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Synthesis of Platinum Nanocages using Liposomes Containing Photocatalyst Molecules

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Experimental Details:

Chemicals: Potassium tetrachloroplatinate(II) (K₂PtCl₄, 99.99%), AA (99+%), DSPC (99%), and cholesterol (99+%) were of the highest purity available and were used as received from Sigma-Aldrich (St. Louis, MO). SnOEP was obtained from Porphyrin Products (Logan, UT) and used without further purification.

Liposome preparation: Stock solutions in chloroform of 5 mL of DSPC (1 mm), 5 mL of cholesterol (1 mm) and 0.2 mL of SnOEP (5 mm) were added to a roundbottomed flask. The flask was connected to a rotary evaporator and dried at 35°C to form a thin lipid film on the inside wall of the flask. The residual traces of solvent were removed by overnight drying under high vacuum. The film was then hydrated in 10 mL of an aqueous solution of AA (150 mm) for one hour at 65°C to form multilamellar liposomes. The multilamellar liposomes were then sonicated briefly in a bath to reduce the average size of the vesicles and then extruded through a 200-nm pore polycarbonate membrane in a LIPEXTM liposome extruder (Northern Lipids Inc. Vancouver, Canada). The liposomes were extruded at least 10 times to ensure uniform size distribution and to filter out the undissolved SnOEP. The liposomes have an average size of 170-nm in diameter, which was measured on a Protein Solutions DynaPro LSR (Lakewood, NJ) at 25 °C with a laser wavelength of 782.4 nm. For the measurement, at least 20 data acquisitions with a baseline error threshold below 1% were obtained and averaged to yield the particle size. The concentration of SnOEP in the as-prepared liposomes is 7.9 µM, according to the absorbance value of the Soret band in its UV-visible spectrum obtained using an HP 8452A diode array spectrophotometer (Colorado Springs, CO). The extinction coefficient was taken to be $3.16 \times 10^5 \text{ cm}^{-1}$.[1]

Synthesis: Irradiation for 30 minutes with incandescent light (800 nmol cm⁻²s⁻¹) led to a mixture with transparent and colourless supernatant and a black precipitate residing at the bottom of the reaction vessel, indicating that reduction of the colored Pt complex was complete. The light intensity was measured with a Hansatech Instruments (Norfolk, England) Quantitherm light meter thermometer. The obtained clear supernatant also suggested that the templating liposomes were associated with the platinum after reduction; otherwise we should still observe the cloudiness caused by the presence of the liposomes as before the reaction was started.

TEM samples were prepared on holey carbon copper grids (SPI, West Chester, PA). For SEM characterizations, the samples were loaded onto a doped silicon wafer and were rinsed with water, ethanol, and chloroform to remove lipids and other reaction by-products to improve conductivity. The samples without cleaning showed a lot of charging effect under SEM beam.

[1] K. M. Smith, *Porphyrins and metalloporphyrins*, 2nd ed., Elsevier/North-Holland Biomedical Press, Amsterdam, The Netherlands, **1976**.

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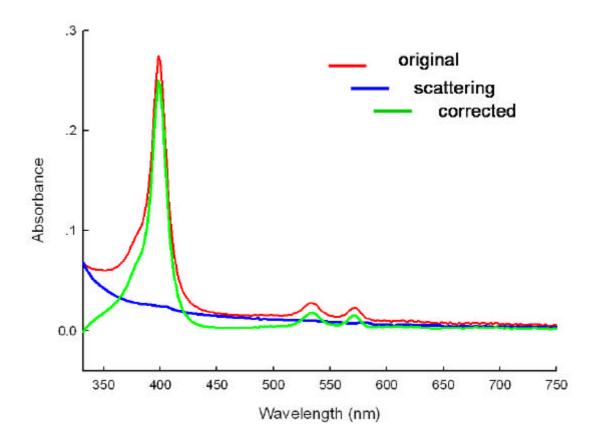


Figure S1 UV-visible spectrum of SnOEP residing between liposomes bilayer in water using 1-mm cell (red line: original data; blue line: scattering; green line: corrected for scattering)

