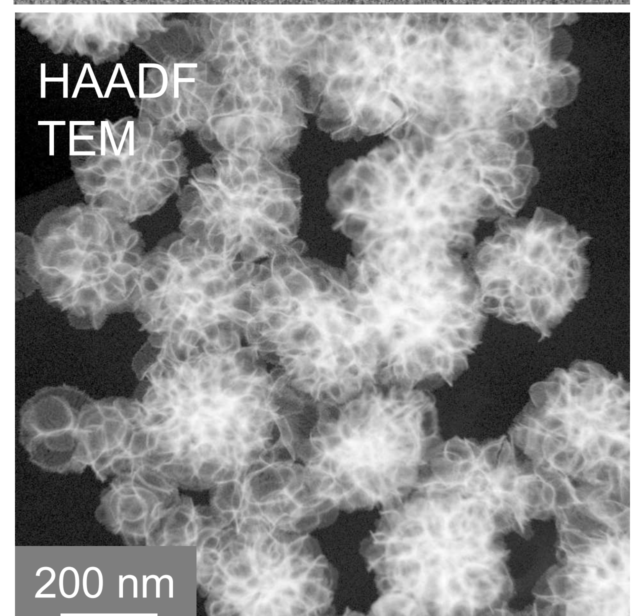
+ K_2PtCl_4 (aq.)

+Ascorbic acid (aq.)

Flat Dendritic Nanosheets

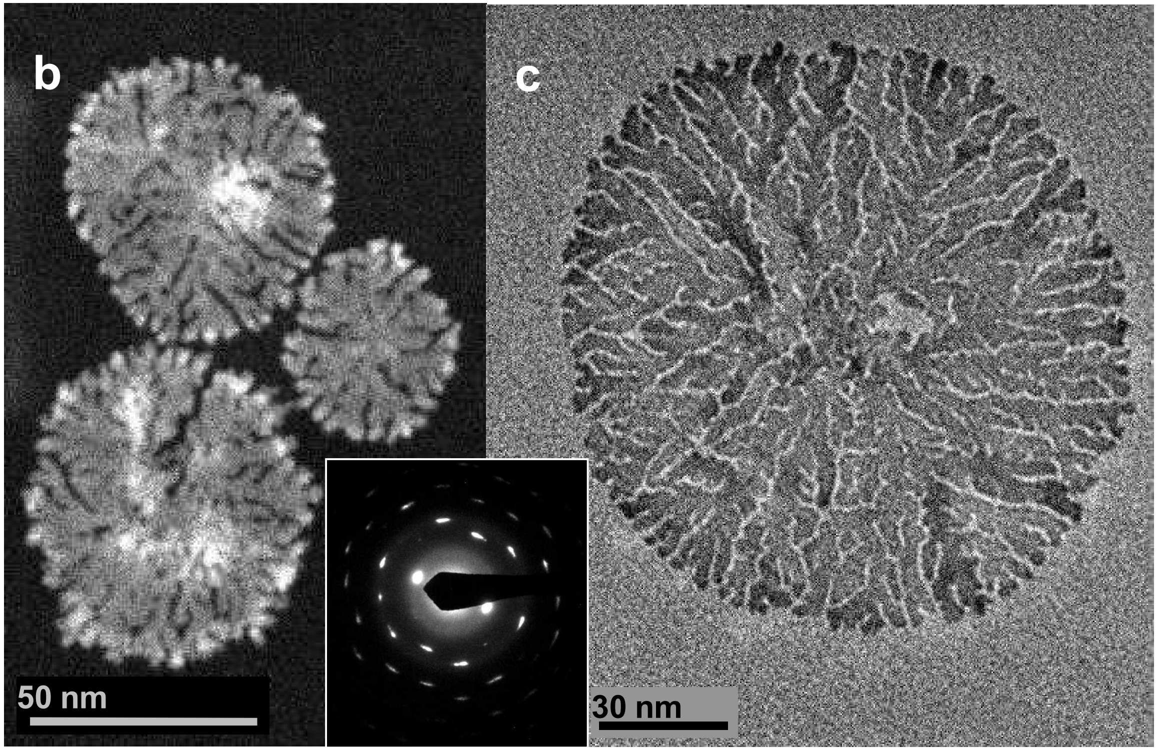


Foam-like Dendritic Nanospheres



Y. J. Song, *et al., J. Am. Chem. Soc.* **2004**, *126*, 635.
Y. J. Song, *et al., Chem. Mater.* **2006,** *18*, 2335.

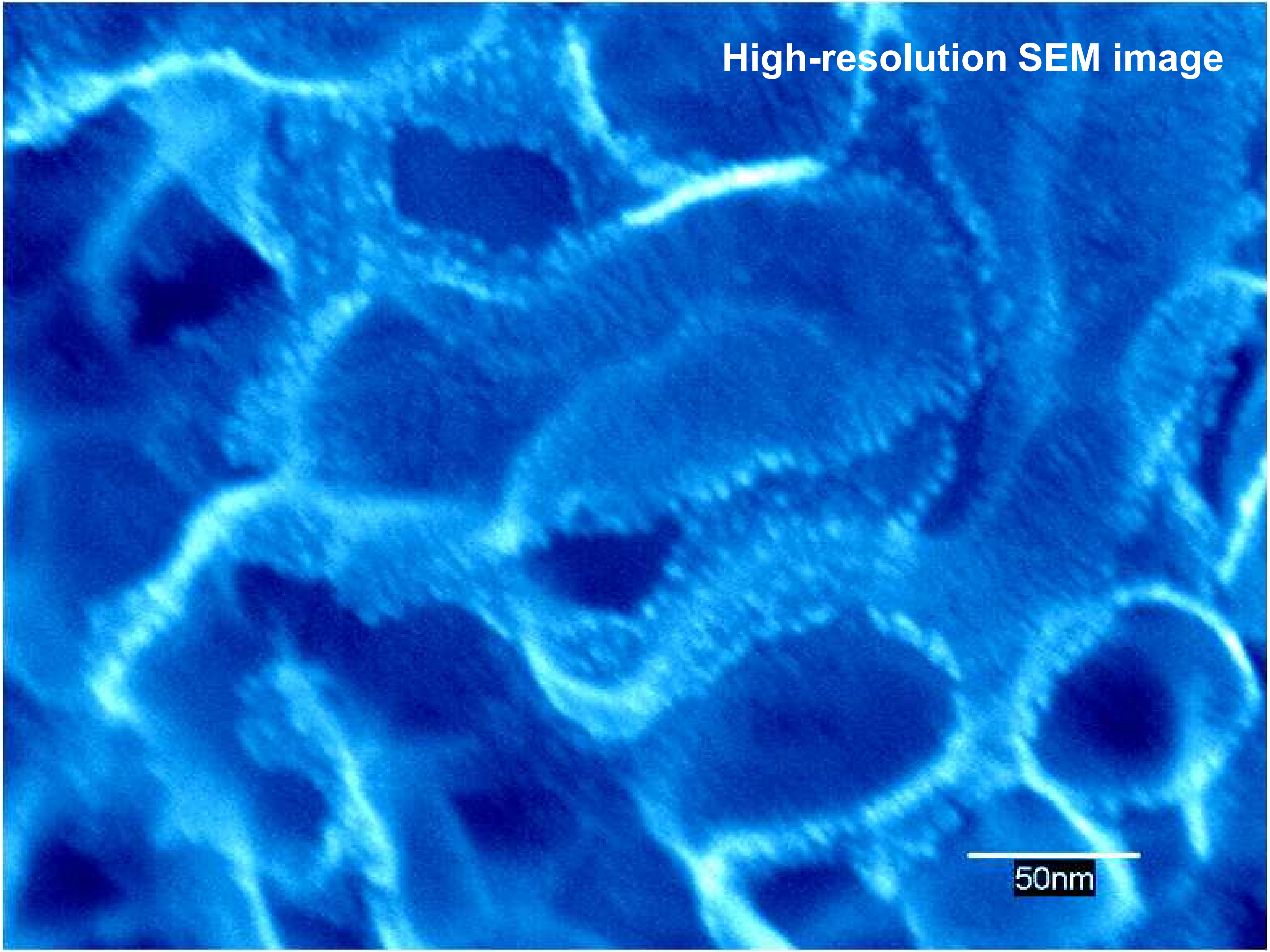
Large Platinum Nanosheets



- 2-nm thick dendritic platinum sheets are single crystals.
- Grown within bilayers of large liposomes or vesicles.
- Diameters can be controlled by light exposure.

Song, Y.; Yang, Y.; Medforth, C. J.; Pereira, E.; Singh, A. K.; Xu, H.; Jiang, Y.; Brinker, C. J.; van Swol, F.; Shelnutt, J. A., *J. Am. Chem. Soc.* **2004**, *126*, 625-635.

Curved Dendritic Pt Nanosheets.

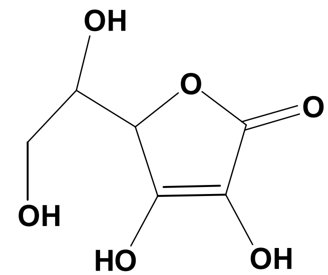


Grown within bilayers of aggregated unilamellar liposomes.

Reduction of platinum complex

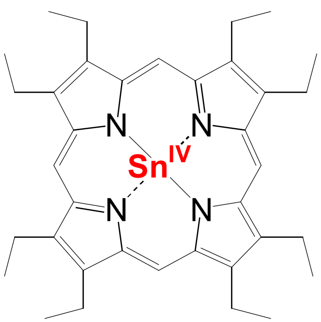
by chemical reduction with ascorbic acid

$$Pt^{2+} + AA \xrightarrow[\text{slow}]{} Pt^{0} + AA_{ox}$$



AA

by photocatalytic reduction



SnOEP

$$SnP + h\nu \rightarrow SnP^{*}$$

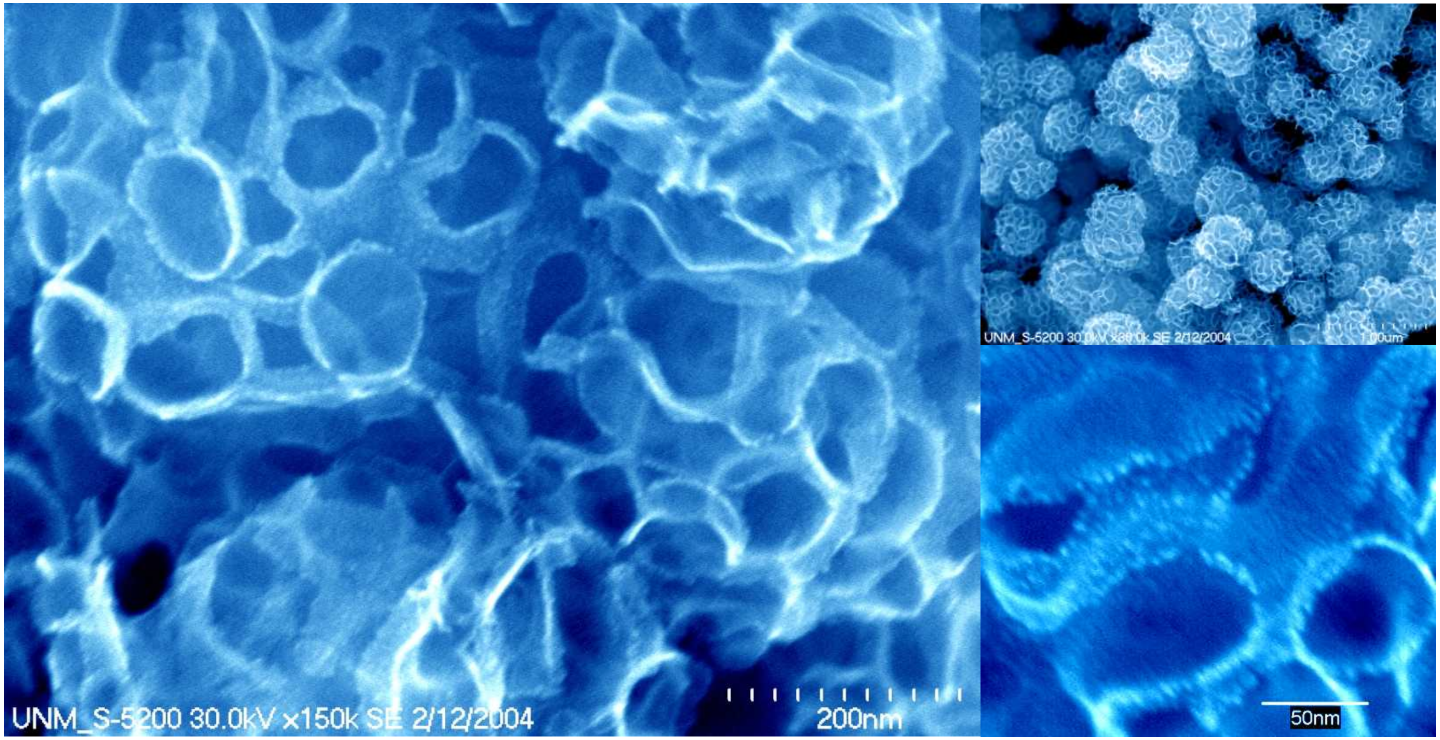
$$SnP^{*} + AA \rightarrow SnP^{-\cdot} + AA_{ox}$$

