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Metal Nanostructuring by Photocatalytically Initiated Dendritic Growth in Soft Templates

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U.S. DEPARTMENT OF ENERGY

2009 R&D 100 Award for NanoCoral

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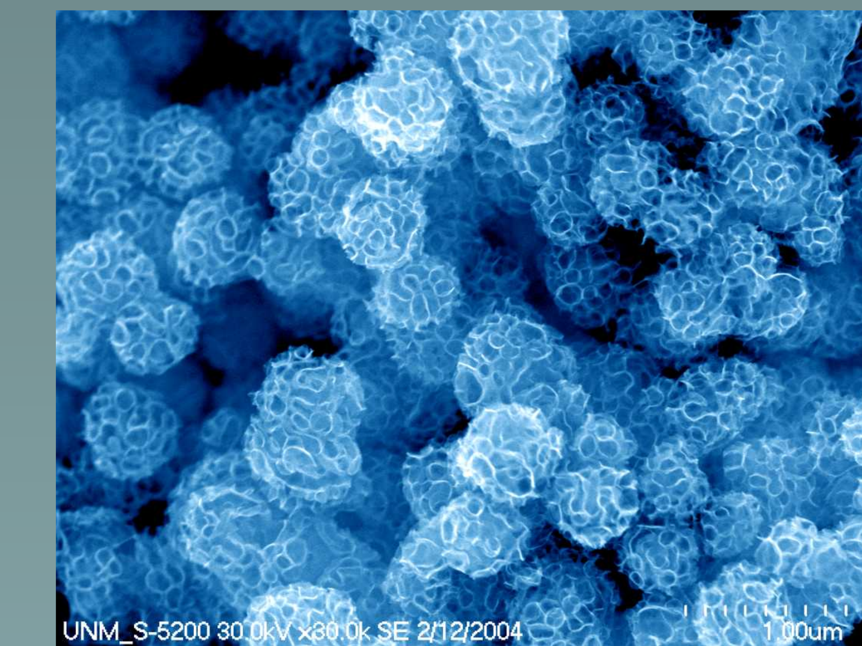
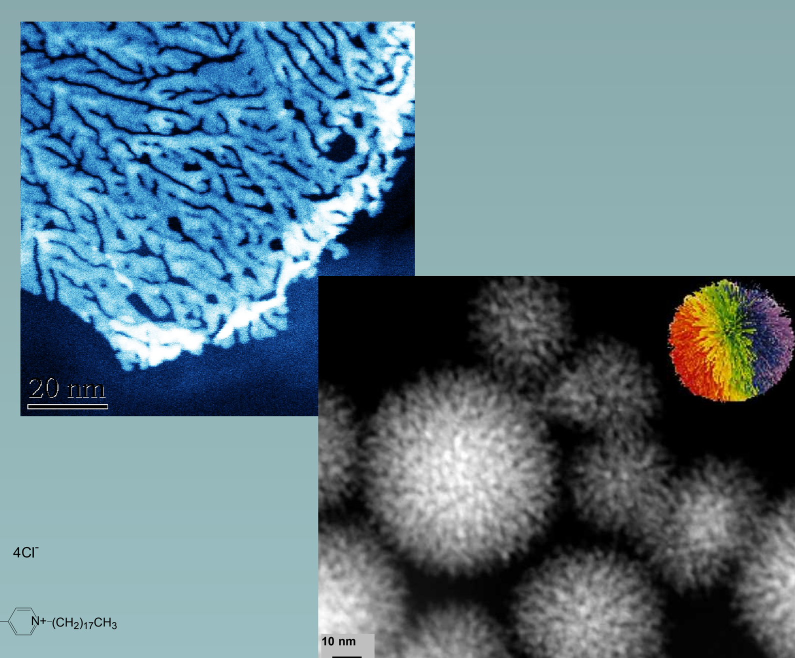
- **Background & Significance**: A new method was developed for producing dendritic metal structures with nanoscale dimensions in various shapes. Dendritic growth of platinum and other metals was discovered at Sandia, and soft templating and photocatalytic seeding methods for controlling the shape and size of the metal nanostructure were also invented at Sandia.
- **Research goals**: Prepare new types of metal nanostructures using catalytic metal like Pt and Pd for applications in renewable energy technologies, especially PEM fuel cells.
- **Major results**: Holey nanosheets: the first ripening resistant nanostructure was discovered.
- **Significance**: The synthesis of a wide variety of new Pt group metal structures is now possible, providing a wide variety of new materials for use in renewable energy applications.