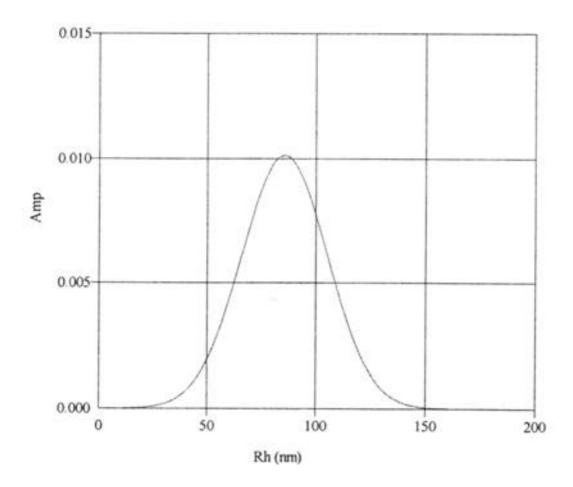


Figure S2 Radii distribution of the liposomes containing SnOEP

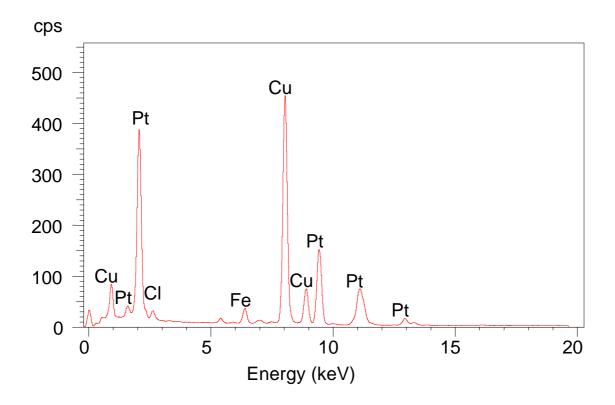


Figure S3 EDX spectroscopy of the hollow platinum nanocages (Copper peaks arise from TEM grid; iron peak is an artifact from background; chlorine peak comes from the metal salts, K₂PtCl₄.)

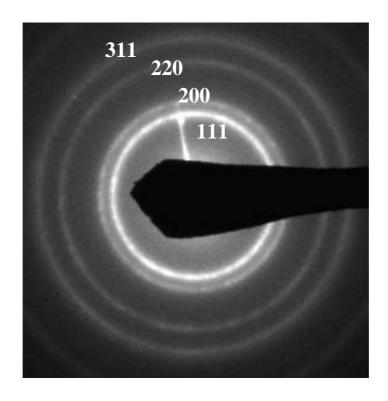


Figure S4 SAED pattern of the hollow platinum nanocages

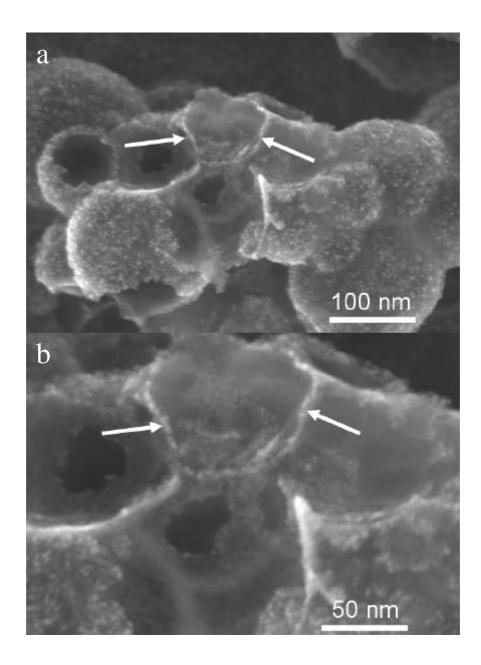


Figure S5 SEM images of partially broken platinum nanocages showing the 2-nm shell, which are pointed by arrows, at low (a) and high (b) magnifications. (Note: Some edges appear thicker than 2-nm in that they are not perpendicular to the electron beam, thus leading to the observed thickening.)

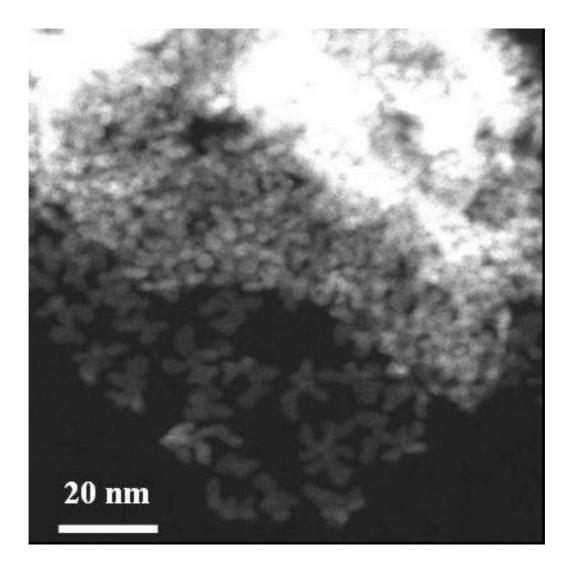


Figure S6 HAADF STEM image of a partially broken platinum nanocages with edges suitable for identification of the constituent dendritic nanosheets.

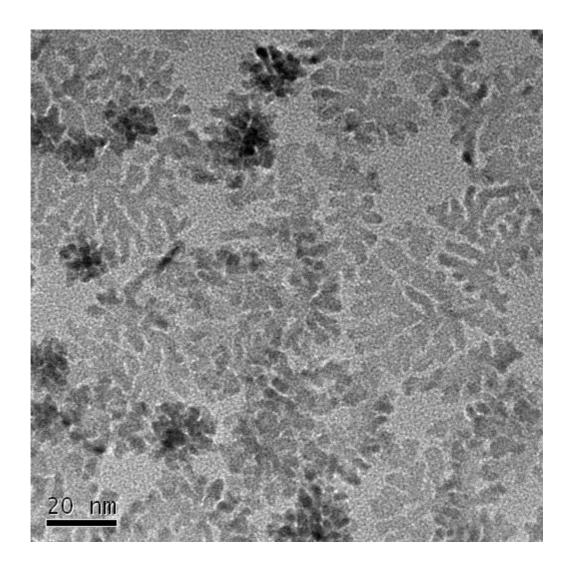


Figure S7 TEM image of the dendritic nanosheets synthesized in the presence of 5 $\,$ mm of platinum complex.