

H₂ Reactivity of Pd Nanoparticles Coated with Mixed Monolayers of Alkyl Thiols and Alkyl Amines for Sensing and Catalysis Applications

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Supporting Information

S.1 Thermogravimetric Analysis (TGA) of C₆S Pd and C₈NH₂ Pd MPCs

Thermogravimetric analysis was used to determine the weight loss of the Pd MPC samples as the temperature was slowly increased from ambient temperature to 800 °C. The weight loss was assumed to correspond to the organic fraction of the Pd MPCs and used in conjunction with the transmission electron microscopy (TEM) determined radius to estimate the average composition of the Pd MPCs. Figure S-1 shows the TGA analysis of pure C₆S Pd and C₈NH₂ Pd MPCs. Frame A exhibits the TGA of pure C₆S Pd MPCs with a fairly rapid 12.72% weight loss occurring between 100 and 200 °C and additional gradual weight loss up to 800 °C, resulting in a total weight loss of 18.83%. Frame B shows the thermal decomposition of the organic portion of C₈NH₂ Pd MPCs. The most rapid weight loss of about 12.29% occurs between 100 and 200 °C with an additional weight loss up to 800 °C for a total of 18.93%. The weight loss between 200 and 800 °C occurs in three fairly discrete steps with steep regions and plateaus in the TGA plot that is distinctly different compared to the gradual weight loss observed for C₆S Pd MPCs throughout the entire 200-800 °C range.

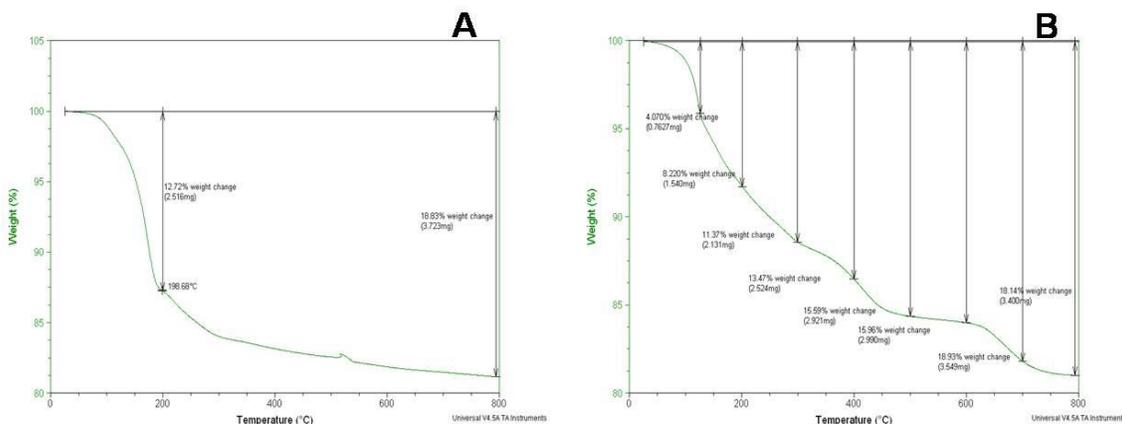


Figure S-1. Thermogravimetric analysis (TGA) of (A) C₆S Pd and (B) C₈NH₂ Pd MPCs.

S.2 Optical Properties of Mixed Monolayers of C8NH₂ and C6S Pd NPs

Figure S-2 shows the UV-vis spectra of dilute toluene solutions containing C8NH₂ Pd, C6S Pd, and C8NH₂/C6S Pd MPCs of varied ratio before exposure to H₂. The spectroscopic measurements of pure C8NH₂ Pd and C6S Pd MPCs were performed immediately after the synthesis of the clusters. In the case of Pd MPCs coated with mixed monolayers of C8NH₂/C6S, the optical properties were obtained in most cases after carrying out the liquid-phase place-exchange reaction for 24 hours. The UV-vis spectra exhibit an absorbance throughout the entire wavelength range that decays exponentially with increasing wavelength, which is expected for metallic Pd⁰ nanoparticles. One exception is the UV-vis spectrum of the 96/81 C8NH₂/C6S Pd MPCs, which shows two small peaks at approximately 330 and 420 nm in the UV-vis spectrum after the 24 hour exchange reaction and very little absorbance greater than 500 nm. This is consistent with the presence of Pd^{II} species instead of Pd⁰. The larger quantity of C6S ligands in this case leads to the oxidation of Pd⁰ to Pd^{II}. To avoid this, we instead performed the place-exchange for only 5 hours, where the spectrum is again consistent with Pd⁰ MPCs as shown in Figure S-2.