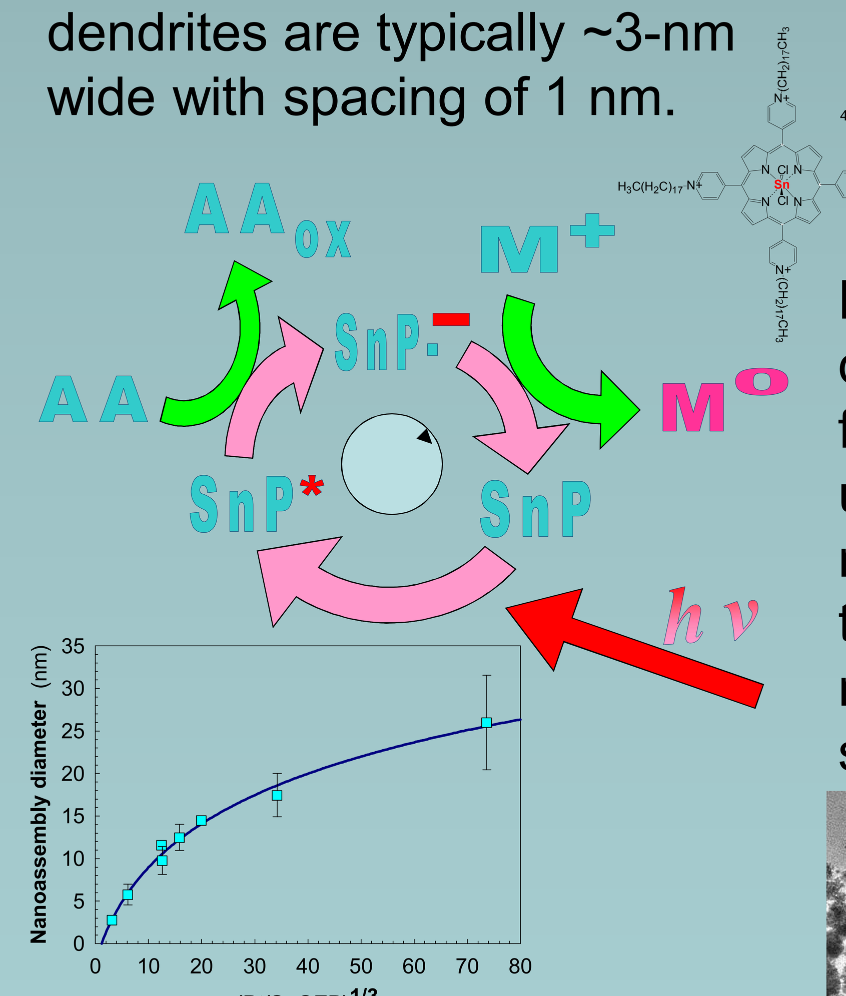


NanoCoral: Dendritic Pt Nanosheets

Research Description

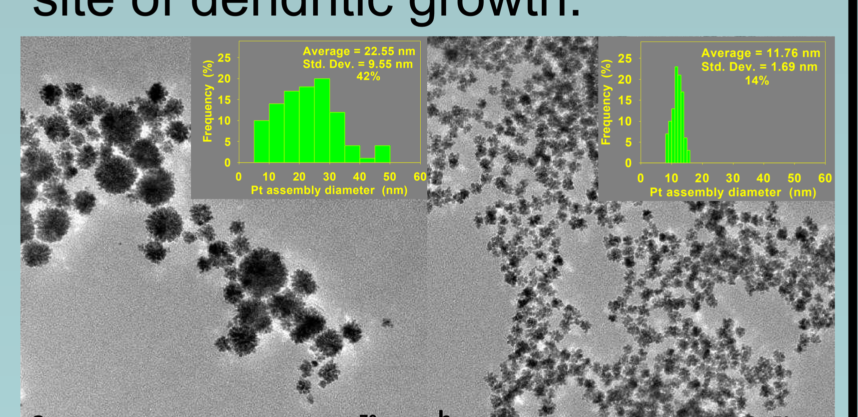
Dendritic metal growth occurs in two or three dimensions. Growth in surfactant bilayers gives dendritic nanosheets (2 nm thick); growth in micelles gives globular dendrites. Arms of the dendrites are typically ~3-nm wide with spacing of 1 nm.