$$2SnP^{-\cdot} + Pt^{2+} \rightarrow 2SnP + Pt^{0}$$

by autocatalytic reduction

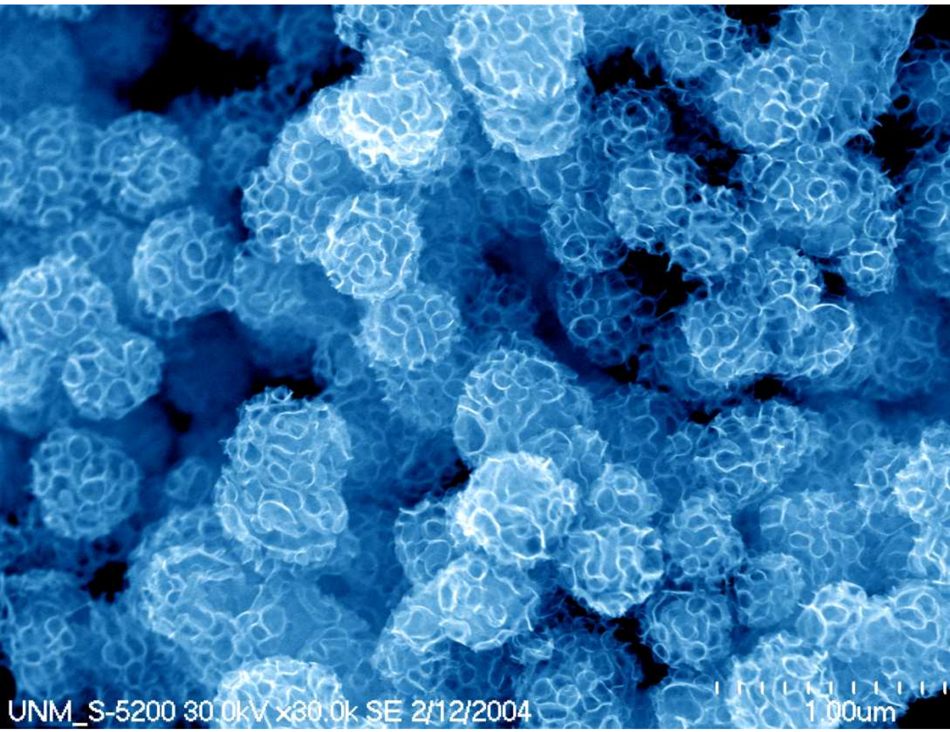
$$Pt^{2+} + AA \xrightarrow[\text{fast}]{Pt^{0}} Pt^{0} + AA_{ox}$$

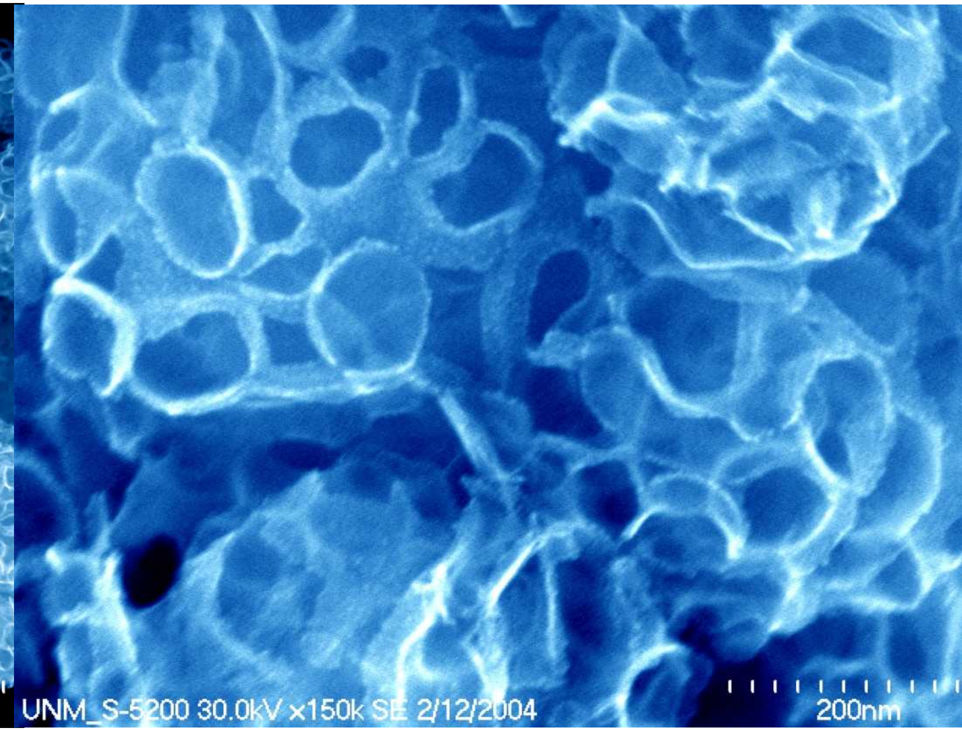
Foam-like Pt Nanospheres



Platinum foam-like nanospheres

- Dendritic platinum sheets grown in aggregated DSPC/cholesterol liposomes.
- High surface area (30 m^2/g).





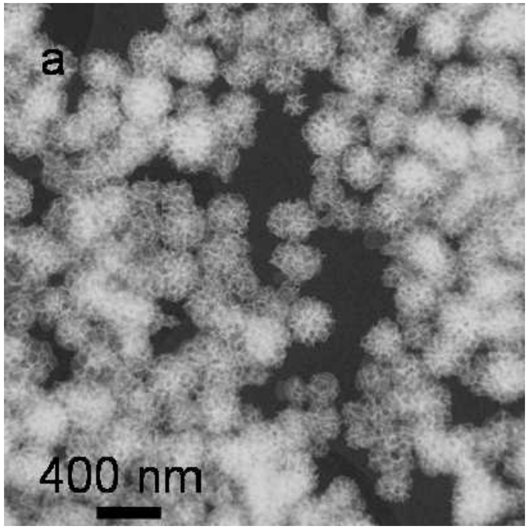
- **10-second visible light exposure**

Song, Y.; Steen, W. A.; Peña, D.; Jiang, Y.-B.; Medforth, C. J.; Huo, Q.; Pincus, J. L.; Qiu,Y.; Sasaki, D. Y.; Miller, J. E.; Shelnutt, J. A., *Chem. Mater.* **2006**, *18*, 2335-2346.

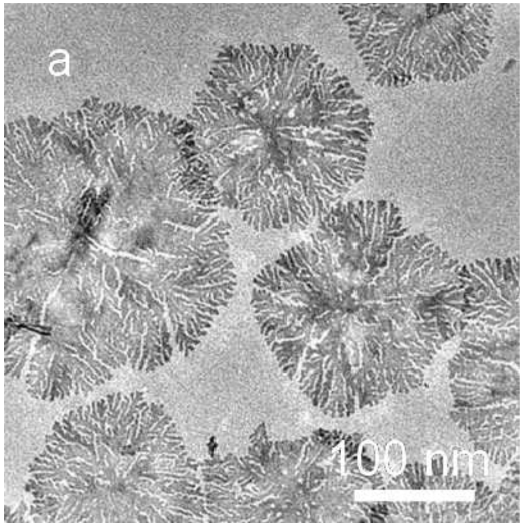
Dendritic Pt Electrocatalysts

- Compare membrane electrode assemblies (MEAs) prepared with *unsupported*:
  - Dendritic platinum nanospheres
  - Circular dendritic nanosheets

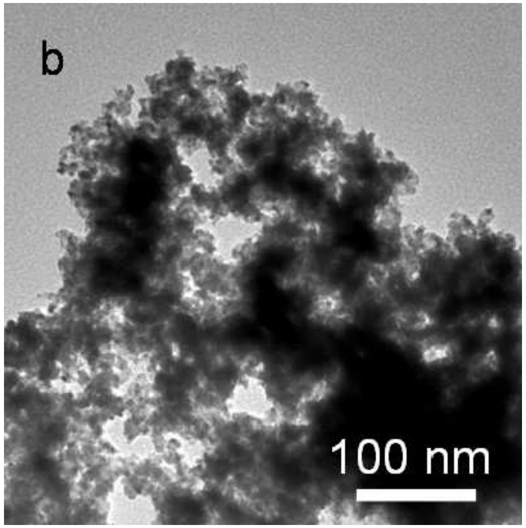
  With *unsupported* platinum black.