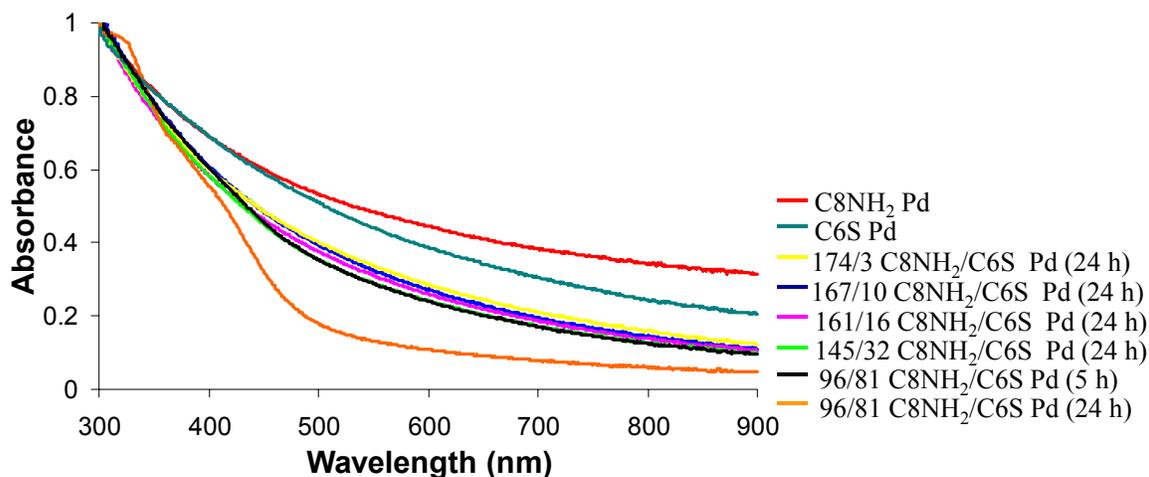


Figure S-2. UV-vis spectra of dilute toluene solutions containing C8NH₂ Pd, C6S Pd, and mixed monolayers of C8NH₂/C6S Pd MPCs before exposure to H₂.

S.3 H₂ Reactivity with solutions of C6S Pd and C8NH₂ Pd MPCs

Diluted toluene solutions containing pure C6S Pd and C8NH₂ Pd MPCs were exposed to 100% H₂ for 60 min at a constant flow of 4.50 ± 0.12 mL/min. Figure S-3 shows a digital picture of vials containing solutions of Pd MPCs coated with C6S and C8NH₂ before and after H₂ bubbling for 60 min. Initially the two solutions of Pd MPCs appeared dark brown in color (Frames A and B). After H₂ exposure for 60 min, the color and

appearance of the solution of C6S Pd MPCs did not change, confirming its low reactivity with H₂ (Frame C). In contrast, the dark color of the solution of C8NH₂ Pd MPCs changed to a colorless solution with a noticeably black solid precipitate of Pd MPCs forming and settling to the bottom of the vial (Frame D). The high reactivity of C8NH₂ Pd MPCs with H₂ leads to PdH_x formation, which leads to the irreversible aggregation of the MPCs as described in the main paper.