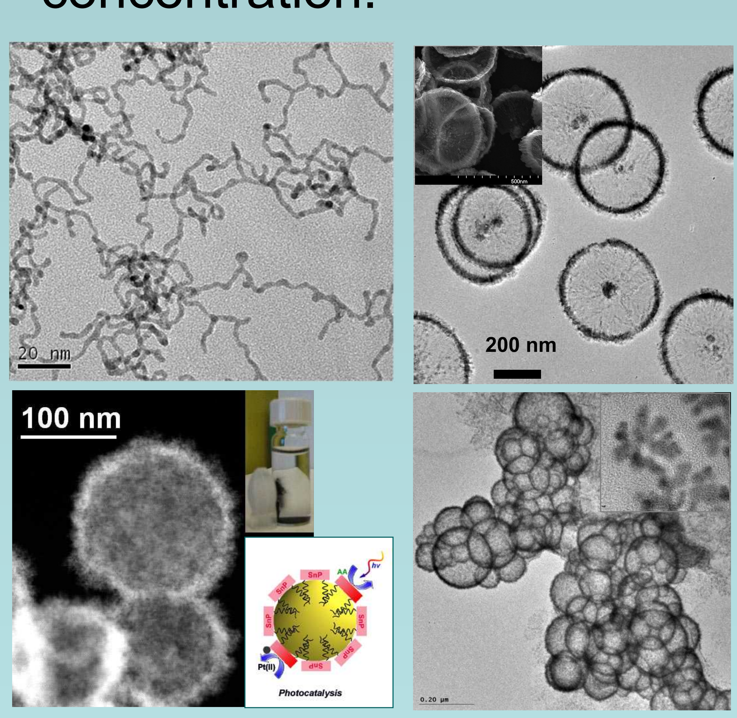


Photocatalytic seeding of dendrite growth was developed for controlling the size and uniformity of the metal nanostructures. The location of the porphyrin photocatalyst molecule can also determine the site of dendritic growth.

Size can be controlled by varying light exposure time, porphyrin concentration, or Pt concentration.



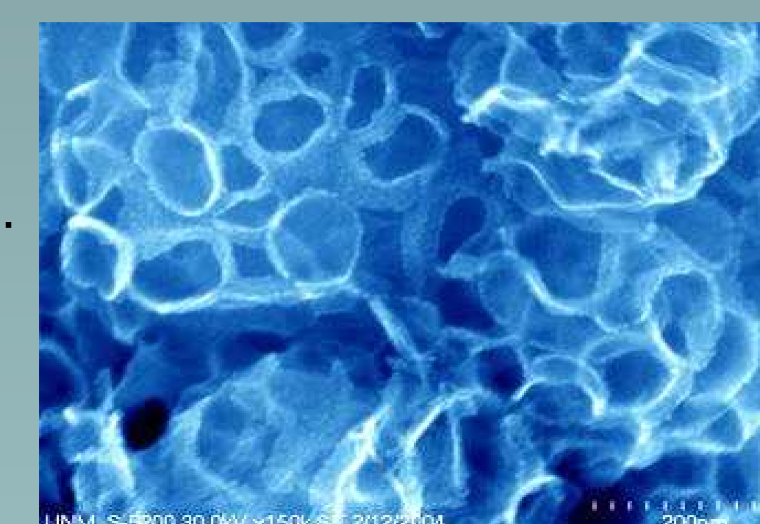
TEM images of globular dendrites grown with (right) and without (left) photocatalyst and light.