Platinum-Foam Nanospheres

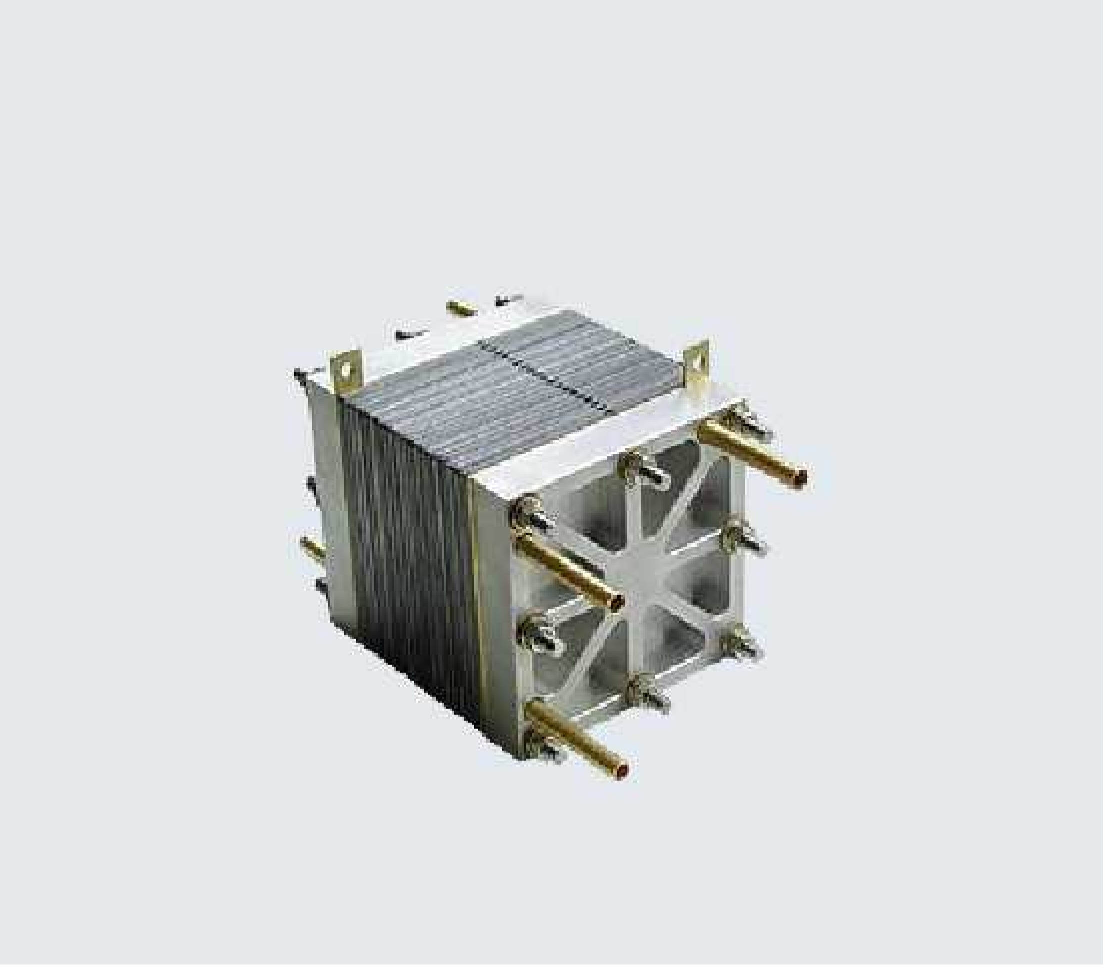


Dendritic Platinum Nanosheets



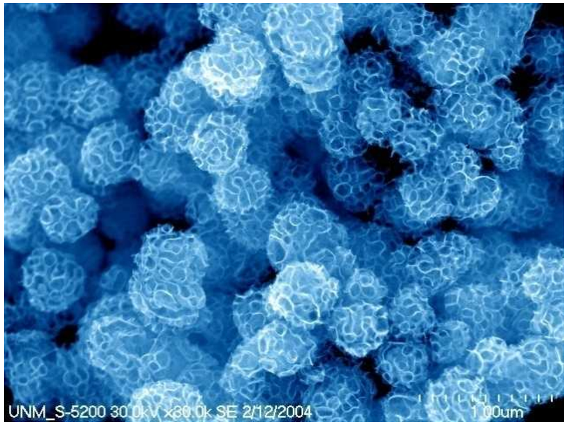
Platinum Black (ETEK)

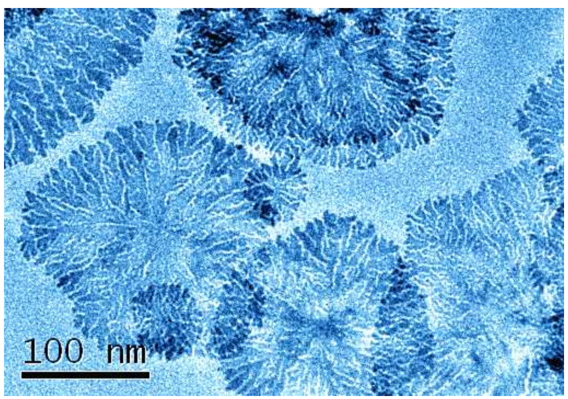
High Performance Electrocatalysts for PEM Fuel Cells

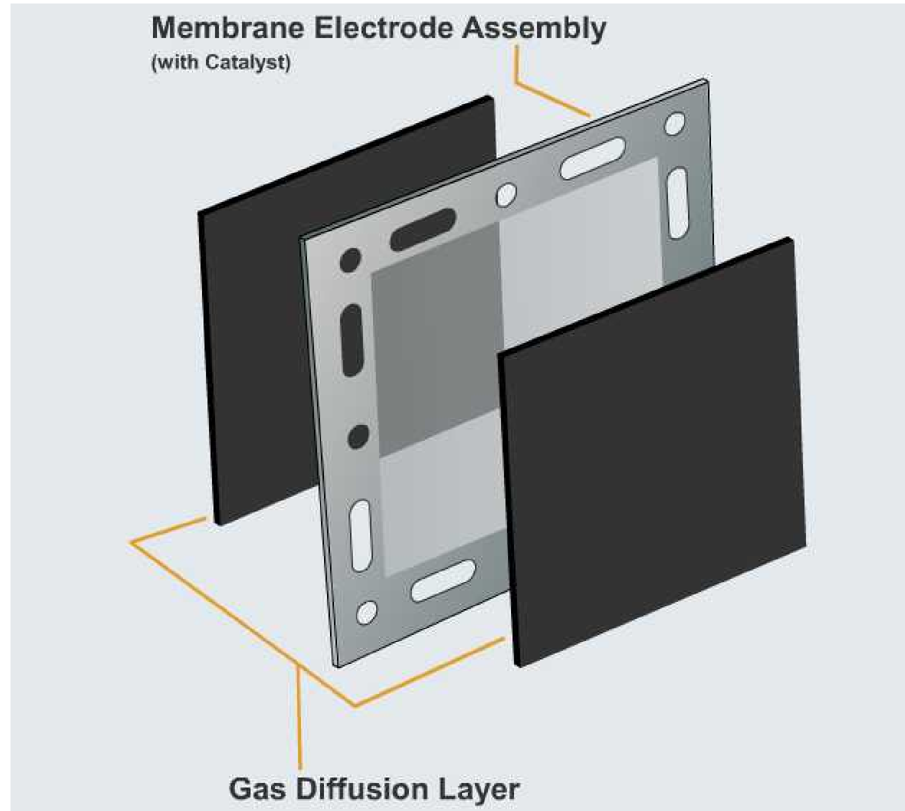


SGL Technologies

Membrane Electrode Assembly (MEA)



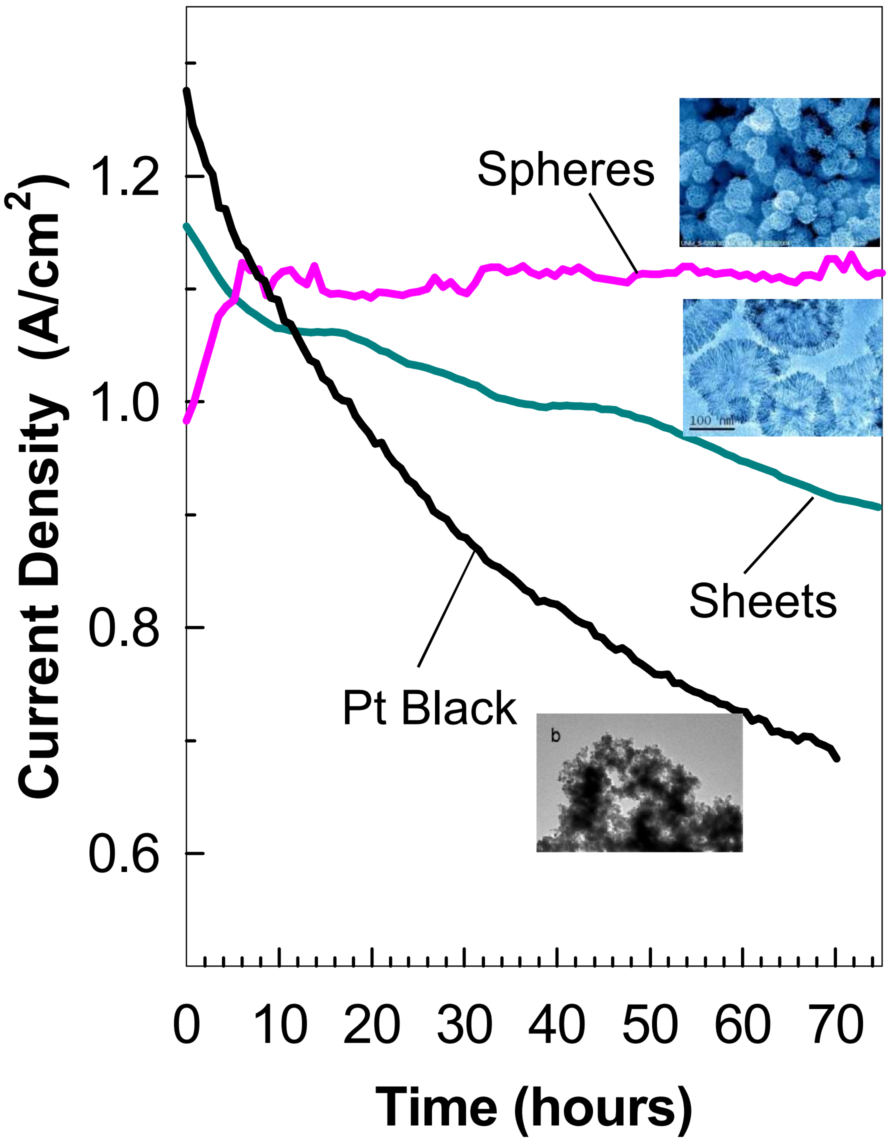




PEM Fuel Cell

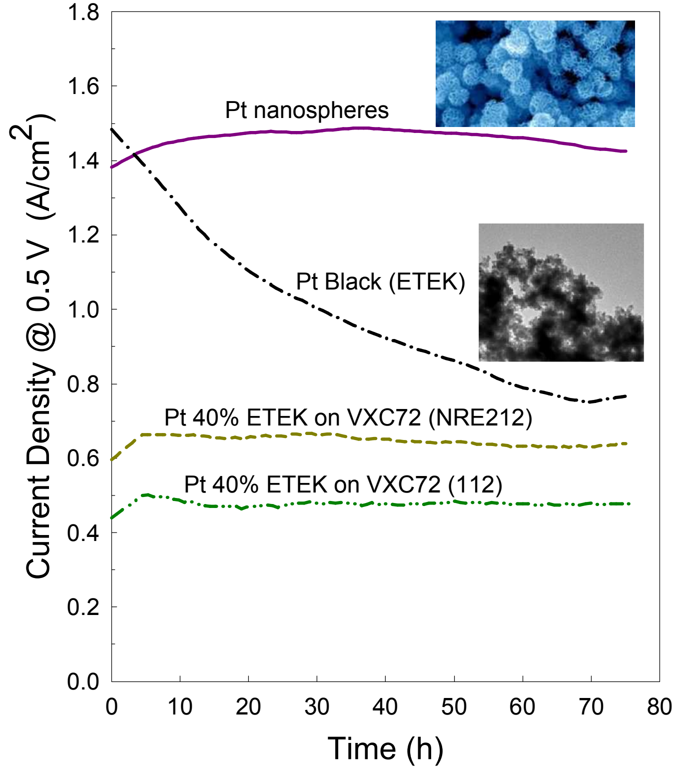
- Pt is typically supported on carbon black, but no carbon support for this study.
- Electrocatalyst layers applied to Nafion membrane using an aqueous slurry of the Pt nanomaterial with Nafion polymer.

