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Electronic Supplementary Information For:

Effects of Lipid Bilayer Encapsulation and Lipid Composition on the Catalytic Activity and Colloidal Stability of Hydrophobic Palladium Nanoparticles in Water

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I. Materials

II. Instrumentations

III. Synthesis and characterization of sodium S-dodecanethiosulfate ligand

IV. Characterization of Pd nanoparticles synthesized by alkyl thiosulfate method

V. Characterization of lipid and lipid-Pd nanoparticles assemblies

VI. Catalytic reaction

I. Materials

The following reagents were purchased from the specified suppliers and used as received without further purification: Sodium thiosulfate pentahydrate (Na₂S₂O₃•5H₂O), ethanol, toluene, methanol, acetone, and chloroform were purchased from Fisher Scientific. Tetra-*N*-octylammonium bromide (TOAB), potassium tetrachloropalladate (II) (K₂PdCl₄), sodium borohydride (NaBH₄), 1-octene, *E*-2-octene, and *Z*-2-octene were purchased from Acros Organics. 1-Bromododecane (C₁₂H₂₅Br) and sodium thiosulfate pentahydrate (Na₂S₂O₃•5H₂O) were purchased from Sigma-Aldrich. Deuterium oxide (D₂O) and chloroform-D (CDCl₃) were purchased from Cambridge Isotope Laboratories, Inc. 1,2-Distearoyl-sn-glycero-3-phosphocholine (DSPC) and chlorofor were purification system.

II. Instrumentations

¹**H NMR.** Sodium S-dodecylthiosuflate ligand was dissolved in D₂O. PdNP and PdNP-DSPC hybrid samples were dissolved in CDCl₃. ¹H NMR spectra were obtained by a Bruker Fourier 300-MHz NMR.

Fourier transform-infrared spectroscopy. The solid-state IR spectrum of sodium *S*-dodecylthiosulfate was collected using a Bruker FT-IR spectrometer.

UV-Vis spectroscopy. The UV-Vis spectrum of the purified PdNP was collected using a Shimadzu UV-2450 spectrometer with chloroform as solvent.

Transmission electron microscopy. Core size and size distribution of the PdNPs were determined by magnification under a JEOL 1200 EX II electron microscope operating at 100kV. PdNPs were dispersed in THF then deposited onto 200 mesh carbon-coated copper grids with

Formvar film (Ted Pella, inc.) and left to air dry. PdNP-DSPC hybrid samples were diluted in deionized water to 100X of original concentration and loaded dropwise on the same TEM grid. Images of PdNPs were analyzed for particle size distribution via Scion Image Beta Release 2. **Thermogravimetric analysis - differential scanning calorimetry (TGA-DSC)**. DSPC-PdNP LNA sample was placed in a furnace at 150 °C to remove residual moisture from the sample. A 40 μ L Tzero alodined pan containing ~5 mg of DSPC-PdNP was placed into the thermogravimetric analyzer beam. Analysis was done within the following parameters: temperature ramp rate of furnace set at 10 °C/min recording data from 30 – 240 °C under argon gas with a flow rate of 50 mL/min. TRIOS software was used to obtain data through a TA SDT650 instrument.

Dynamic light scattering (DLS) for size distribution. A 1.2 mL aliquot of sample was injected in a disposable polystyrene cuvette before measurement analysis using a Nano ZS90 Zetasizer instrument (or Malvern Zetasizer with 13° backscattering). The measurement parameters are the following: the dispersant material was water at 25 °C/scan per sample. This technique measures the intensity of light scattered by the sample over a period to estimate the hydrodynamic radius of colloidal particles. The amount of light scattered by a particle increases with its surface area, so larger particles are more heavily weighted than in number or volume distributions.

Gas chromatography - mass spectrometry. Chromatograms of purified catalysis products were collected using a Thermo Fischer GC-MS. The mobile phase was a stream of inert helium gas and stationary phase was a capillary column for the high sensitivity required to separate the catalytic reaction products. The identity of each peak-generating compound was determined by an algorithm matching experimental data to a spectral database. Chromeleon software was used to operate the GC-MS, analyze chromatograms, and identify peaks.

III. Synthesis and characterization of sodium S-dodecylthiosulfate ligands

Synthesis of sodium S-dodecyl thiosulfate ligand. Sodium S-dodecylthiosulfate was successfully synthesized via an S_N2 reaction between 1-bromododecane and sodium thiosulfate.¹ 1-Bromododecane (25 mmol) was added and dissolved in 50 mL of ethanol. Sodium thiosulfate pentahydrate ((Na₂S₂O₃•5H₂O) (25 mmol) was dissolved in 50 mL of water. The two solutions were mixed in a 1000 mL round-bottom flask. The mixture was connected to a condenser and refluxed for 3 hr. Insoluble components were separated from the reaction mixture by gravity filtration then discarded. Crude product was isolated by rotary evaporation of the filtrate. Crude ligand was dissolved in hot ethanol and recrystallized overnight. ¹H NMR (300 MHz, D₂O): δ 3.01 ppm (triplet, α -CH₂-S-SO₃-, 2H), δ 1.67 ppm (quintet, β -CH₂-, 2H), δ 1.32 ppm (broad quintet, γ -CH₂-, 2H), δ 1.9 ppm (multiplet, -CH₂-, 16H), δ 0.77 ppm (triplet, -CH₃, 3H).