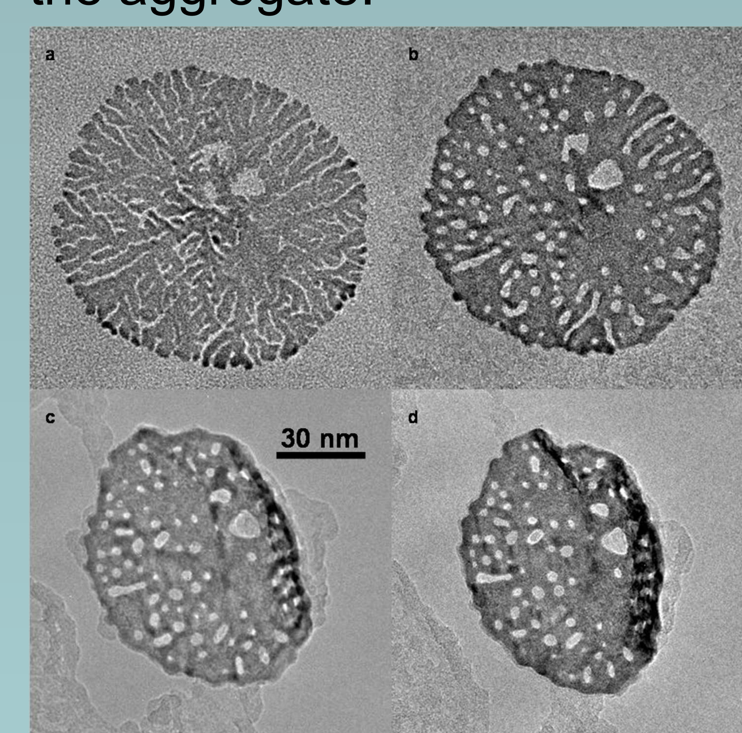
Shape control comes from the shape of the templating structure. Both hard and soft templates are effective. Examples include surfactant assemblies (liposomes, vesicles, bicelles, worm-like micellar networks, nanoemulsions) and hard spheres (silica, polystyrene).

Major Results & Impact

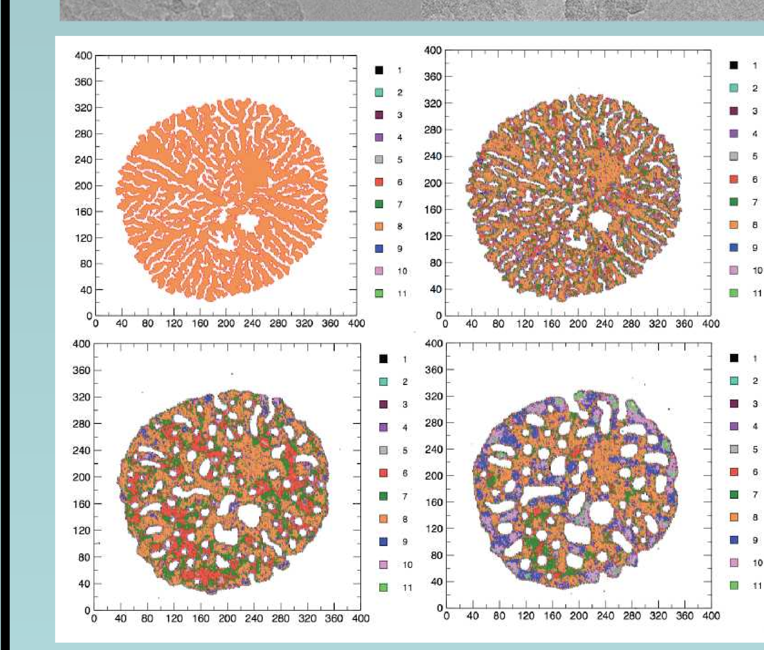
The dendritic Pt nanosheets form highly extended structures when templated on aggregated liposomes. Initiation of a Pt nanoparticle seed, spontaneously or photocatalytically, starts growth of dendritic sheet in the liposomal bilayer and then spreads to adjacent liposomes in the aggregate.