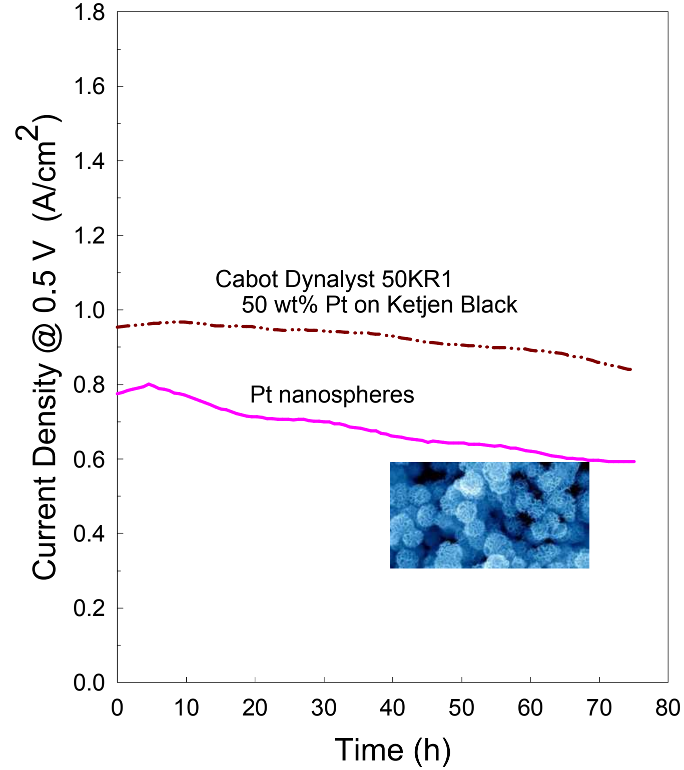
Catalysts Durability (~75 h)



- Durability tests of MEAs at 0.5 V for the 7 mg Pt/cm^2 loadings.
- Similar results for lower Pt loadings of 2 mg/cm^2 and 0.4 mg/cm^2.
- No carbon support.

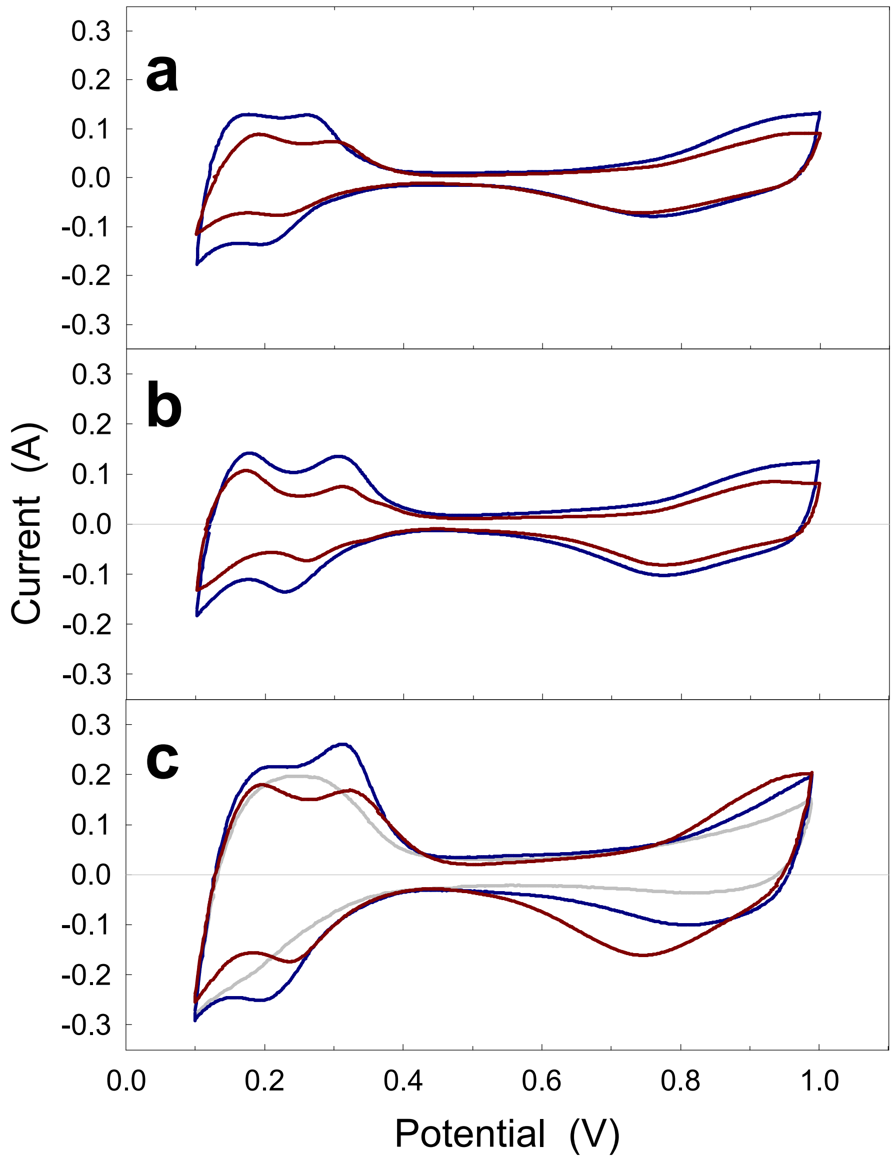
Comparison with ETEK
(particles on Carbon Black)





- (left) Electrocatalyst stability tests at 0.5 V potentiostatic hold for MEAs made with **2 mg/cm^2** Pt loading for unsupported Pt nanospheres (solid line), Pt black (- . -), and ETEK 40wt.% on VXC72 carbon black (NRE 212 [- - -] and 112 membranes [- . . -]).
- (right) Durability tests at 0.5 V for MEAs prepared with **0.4 mg/cm^2** Pt loading for unsupported Pt nanospheres (solid line) and (carbon supported) Cabot Dynalyst 50KIR1/50 wt.% Pt on Ketjen Black on NRE212 membranes (- . . -).

Cyclic Voltammograms



- Cyclic voltammograms for (a) Pt black, (b) flat Pt nanosheets and (c) Pt nanospheres at a loading of 7 mg/cm^2.
- Blue curves are at time 0 after break-in and the red curves are at 75 h after break-in.
- In (c) the gray line is before the break-in period removes the residual surfactant from the nanospheres.

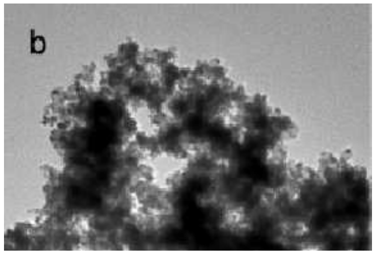
Catalyst Stability & Surface Areas

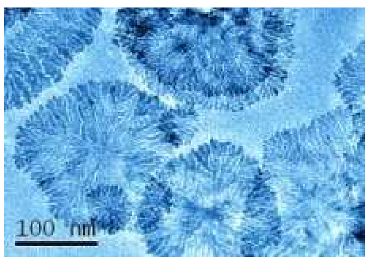
Nanomaterial	Current Density Percent Change	Initial Electrochemical Surface Area (m^2/g)	Electrochemical Surface Area Percent Change
Nanospheres	0 % (86 h)	11.3	27 %
Flat Nanosheets	20 % (75 h)	6.4	36 %
Platinum Black	47 % (70 h)	5.9	42 %

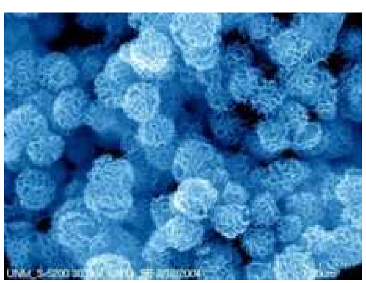
Decrease in performance follows the same trend as the decrease in electrochemically active surface area.

