

Strongly hyperpolarized gas from parahydrogen by rational design of ligand-capped nanoparticles

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Supporting Information

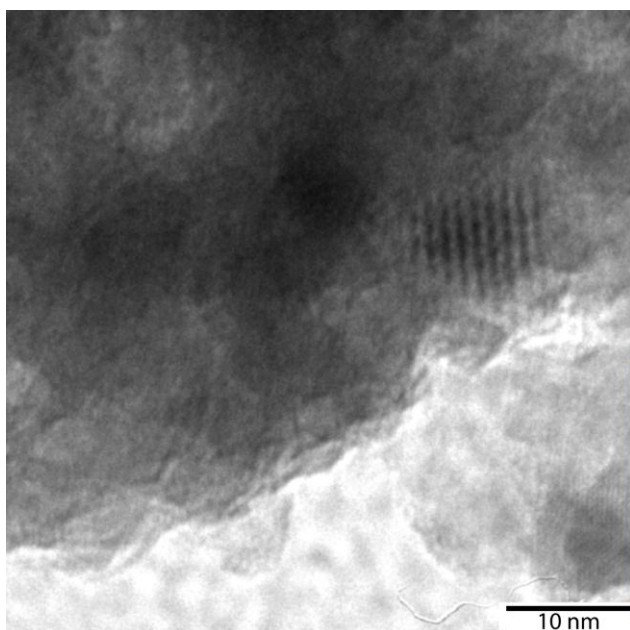


Figure S1. TEM image of bare Pt NPs obtained by incipient wetness impregnation through *in situ* reduction of hexachloroplatinic acid on TiO₂ support using hydrogen gas at 140 °C. The very low concentration (0.02-wt% Pt/TiO₂) led to few NPs within the field of view. The TEM sample was prepared by grinding the support gently using mortar and pestle in the presence of water.

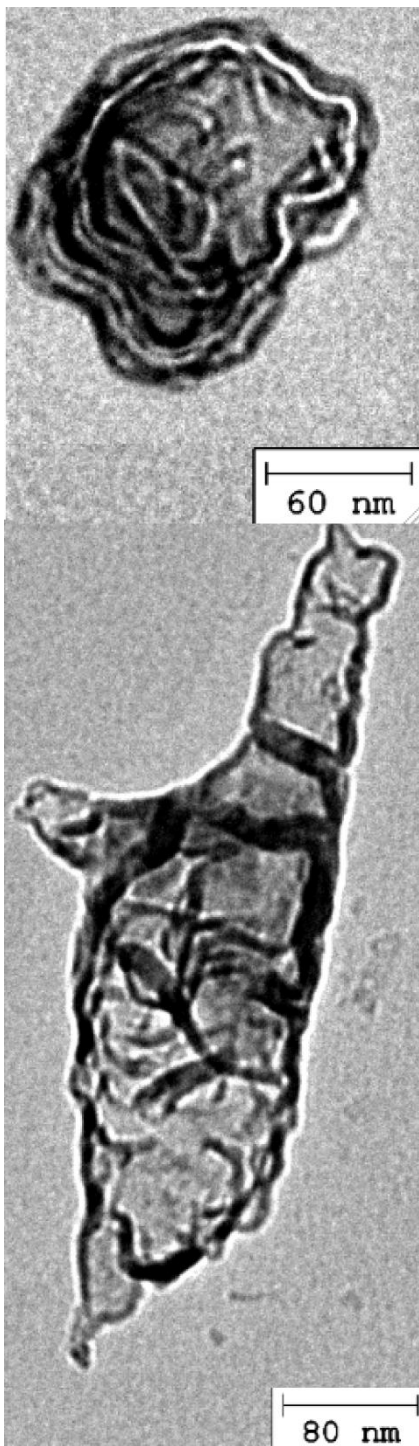


Figure S2. TEM image of Pt particles obtained from ground metal film on SiO₂. The TEM sample was prepared by grinding the black metal film on SiO₂ support using mortar and pestle in the presence of water.