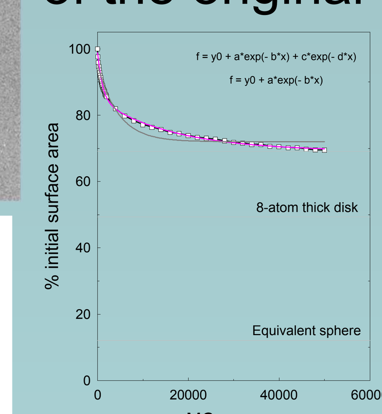


The isotropic growth stops when the Pt complex is exhausted leaving unfinished spheres at the surface.



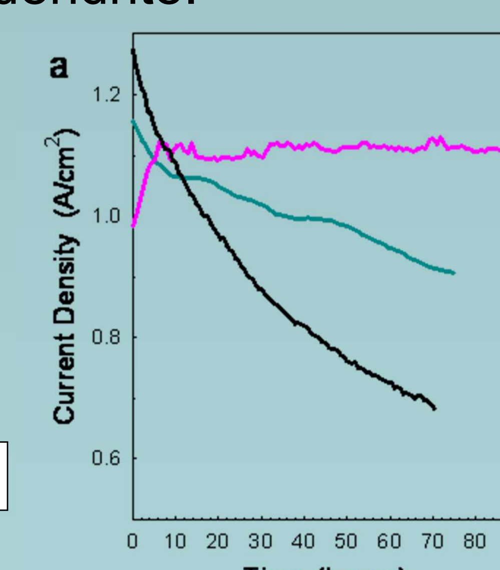
Dendritic Pt nanosheets ripen/sinter to form a holey nanosheet with some lose of surface area. The holey sheet is a metastable structure due to the persistence of the holes formed along the spaces between the arms of the original dendrite.



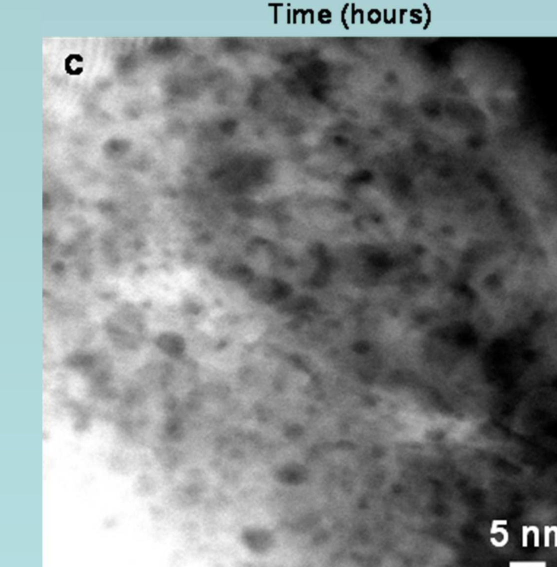


$$\tilde{\mu}_{Pt^0}(r) = \mu^{o}_{Pt^0}(\infty) + \frac{2\gamma V_m^{Pt}}{r} + 2F\phi(r)$$

Monte Carlo simulations of ripening dendritic sheet show the metastability of the holey sheet.



Fuel cell membrane electrode assemblies (MEAs) made with the dendritic nanospheres (NanoCoral) show enhanced durability compared to flat nanosheets and unsupported Pt black. The enhanced durability correlates with the smaller loss of surface area for NanoCoral.



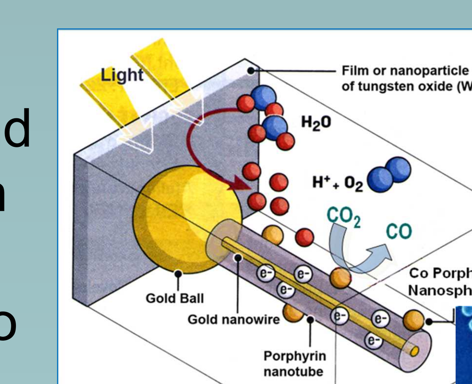
Holes in nanosheet formed after running MEA at 0.5 V for 75 h.