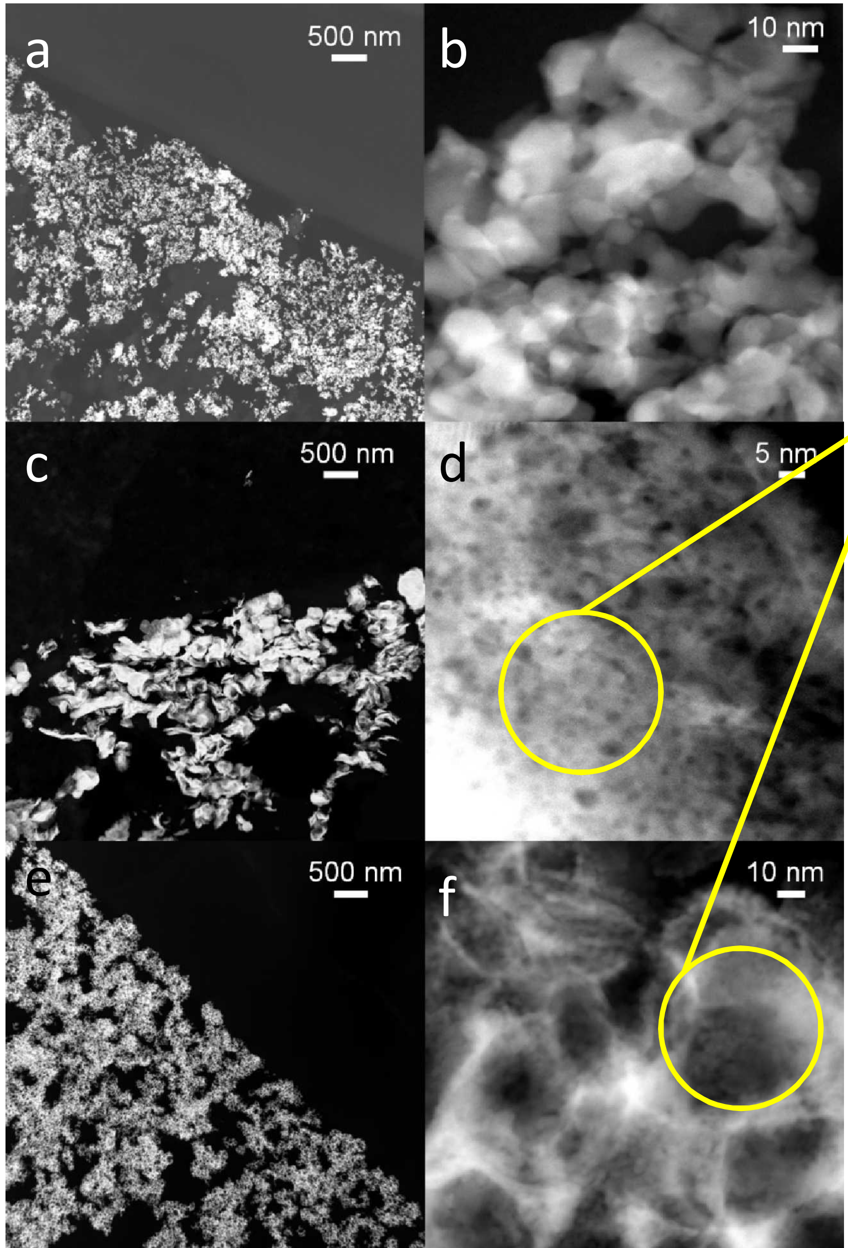
- 7 mg/cm^2 loading

MEA Cross-section After 75-hour Tests







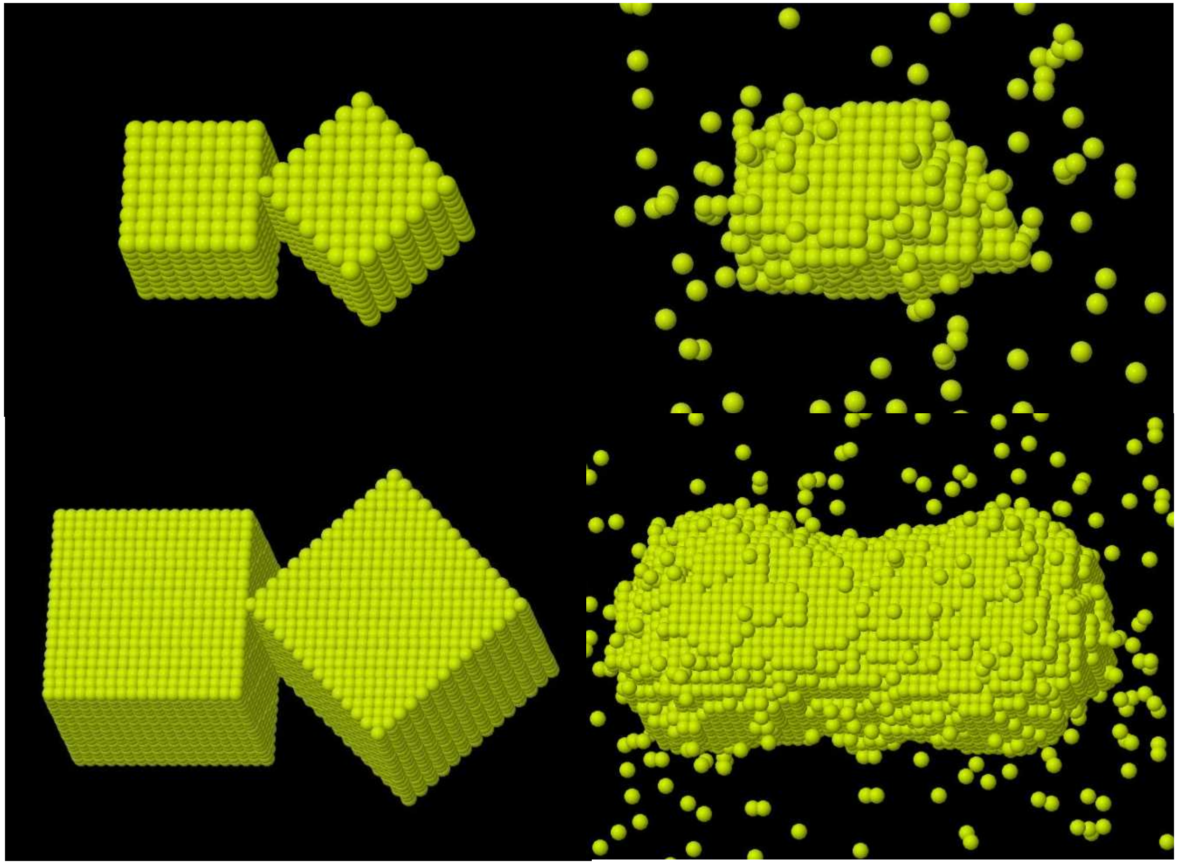


MEA Cross-sections:
HAADF STEM Images

For the dendritic platinum nanostructures, sintering during the durability test leaves ***persistent nanoscale pores*** resulting in enhanced retention of surface area.

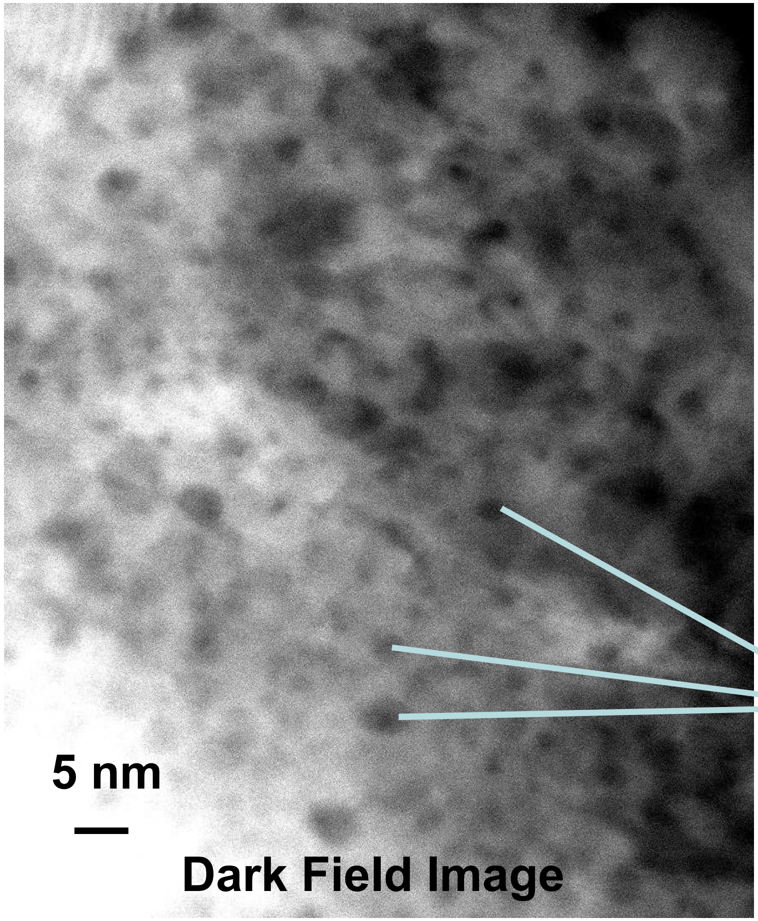
Nanoscale Platinum Sinters/Ripens Decreasing ECA.

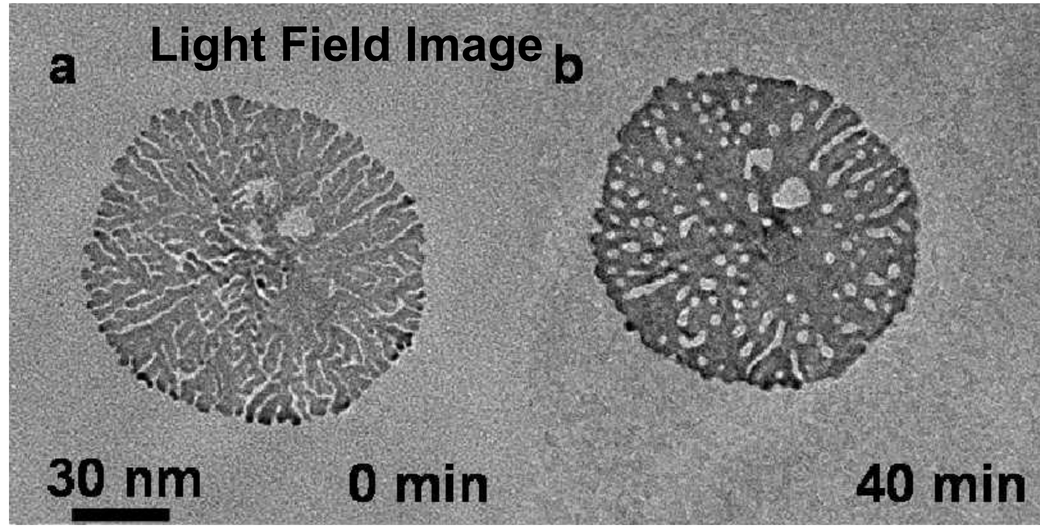
Sintering of Particles



- Typical Monte Carlo simulations of the diffusion of atoms of two touching 3-nm (top) and 6-nm (bottom) cubical nanoparticles of Pt black. The temperature is *kT/e* = 0.5 in units where the roughening temperature is 0.63. Starting structures (left) and after 16,000 MC sweeps (right).

Sintering Decreases ECA



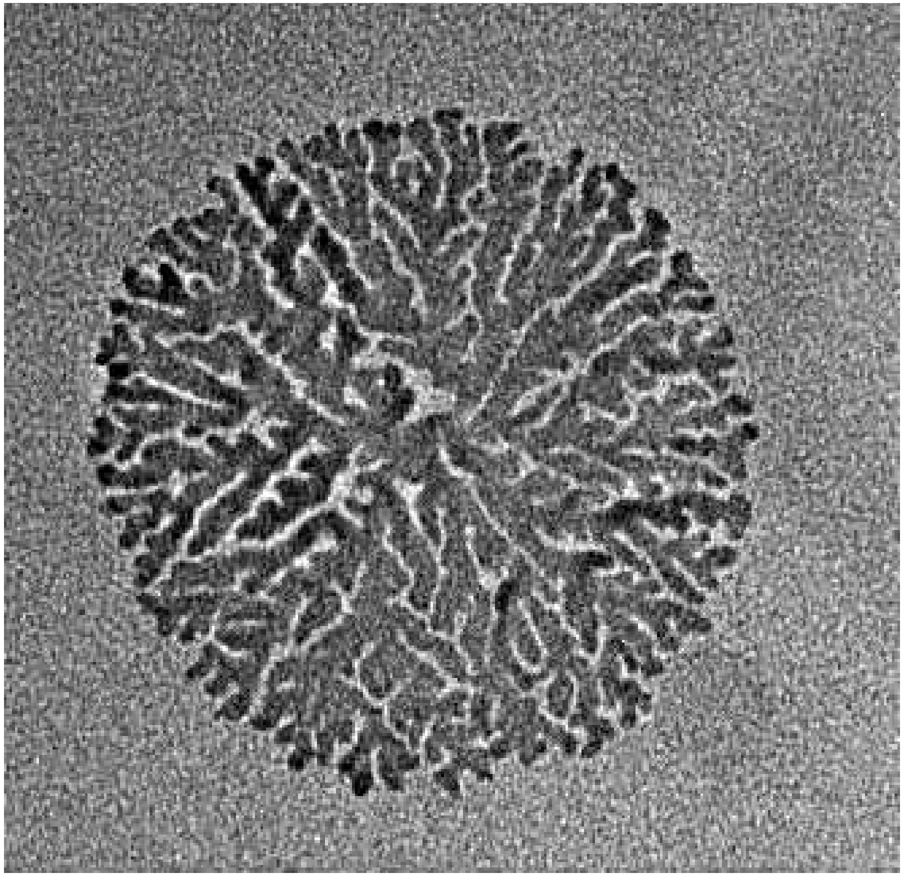


Heating by an intense electron beam results in sintering and formation of *persistent nanoscale pores*.

$$\tilde{\mu}_{Pt^{2+}}(r) = \mu^{o}_{Pt^{2+}}(\infty) + \frac{2\gamma V_m^{Pt}}{r} + 2F\phi(r)$$

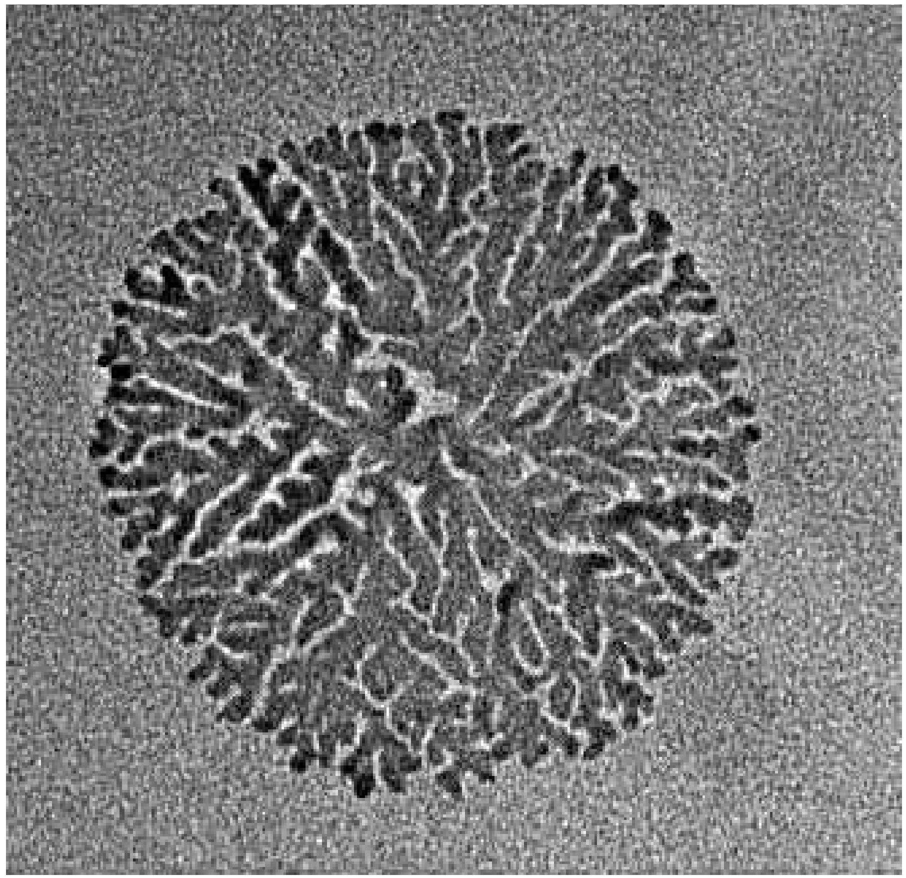
- HAADF-TEM images of a section of the MEA made with the circular nanosheets after a 75-h run.
- TEM image of a dendritic Pt nanosheet after annealing in the electron beam.