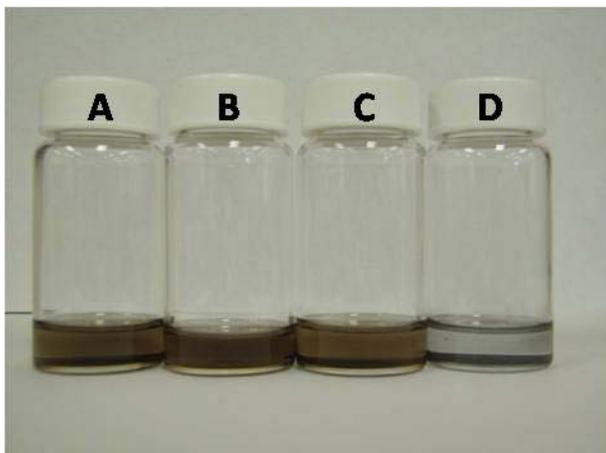


Figure S-3. Dilute toluene solutions of (A, C) C6S Pd and (B, D) C8NH₂ Pd MPCs before (A, B) and after (C, D) H₂ bubbling for 60 min at a constant flow of 4.50 ± 0.12 mL/min.

S.4 Response of the 96/81 C8NH₂/C6S Pd MPC Sensor

The analytical signal used for the detection of H₂ is % response as described by the following equation:

$$\% \text{ response} = (i_r - i_b)/i_b \times 100\% = \Delta i/i_b \times 100\%$$

where i_b is the initial baseline current in 100% N₂, i_r is the current in the presence of the H₂/N₂ mixture, and $\Delta i = (i_r - i_b)$. Figure S-4 shows three calibration curves plotting the % response (y -axis) versus the H₂ concentration (x -axis) for three different sensor devices containing 96/81 C8NH₂/C6S Pd MPCs. Frames A and B show the % response of the devices as function of H₂ concentration from 0.3 to 9.6% and from 0.3 to 1.0% H₂, respectively. All of the devices display fairly linear behavior below 1.0% H₂ (not forced through the origin) and detect H₂ below the explosive limit with a limit of detection of about 0.3%. The device-to-device reproducibility is also good.

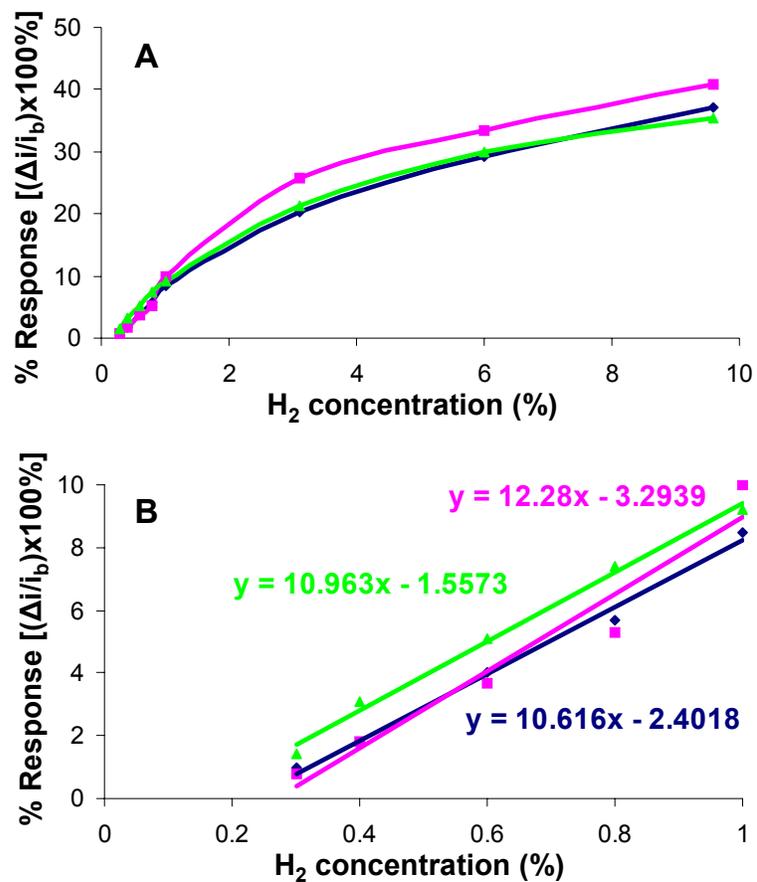


Figure S-4. Calibration curves showing the % response versus H₂ concentration from 0.3 to 9.6% (**A**) and 0.3 to 1.0% (**B**) for each sensor containing 96/81 C₈NH₂/C₆S Pd MPCs.