Electronic Supplementary Information

In Situ Synthesis of Ultra-small Platinum Nanoparticles Using Water Soluble Polyphenolic Polymer with High Catalytic Activity

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Catalysis of borohydride reduction of 4-nitrophenol by colloidal Bare-Pt NPs

At first, 2 mL of the as prepared colloidal Bare-Pt NPs (5.7x10^-4 mmol) taken into a 3 mL quartz cuvette followed by the addition of 0.8 mL water, and an aqueous 4-NP solution (0.1 mL, 3 mM) to that solution. The catalytic reduction of 4-NP was then studied in a spectrophotometer at 25 °C with a stirring speed of 500 rpm by final addition of an aqueous NaBH₄ solution (0.1 mL; 300 mM).

Catalysis of borohydride reduction of 4-nitrophenol by colloidal PVPh-PtBH₄ nanocatalyst

First a stock aqueous colloidal Pt NPs suspension was prepared by dilution of 0.5 mL as-synthesised colloidal Pt NPs to 2.5 mL with Milli-Q water. From this, 2 mL (5.1x10^-4 mmol) solution was taken into a 3 mL quartz cuvette. To that solution 0.8 mL water, and an aqueous 4-NP solution (0.1 mL, 3 mM) were added and placed the cuvette in a spectrophotometer at 25 °C with stirring at a speed of 500 rpm. To this reaction mixture, an aqueous NaBH₄ solution (0.1 mL; 300 mM) was finally added to study the reduction of 4-NP.
Figure S1. TEM images of (A) colloidal Bare Pt NPs (B) PVPh-Pt$_{BH4}^{-}$ nanoparticles. Insets in each panel showed the HRTEM of single Pt nanoparticle.

Figure S2. Energy dispersive X-ray (EDX) analysis of (A) PVPh-Pt$_{1.3}$ (B) PVPh-Pt$_{5}$. 
**Figure S3.** Plot showing log-normal distributions of the sizes of the Pt NPs (PVPh-Pt$_5$) from DSL measurements.

**Figure S4.** Plot showing log-normal distributions of the sizes of the Pt NPs (PVPh-Pt$_{1.3}$) from DSL measurements.
Figure S5. Time-dependent absorption spectra of the 4-NP reduction in the presence of PVPh-Pt\textsubscript{1.3} at (A) 30 °C (B) 40 °C.
Figure S6. Time-dependent absorption spectra of the 4-NP reduction in the presence of PVPh-Pt$_5$ at (A) 30 °C (B) 40 °C.

Figure S7. Time-dependent absorption spectra of the 4-NP reduction at 25 °C in the presence of (A) colloidal bare Pt NPs (B) PVPh-Pt$_{BH4^-}$.
Figure S8. Plots of ln A (A = absorbance at 400 nm of p-nitrophenolate ion) versus time for the reduction of p-nitrophenol at 25 °C using catalyst (A) ▲ PVPh-Pt \(^{1.3}\) (B) ● PVPh-Pt\(_{\text{BH}_4}\) (C) ■ Colloidal bare Pt NPs

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\begin{align*}
\text{H}_2\text{C} & - \text{CH}_3 \\
\text{c} & - \text{c} \\
\text{d} & - \text{d} \\
\text{e} & - \text{e}
\end{align*}
\]

Figure S9. \(^1\)H NMR spectrum of ethyl benzene. \(^1\)H NMR (500 MHz, CDCl\(_3\), \(\delta\) ppm): 1.27 (t, 3H, CH\(_3\)), 1.88 (q, 2H, CH\(_2\)), 7.20 (dd, 1H), 7.23 (m, 2H), 7.30 (m, 1H, CH), (The \(^1\)H NMR peak at \(\delta\) 7.26 ppm corresponds to CHCl\(_3\) present in CDCl\(_3\)).
**Figure S10.** $^{13}$C NMR spectrum of ethyl benzene. $^{13}$C NMR (500 MHz, CDCl$_3$, $\delta$ ppm): 15.70 (a-CH$_3$), 29.02 (b-CH$_2$), 125.71 (e-CH), 127.9 (d-CH), 128.4 (c-CH), 144.4 (f-CH) (The $^{13}$C NMR peak at $\delta$ 77.26 ppm corresponds to CHCl$_3$ present in CDCl$_3$).

**Figure S11.** $^1$H NMR spectrum of aniline. $^1$H NMR (500 MHz, CDCl$_3$, $\delta$ ppm): 3.36 (2H, Nh$_2$), 6.70 (d, 2H), 6.78 (t, 1H), 7.17 (t, 2H) (The $^1$H NMR peak at $\delta$ 7.26 ppm corresponds to CHCl$_3$ present in CDCl$_3$).
Figure S12. $^{13}$C NMR spectrum of aniline. $^{13}$C NMR (500 MHz, CDCl$_3$, δ ppm): 115.65 (b-CH), 119.09 (e-CH), 129.83 (d-CH), 146.92 (a-CH) (The $^{13}$C NMR peak at δ 77.26 ppm corresponds to CHCl$_3$ present in CDCl$_3$).

Figure S13. Mass spectra of GC-MS of ethyl benzene obtained after removal of catalyst.
Figure S14. Mass spectra of GC-MS of aniline obtained after removal of catalyst.
**Figure S15.** Time-dependent absorption spectra of the 4-NP reduction in the presence of PVPh-Pt\textsubscript{1.3} at (A) 2\textsuperscript{nd} cycle, (B) 3\textsuperscript{rd} cycle and (C) 4\textsuperscript{th} cycle of catalysis.

**Figure S16.** Plots of ln A (A = absorbance at 400 nm of p-nitrophenolate ion) versus time for the reduction of p-nitrophenol sample at 25 °C using PVPh-Pt\textsubscript{1.3} for (A) ▼ 1\textsuperscript{st} cycle (B) ■ 2\textsuperscript{nd} cycle (C) ● 3\textsuperscript{rd} cycle (D) ▲ 4\textsuperscript{th} cycle of catalysis.
Figure S17. Plot showing the variation in normalized rate constant in different cycles of the borohydride reduction of p-nitrophenol using PVP-Pt$_{1.3}$ sample.
Figure S18. TEM image of the sample PVPh-Pt_{1.3} after 3\textsuperscript{rd} cycle of the catalysis