Electron Beam Sintering



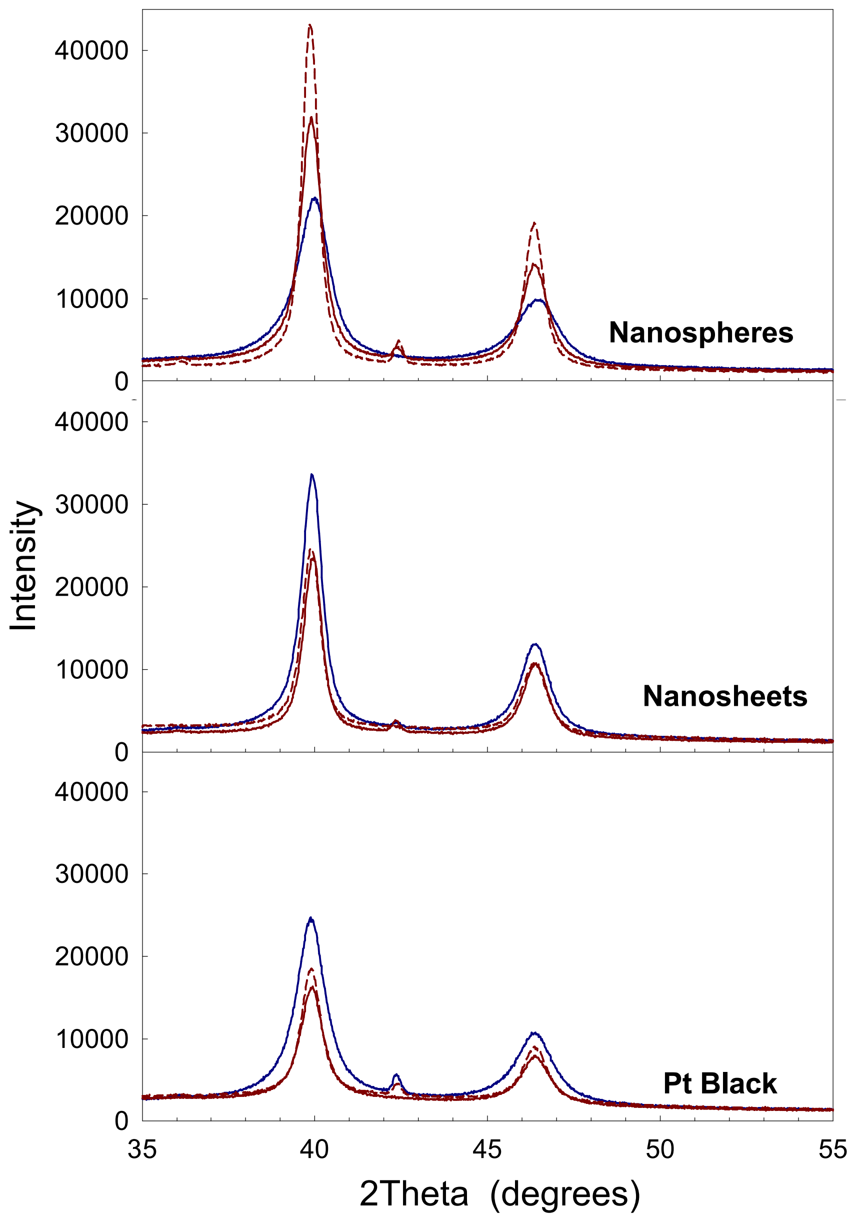
- Formation and persistence of holes preserves surface area.

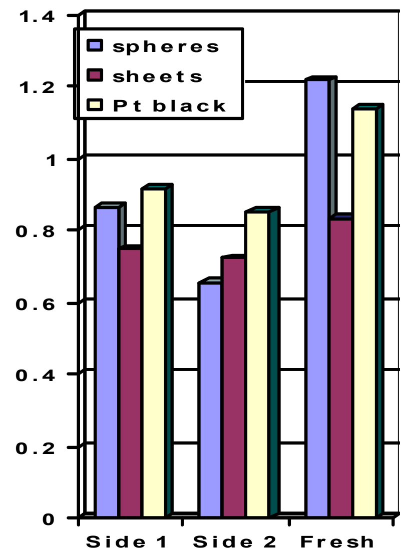
Electron Beam Sintering

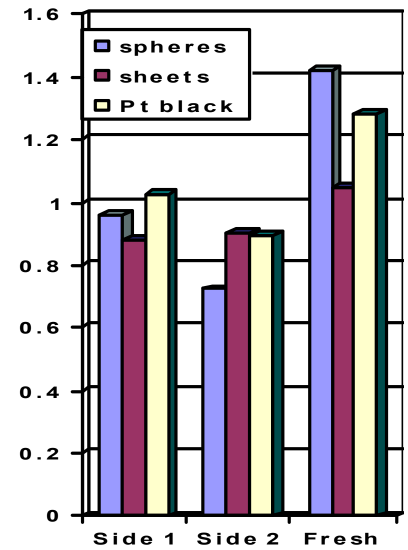


- Formation and persistence of holes preserves surface area.

XRD







- Typical XRD patterns of the MEAs with 7 mg Pt/cm^2 made with the Pt nanospheres (top), flat Pt nanosheets (middle), and Pt black (bottom) before and after the stability test.
- The charts illustrate the decreases in widths of the lines at 40° and 47° for the two sides of the electrodes, which suggests an increase in Pt crystallinity for all three nanomaterials.

Rapid formation of holey nanosheets and persistence of the holes

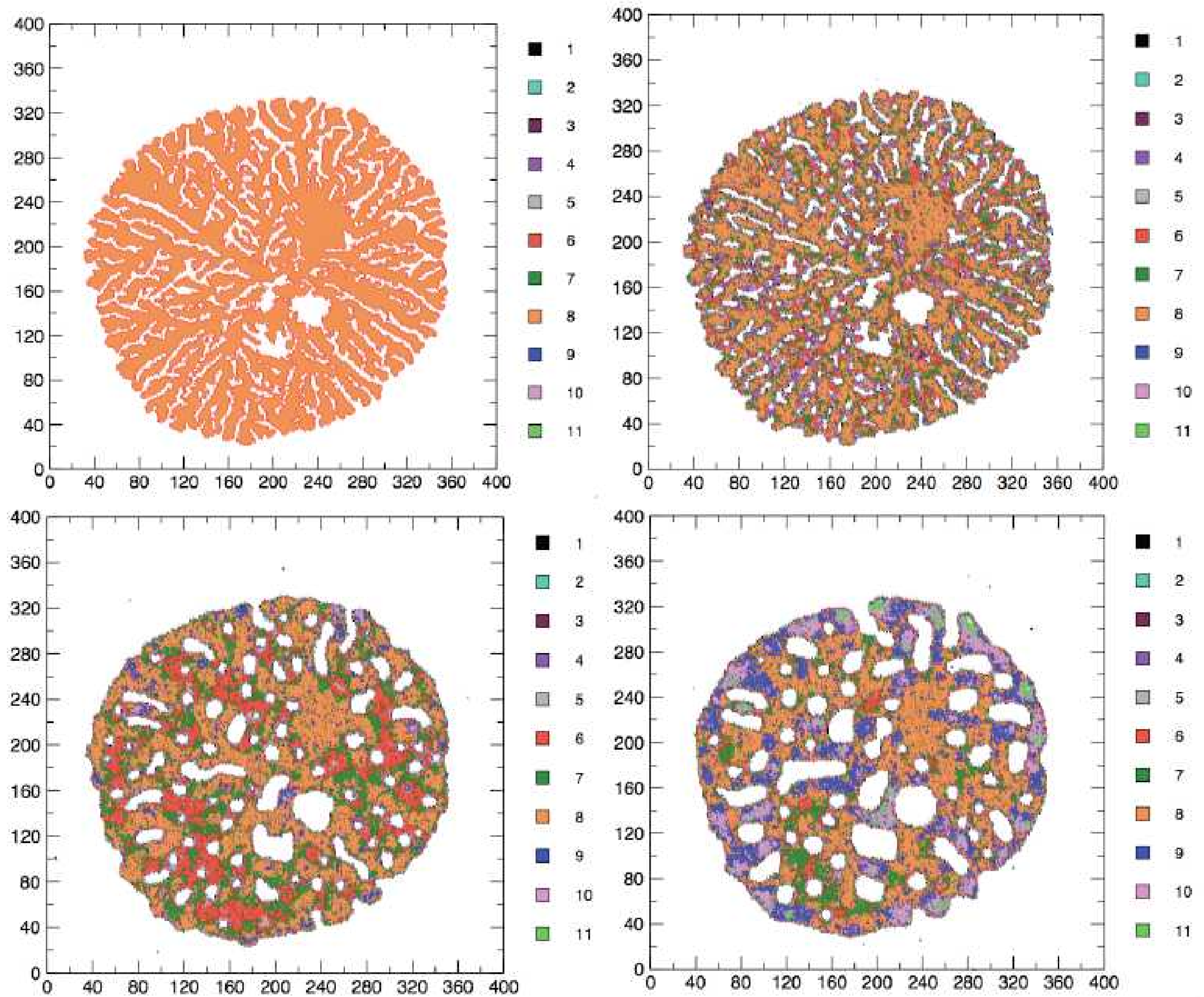
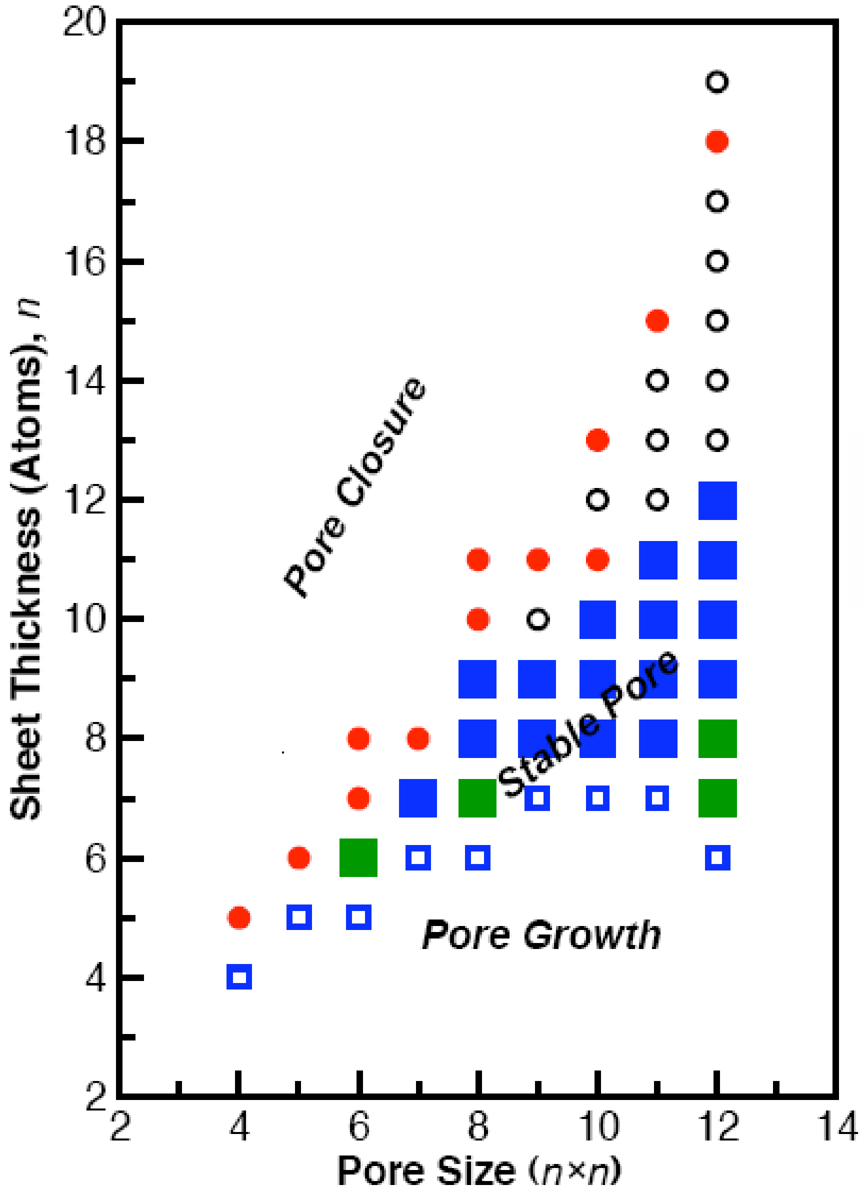