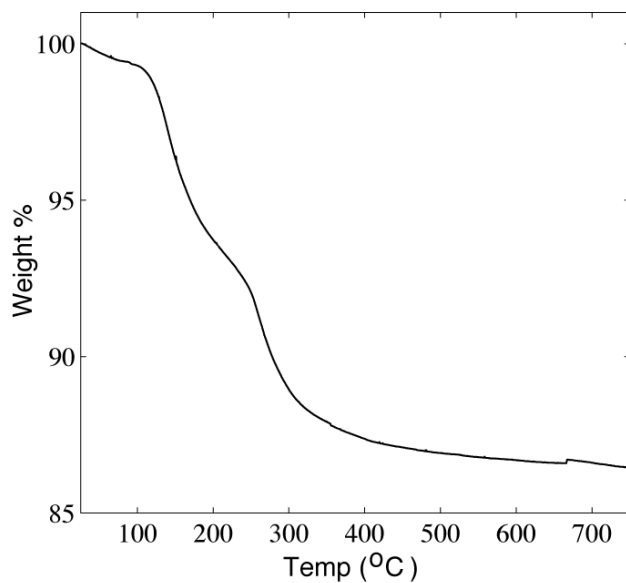


Figure S3. The composition analysis by TGA in p-MBA-capped 2.5 ± 0.4 nm Pt NPs shows 13% ligands and 87% Pt. The surface-bound ligands decompose completely after heating to ~ 400 °C.

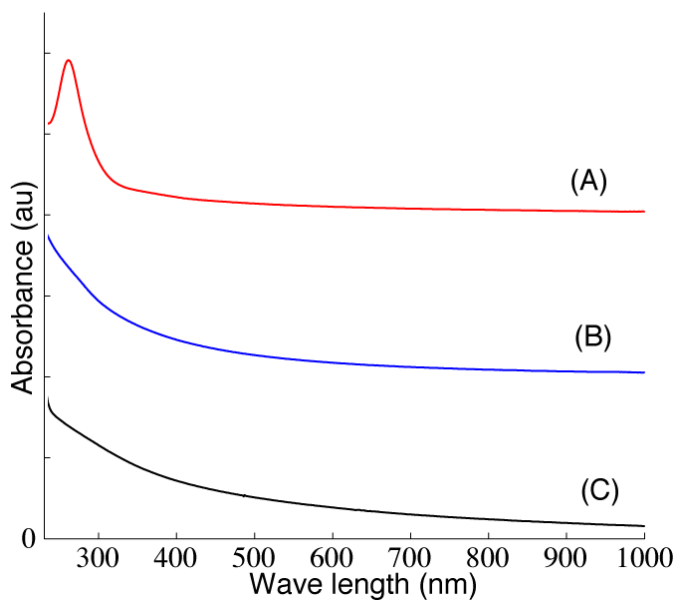


Figure S4. UV-Vis spectra of (A) dilute solution of hexachloroplatinic acid dissolved in water, (B) dilute p-MBA-capped Pt NPs dissolved in water and (C) solution obtained from agitating SiO₂ support containing 1% Pt NPs made through the reduction of hexachloroplatinic acid by passing H₂ gas at 140°C inside the NMR tube. Lack of absorption peak at 262 nm confirms absence of Pt ions used as starting material to produce particles in (B) and (C).

PHIP Enhancement Factor

Figure S5 (same as Figure 1, but magnified) shows two spectra collected consecutively (i.e. back-to-back) for parahydrogen-polarized propane (bottom) and thermally polarized propane (top) from a hydrogenation reaction of propene. The peak assignments for gaseous propane protons are: CH₃, 1 ppm; CH₂, 1.5 ppm. In addition, both spectra show peaks from gaseous propene which is a reactant in the hydrogenation reaction. The propene peak assignments are as follows: CH₃, 1.7 ppm; CH₂ 5 ppm; CH 5.8 ppm. The top and bottom spectra were collected with same experimental setup apart from one difference—the number of scans (NS) is 4,000 for the top spectra and NS=4 for the bottom spectra. Labeled in the top spectra are CH₃ propene as a reference peak (N1) and thermally-polarized propane peak (N2), respectively. In the bottom spectra, the CH₃ propene is labeled as a reference peak (P1) and the parahydrogen-polarized propane peak is labeled (P2), respectively.