The lack of a S-H stretching peak at ~ 2500 cm⁻¹ on the IR spectrum in Figure S1 suggests there are no free thiol ligands. The use of alkanethiol ligands in NP synthesis is known to yield nanoparticles with surface coverage that is denser than those prepared using the thiosulfate counterpart. Having a NP surface with a less dense ligand coating is crucial for imparting high catalytic activity so the purity of the sodium *S*-dodecylthiosulfate ligand is essential for production of effective catalyst.



Figure S1. The characteristic IR spectrum of *S*-sodium dodecyl thiosulfate supports the absence of free thiols in the synthesized ligand.

IV. Characterization of Pd nanoparticles synthesized by alkyl thiosulfate method

UV spectroscopy results shown in Figure S2 indicated the synthesized PdNPs exhibit a feature of small metal nanoparticles without surface plasmon band. The absence of higher energy absorbance bands at ~445 nm indicated the successful formation of PdNPs without the presence of Pd (II) ions.¹



Figure S2. UV-Spectrum of PdNP in chloroform showing absorbance of Pd (0) at its respective wavelength.

The ¹H NMR result of Pd nanoparticles capped with dodecanethiolate is shown in Figure S3. Peaks appearing at ~0.9 ppm and ~1.1 – 1.5 ppm indicate the presence of the methyl (-CH₃) and methylene (-CH₂-), respectively. The broad chemical shifts and the absence of α and β CH₂ chemical shifts exhibit characteristic of surface-bound alkanethiolate ligands. The absence of any other peaks corresponding to the precursor, S-dodecanethiosulfate indicates the purity of the synthesized Pd nanoparticles. ¹H NMR (400 MHz, CDCl₃): δ 1.5-1.1 (m, 18H, CH₂) and δ 0.89 (m, 3H, CH₃).



Figure S3.¹H NMR spectrum of dodecanethiolate-capped Pd nanoparticles in CDCl₃. The broad signal at ~1.55 ppm is due to the presence of water in NMR solvent.

Thermogravimetric analysis (TGA) was used to determine the ratio between the organic ligand and the metal nanoparticle surface. The organic weight fraction of synthesized PdNP comprised around 33% of the weight, whereas the metal (Pd) accounted for about 67% of the weight (Figure S4). Additional TEM image used for the determination of the average core size of the nanoparticles is shown in Figure S5.



Figure S4. Thermogravimetric analysis of PdNPs showing the organic-Pd compositions.



Figure S5. Additional TEM image of PdNPs.

V. Characterization of lipid and lipid-Pd nanoparticles assemblies

| Name | Formula | MW(g/mol) | [X](g/L) | [X](mol/L) |
|-------------|---|-----------|----------|-----------------------|
| DSPC | $\mathrm{C}_{44}\mathrm{H}_{88}\mathrm{NO}_{8}\mathrm{P}$ | 790.15 | 10.00 | 1.27x10 ⁻² |
| cholesterol | C ₂₇ H ₄₆ O | 386.65 | 1.00 | 2.60x10 ⁻³ |
| PdNP | $\sim Pd_{586}(SC_{12}H_{25})_{142}$ | ~90,000 | 0.50 | 5.50x10 ⁻⁶ |

Table S1. Three components were dissolved in chloroform to prepare stock solutions.



Figure S6. ¹H NMR of (top) DSPC and (bottom) DSPC-PdNP liposome assemblies.

To test our hypothesis, dehydrated DSPC-PdNP hybrid assemblies were subjected to DSC analysis to measure the heat flow of the samples as a function of temperature. Results for both samples shown in Figure S7, however, showed broad endo heat flow peaks for LNAs instead of a sharp intense peak at the T_{g-to-l} . The temperature at the peak minimum was recorded at 63.8 °C for LNAs. The broad endo heat flow was likely due to the heterogeneity of DSPC-PdNP hybrid assemblies caused by the low structural stability of materials. The T_{g-to-l} at the minimum peak point appears to have slightly increased with the incorporation of PdNPs compared to the known T_{g-to-l} of DSPC (55 °C).^{2,3} It is important to mention that the overall heat flow might have increased due to the heat conductivity of Pd metal.



Figure S7. DSC result of DSPC-PdNP liposome assembly.

VI. Catalytic Reaction

| Catalyst | Substrate | Conversion (%) | Octane | Octene isomers |
|------------------------------|------------|----------------|--------|----------------|
| PdNP in CHCl ₃ | 1-octene | 100 | 10 | 90 |
| PdNP in H ₂ O | 1-octene | 0 | 0 | 0 |
| DSPC-PdNP | 1-octene | 100 | 100 | 0 |
| DSPC-PdNP | Z-2-octene | 100 | 99 | 1 |
| DSPC-PdNP | E-2-octene | 68 | 55 | 13 |
| DSPC-PdNP- Cholesterol | 1-octene | 95 | 70 | 25 |

Table S2. Summary of catalysis results by various catalysts at 24 h and room temperature.

References

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