Figure 5: Thickness of a dendritic circular nanosheet across its surface, left to right in top to bottom, at : Initial, 1000, 16000, and 50000 MC sweeps

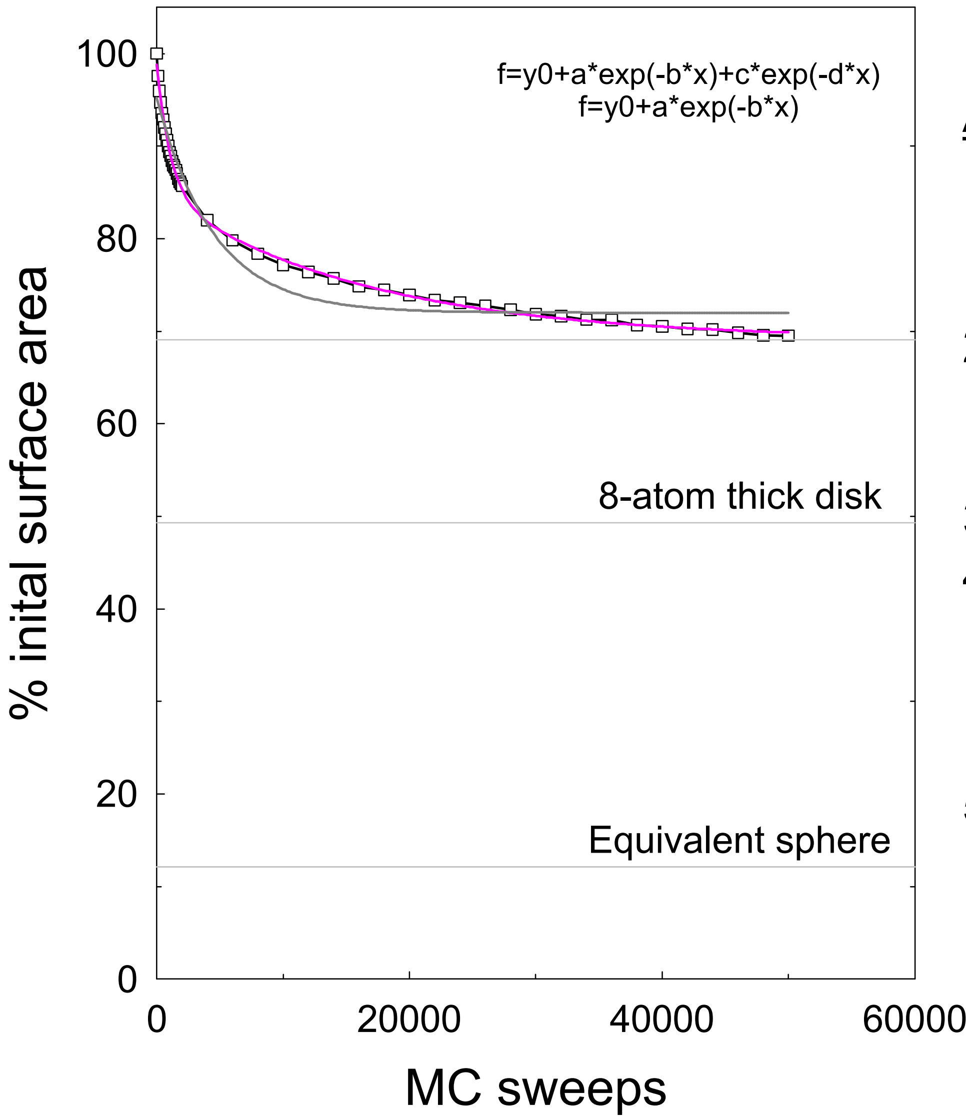
Sintering resistance due to persistent holes.



$$\widetilde{\mu}_{Pt^{2+}}(r) = \mu^{o}_{Pt^{2+}}(\infty) + \frac{2\gamma V_m^{Pt}}{r} + 2F\phi(r)$$

Kelvin equation

Metastable Holey Sheet

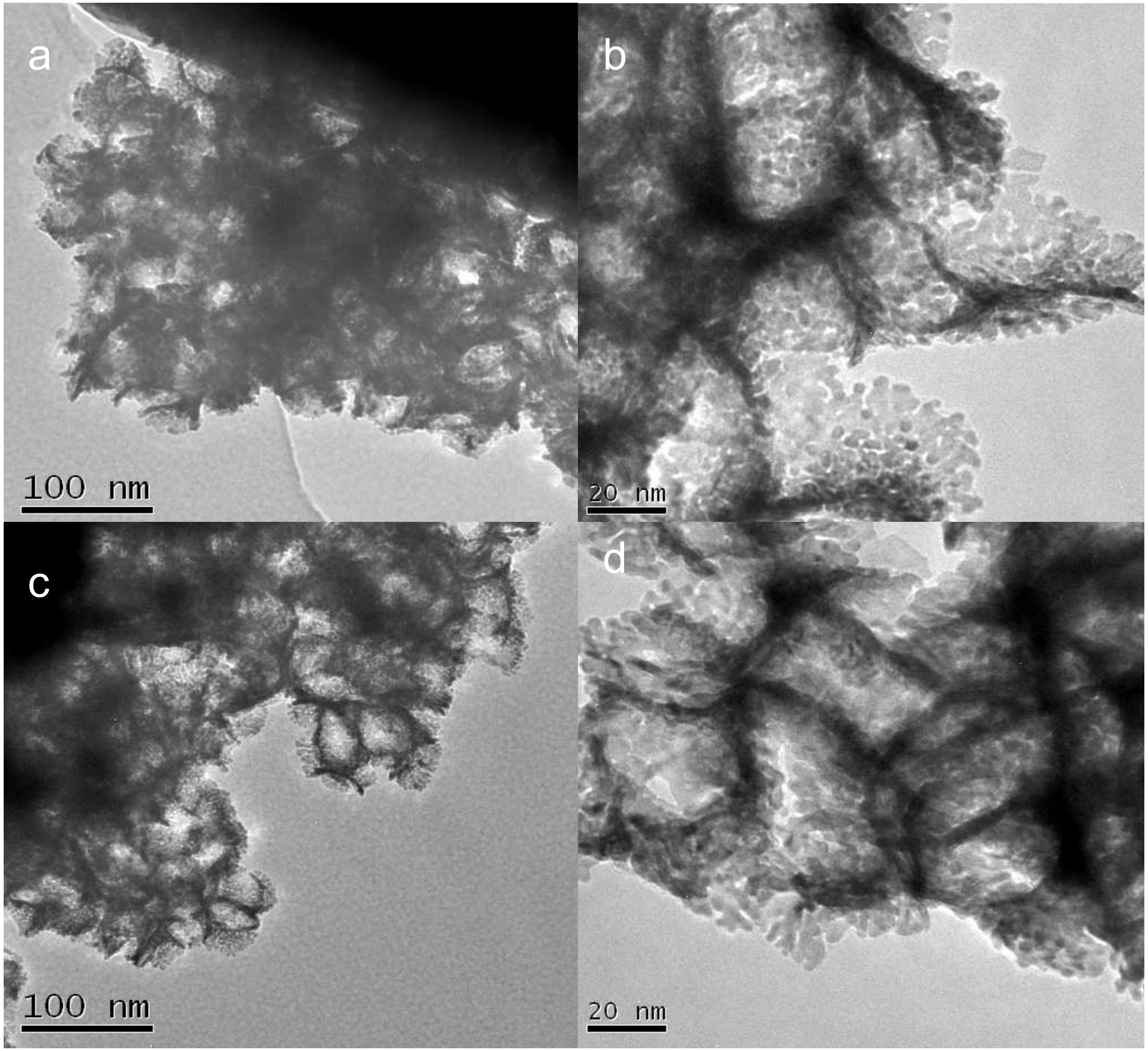


<u>Advantages:</u>

1. Pt nanosheet has near minimum sheet thickness for holey sheet (7 atoms).
2. Dendrite thickness is only twice the minimum for stable solid sheet (4 atoms).
3. Holes can be as small as 2-3 nm.
4. For reasonable hole densities, a holey sheet will have higher surface area than the thinnest solid sheet.
5. Metastability results from the interplay of positive, negative, and infinite curvatures.

- Presence of persistent holes maintains surface area.

MEAs after 75-hour tests



- TEM images of the foam-like nanospheres on either side of the MEA after nominal 75-h test.

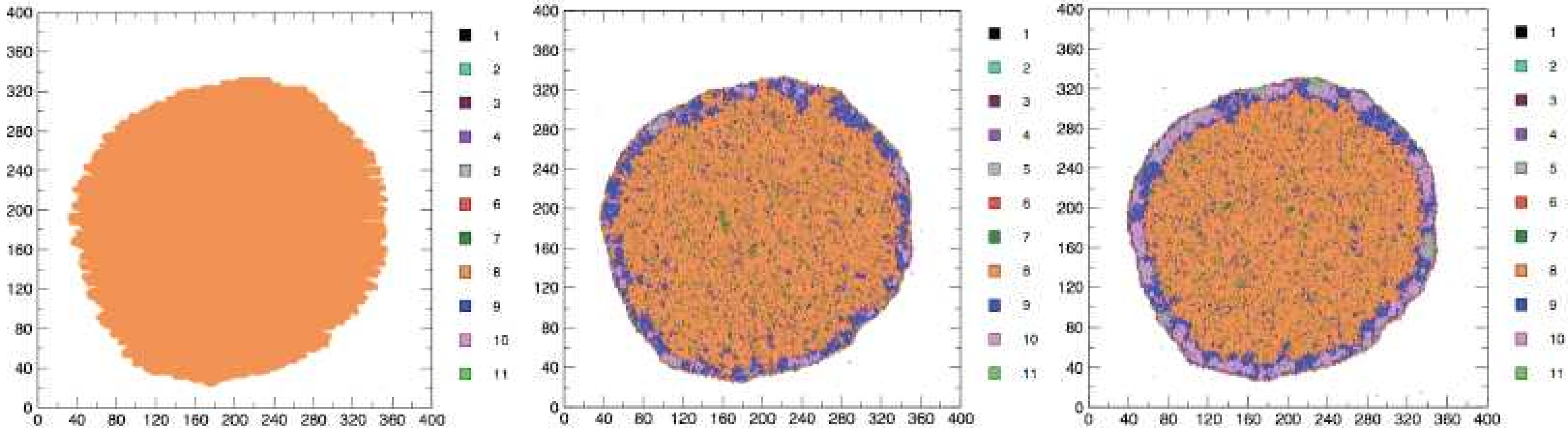


Figure 6: Thickness of a solid nanodisc across its surface, left to right, at : Initial, 30000, and 50000 MC sweeps.