The signal enhancement factor, E , was determined from the NMR spectra of Figure S5 as the ratio

$$E = \frac{R_{PHIP}}{R_{NO\ PHIP}},$$

where R_{PHIP} is the ratio of peak areas P2 to P1 and $R_{NO\ PHIP}$ is the ratio of peak areas N2 to N1. This method of calculating the enhancement factor is accurate because the ratios R_{PHIP} and $R_{NO\ PHIP}$ are taken with respect to a reference peak (P1 or N1, respectively) which is constant in both experiments. The NMR spectra were imported into MATLAB and a Lorentzian line with fixed center frequency ω_0 and baseline subtraction was fitted using the model:

$$f(\omega; \omega_0, I, \gamma, m, b) = I \left[\frac{\gamma^2}{(\omega - \omega_0)^2 + \gamma^2} \right] + (m\omega + b),$$

where I is the height of the peak, γ is its width, m is the slope of the baseline and b , the intercept. With ω_0 fixed (there was actually no advantage to holding ω_0 fixed), there are 4 parameters: $\vec{a} = (I, \gamma, m, b)$. Only the data in the neighborhood of each peak was fitted as there is nothing to be gained from fitting the entire spectrum at once. The peak areas are proportional to the product $I \times \gamma$. The fit was performed using the nonlinear least squares (trust-region-reflective algorithm which is part of the `lsqcurvefit` function in MATLAB) with reasonable constraints, such as non-negativity of I, γ . The result from this analysis was:

$$E = 508.$$

The precision can be estimated from the covariance matrix. The function `lsqcurvefit` returns the Jacobian matrix at the end of the fitting procedure:

$$J_{ij} = \partial f(\omega_i) / \partial a_j,$$

where a_j is the j -th entry of \vec{a} . The covariance matrix is estimated from J_{ij} as follows:

$$C = (J^T J)^{-1}.$$

The standard errors α_i for each fitted parameter are obtained from the diagonal elements of C , and the degrees of freedom in the fit:

$$\alpha_i = \frac{\sigma_i}{\sqrt{\nu}} = \frac{\sqrt{C_{ii}}}{\sqrt{\nu}}, \quad \nu = N - 4,$$

where N is the number of data points fitted and 4 is the number of parameters in the fit. All peaks fitted had a degree of freedom of at least 40. The above model $f(\omega; \omega_0, I, \gamma, m, b)$ provided a good fit to all the peaks. We have also fitted the data with fewer parameters, for example, by allowing the user to specify the baseline position. And we also tested global optimization fitting routines based on simulated annealing and genetic algorithms. In all cases, the results were consistent.

For negligible correlations between the parameters I and γ , the error in the area $A = I \times \gamma$ is given by the sum of squared relative errors in I and γ :

$$\alpha_A = A \sqrt{\left(\frac{\alpha_\gamma}{\gamma}\right)^2 + \left(\frac{\alpha_I}{I}\right)^2}.$$

The error in the ratio $R_{PHIP} = A_{P2}/A_{P1}$ is then obtained in a similar way, by adding the squares of relative errors in A_{P2} and A_{P1} . Finally, the error in E is obtained identically – i.e. by adding the relative errors of R_{PHIP} and $R_{NO PHIP}$ in quadrature. The result for the standard error in E is $\alpha_E = 78$, and we get, for the one-sigma (1σ) confidence limits, $E = 508 \pm 78$, i.e. $E \in [430, 586]$.

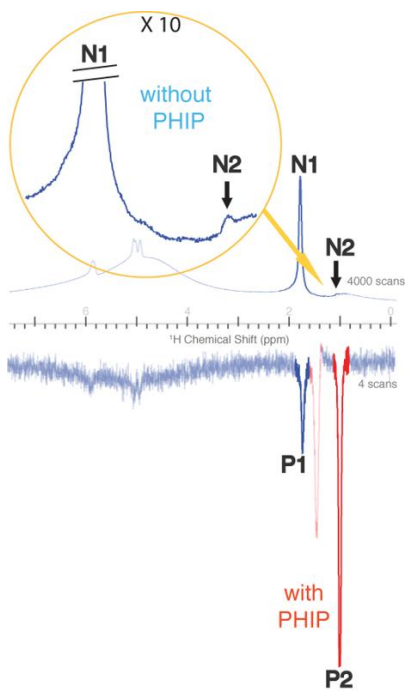


Figure S5. NMR spectra from Figure 1, magnified.