Supporting Information

Kinetics of the reaction of H_2 with Pt^0-nanoparticles in aqueous suspensions monitored by the catalytic reduction of $PW_{12}O_{40}^{3-}$

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Sample Preparation for High-Resolution TEM (HR-TEM)

The Pt^0 NPs and Pt^0-POM nanoparticles were characterized using HR TEM (JEOL 2100, operated at 200 KeV,) equipped with an EDS system for composition analysis. The samples were prepared by dispersing the NPs in an isopropanol-water mixture and placing one drop of the suspension onto a 400 mesh copper grid. The grids were dried in air prior to the measurement.

Samples preparation for Transmission Electron Microscopy (Cryo-TEM).

A FEI Tecnai 12 G^2 transmission electron microscope (120 kV), equipped with a Gatan slow-scan camera (for imaging) was used for Cryo-TEM measurements. Cryogenically frozen samples were prepared using a fully automated vitrification device (Vitribot, FEI). First, 5 µL of the POM protected Pt^0 nanoparticles suspension was placed by pipet onto a glow discharged Cu grid covered with a lacey-carbon film, held inside a 100%-humidity chamber. The grid was mechanically "blotted" and immediately plunged into liquid ethane (mp 90.34 K) cooled by liquid nitrogen (77.2 K).

NMR Spectroscopy

The NMR spectra were measured on a 400 MHz Bruker Avance III HD (^1H 400MHz,^{31}P 162MHz, and ^{195}Pt 86 MHz) spectrometer equipped with a 5 mm tunable broadband probe (BBFO). All the samples were dissolved in solutions of H_2O (90%)/D_2O (10%) and the NMR experiments were performed at 300 K.

^{1}H NMR spectra were acquired using a pre-saturation experiment (*zgpr*) and the remaining signal for water was used as an internal reference, (4.79 ppm for H_2O), for the chemical shifts**.** ([Pt] = 0.50 mM)

^{31}P{^{1}H} NMR spectra were acquired using a proton decoupling experiment (*zgpg*) with an equal number of scans among all the samples. A solution of 85% H_3PO_4 in H_2O (0 ppm for $^{31}PO_4$) was used as an external reference. ([Pt] = 0.25 mM, [POM] = 10.0 mM)

^{195}Pt NMR spectra were acquired in different arrays through the large chemical shift range of the ^{195}Pt nucleus (approximately 10,000 ppm). The pulse sequence was a simple 1D pulse of 90° (*zg*) and the acquisition time of each experiment took an hour. The chemical shifts were determined compared to the external reference of 0.1M K_2PtCl_4 in D_2O (-1623 ppm relative to Na_2PtCl_6 in H_2O). The final pH of the solution was ~ 1.6. ([Pt] = 5 mM, [POM] = 10.0 mM)

Calculations for the number of Pt atoms on the surface

[NP] = C/ n, where C = 0.5 mM = 0.5×10^{-3} M where C = Concentration of Pt^0, based on the [K_2PtCl_4], n = number of Pt atoms per particle

$$n = \frac{4}{3}\pi r^3 \frac{N}{M.W}\rho$$

For Pt,

ρ_{Pt} = 21.4 g/cm^3

M.W. = 195 g/mol

Diameter of Pt nanoparticle = 2.0 nm r = 1.0 nm = 1.0×10^{-7} cm

From the calculations,

n = 276.8 Pt atoms/ Pt NPs

Therefore,

$[NP] = \frac{0.5\times10^{-3}\,mol/L}{276.8}$

$[NP] = 1.81\times 10^{-6}\, [\frac{\text{mole of Pt nanoparticles}}{L}]$

Number of Pt atoms on the surface of the NPs (n_s),

$n_s = n[\frac{r^3-(r-2r_{(Pt)})^3}{r^3}]$ $\quad r_{Pt} = 1.39\,Å = 1.39\times10^{-8}$ cm $\quad r = 1.0\times10^{-9}$ m $= 1.0\times10^{-7}$ cm

n_s = 170 Number of Pt atoms on the surface of one NP. This is for Pt with radius 1nm.