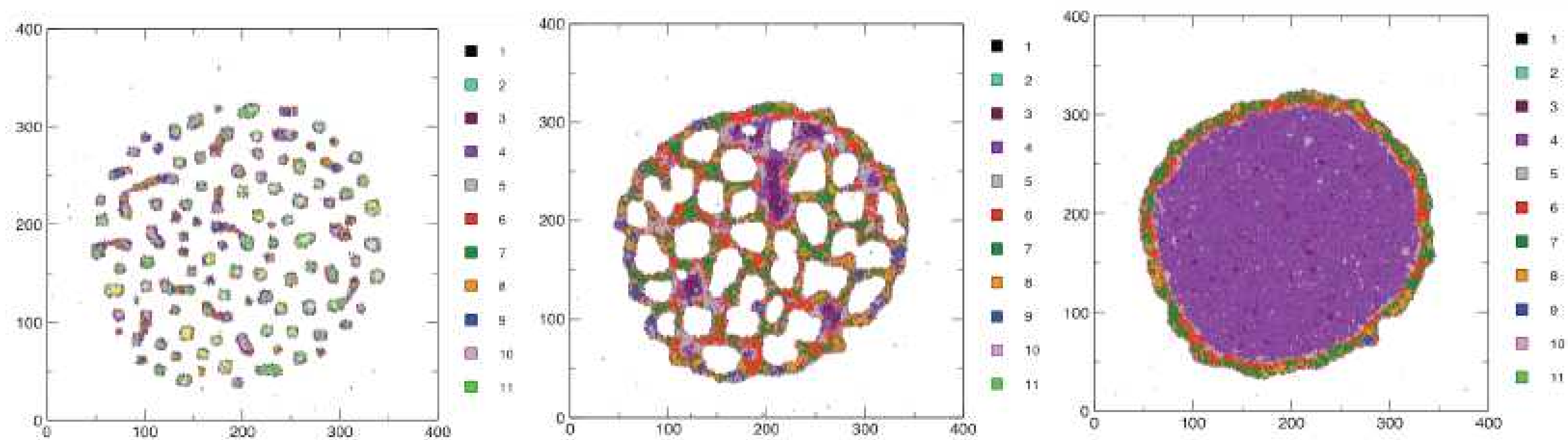
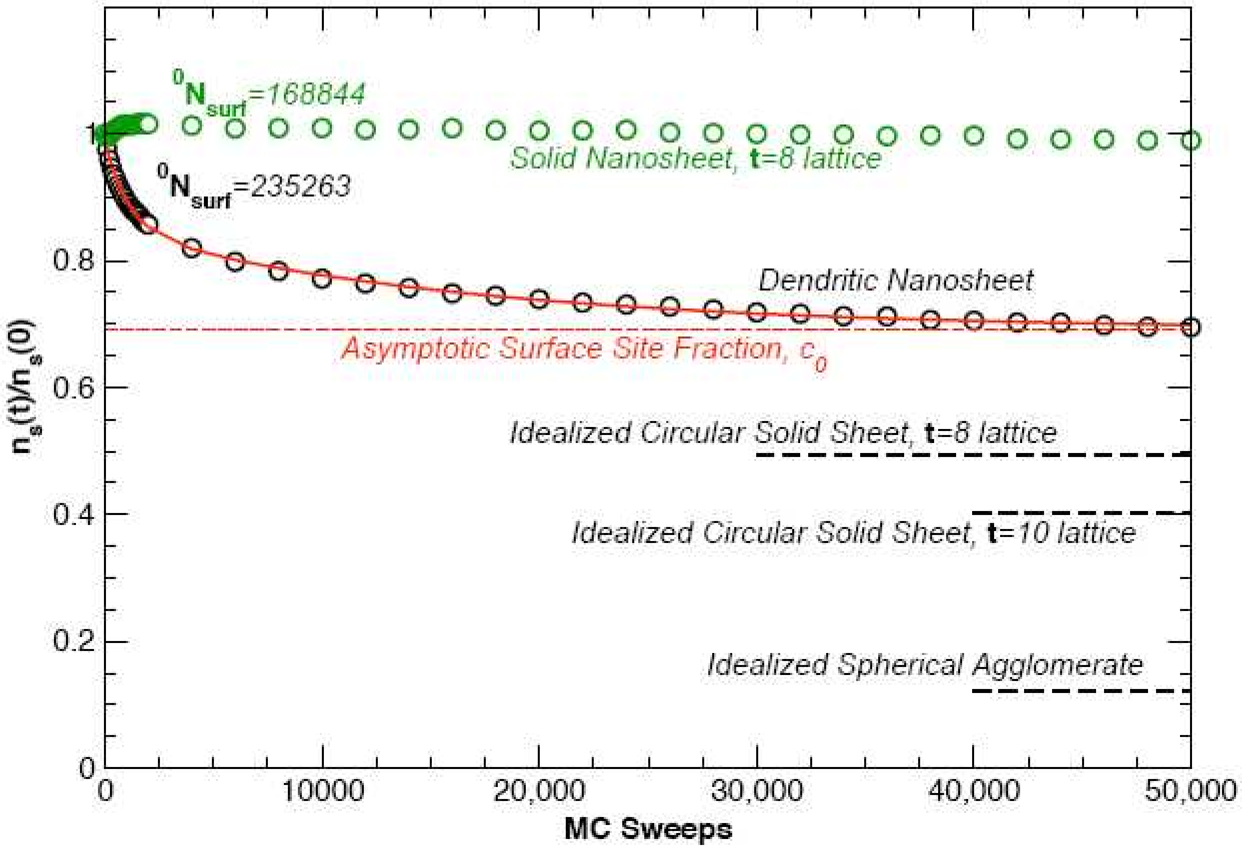
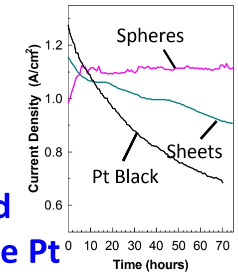


Figure 7: Thickness at 50000 MC sweeps of a solid nanodisc of different starting thicknesses: 2 sites, 3 sites, and 4 sites, left to right.



$^{0}N_{surf}$=168844
Solid Nanosheet, t=8 lattice
$^{0}N_{surf}$=235263
Dendritic Nanosheet
Asymptotic Surface Site Fraction, c_0
Idealized Circular Solid Sheet, t=8 lattice
Idealized Circular Solid Sheet, t=10 lattice
Idealized Spherical Agglomerate
$n_s(t)/n_s(0)$
MC Sweeps
0
0.2
0.4
0.6
0.8
1
10000
20,000
30,000
40,000
50,000

Nanoengineered Electrodes for Fuel Cells

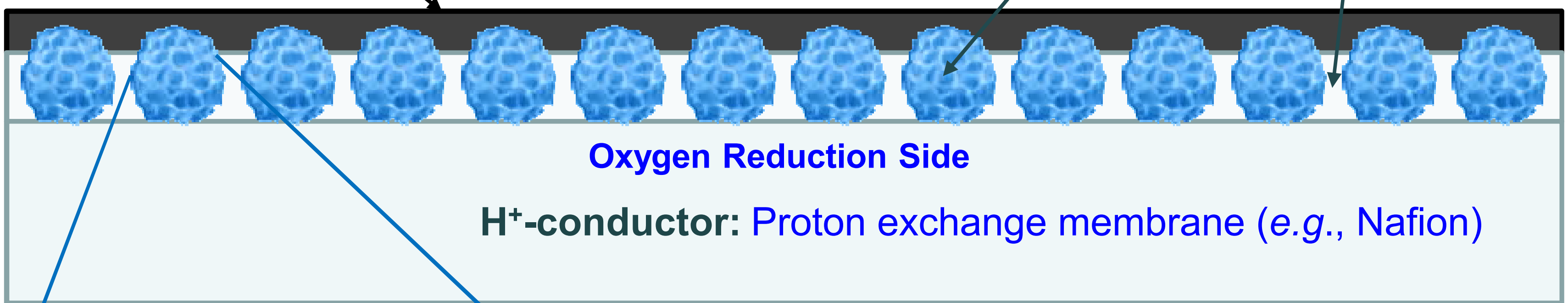


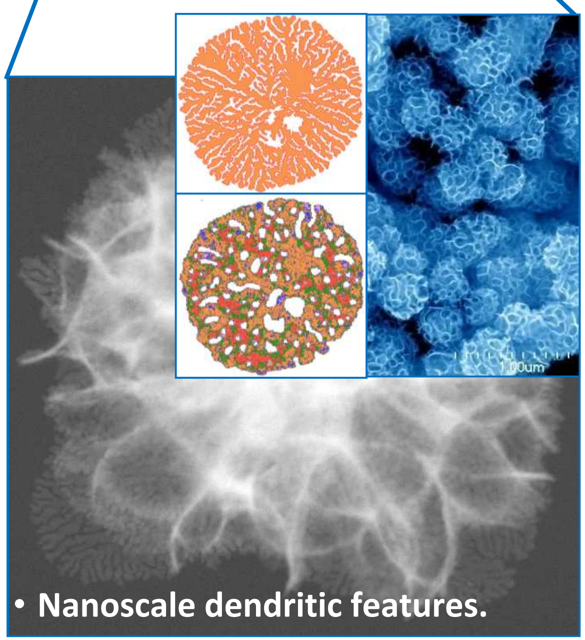
Fuel Cell Electrodes for Efficient and Durable Power Generation:

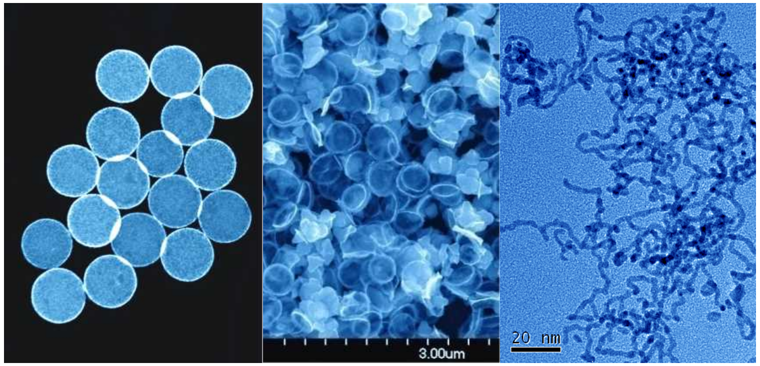
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

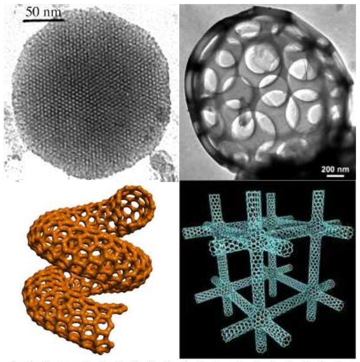
Electronic conductor: **Carbon or CNTs with controllable pores for O_2 and H_2O diffusion**

Catalyst layer: **Controled thickness (*e.g.*, foam-like Pt nanospheres in Nafion slurry)**









- **Variety of Pt & C morphologies exists for FC electrode nanoengineering.**
- **Sandia-discovered sintering/ripening-resistant nanoscale morphologies, *e.g.*, holey sheet.**
- **Simulations and experiments to determine best morphologies and hierarchical nano-architectures.**