The Future

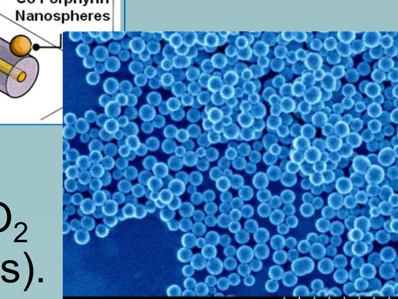
There are still many new nanostructures that can be made using various templating forms and fundamental questions about how metal grows dendritically—a process that is still not adequately understood. While continuing to develop a basic understanding of the dendritic and photocatalytic metal growth processes, we will shift the technological focus toward utilizing the methods developed to generate hierarchical composite solar nanodevices.

Future studies should include:

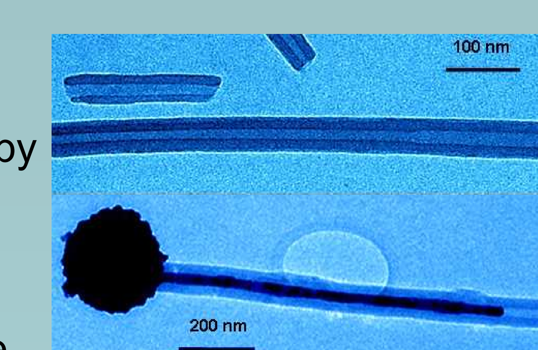
Combining porphyrin structures that carry out light-harvesting and charge-separation functions with metal catalysts and electrical components (connectors, etc.) to produce solar nanodevices.



A possible CO_2 reducing nanodevice.



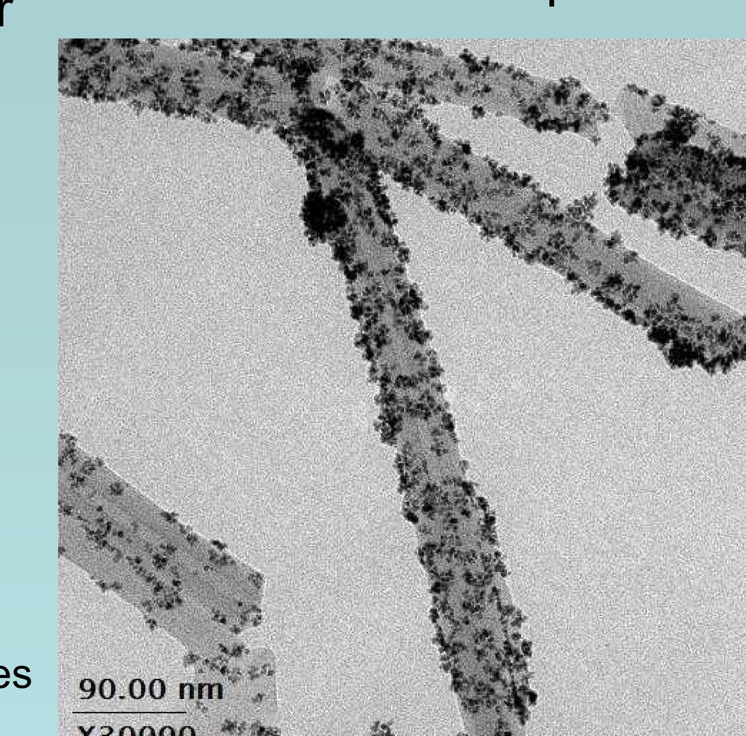
Co porphyrin structures as (CO_2 reduction catalysts).



Photocatalytic reduction of a Au(I) complex by the porphyrin nanotubes results in a nanowire in the core of the tube.

Photocatalysis mediated by the porphyrin nanostructure reduces metal complexes, depositing the metal onto the structure and thus self-generates the required additional metal components.

To fully realize the potential uses of the porphyrin structures (see adjoining poster) we need to better understand their light-harvesting and photocatalytic properties better. We intend to also study the growth of metals on the porphyrin structures to determine what controls the locations at which metal deposits, providing better control over metal deposition.



Photocatalytic reduction of a Pt(II) complex by the porphyrin nanotubes results in Pt nanoparticles on the exterior of the nanotubes.

NNSA National Nuclear Security Administration

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