For, **r=2** nm by same calculations, n= 2213 atoms per particle and **n_s** = 800 atoms/particle

^{1}H NMR

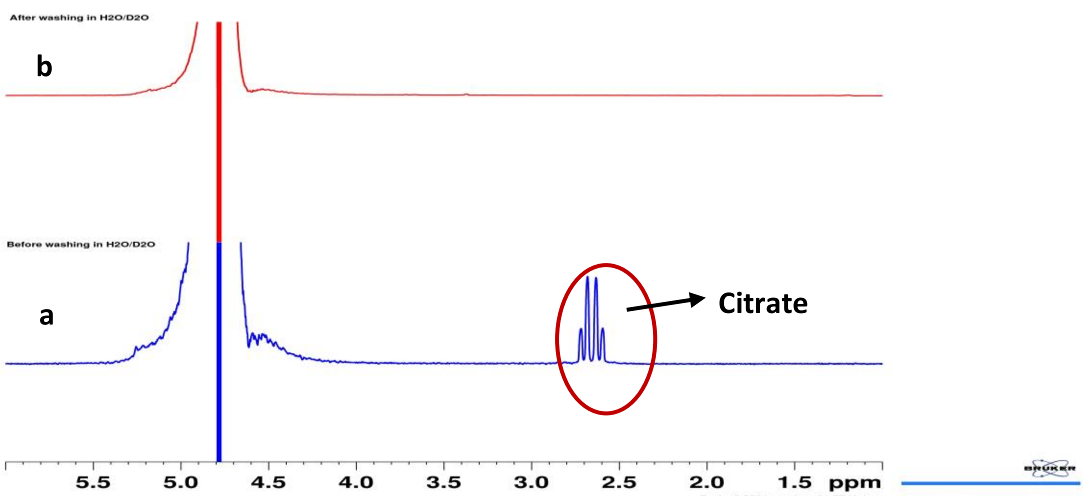

Figure S1. ^{1}H NMR **(**400 MHz, 90 % H_2O/10 % D_2O, 300 K) spectrum of synthesized Pt nanoparticles (0.50 mM)

- **(a)** before washing (blue color)
- **(b)** after washing with resin (red color)

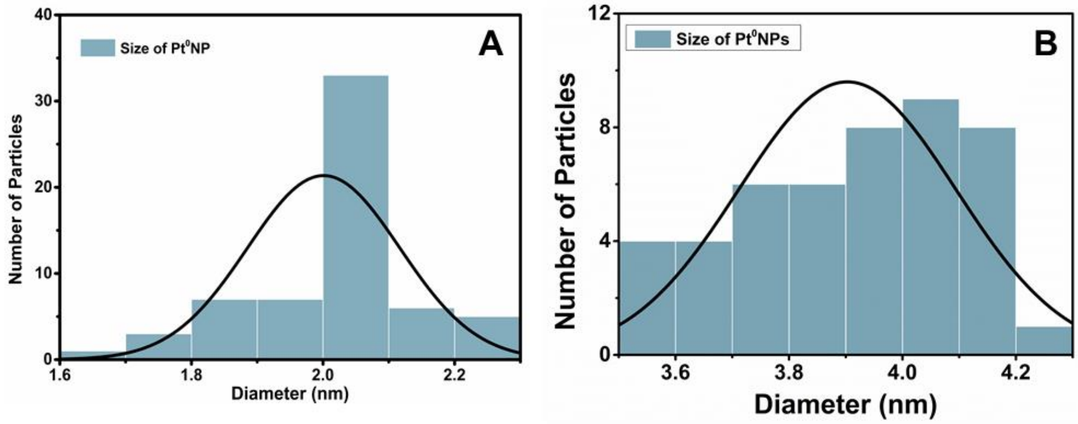

Figure S2. Size distribution curve of synthesized Pt^0 NPs (From HR-TEM)

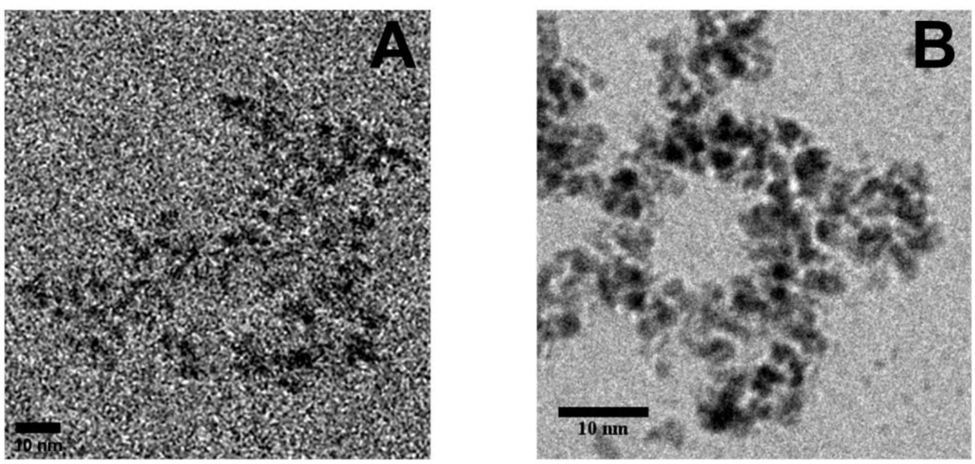

Figure S3. Cryo-TEM images (A) citrate-protected and (B) $PW_{12}O_{40}^{3-}$ protected Pt°-NPs

$Pt^0NP@POM-H_2$ (2 nm Pt)

POM dependence

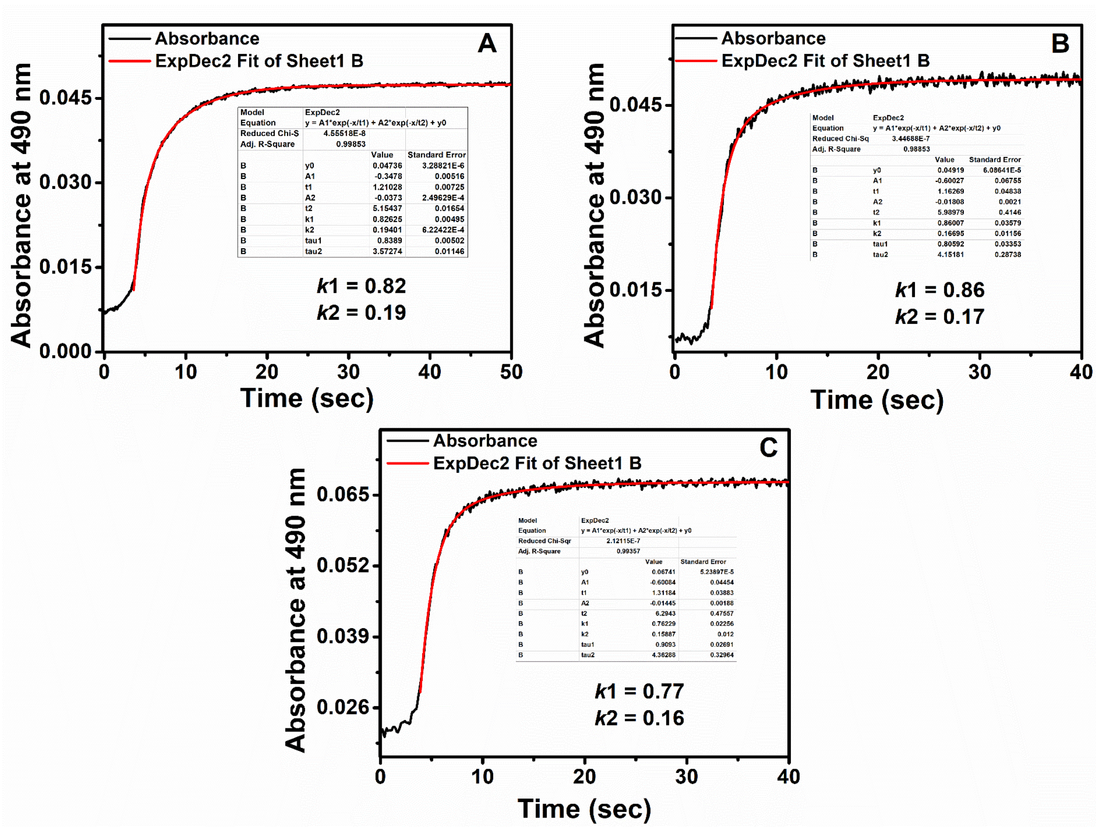

Figure S4. Typical kinetic curves of the reaction of Pt°-NP@$PW_{12}O_{40}^{3-}$ with three different concentrations of $PW_{12}O_{40}^{3-}$ with H_2 saturated water (pH – 1.5) at 490 nm.

Table S1. The k_{obs} values and the ratio of their absorbance for three different concentrations of $PW_{12}O_{40}^{3-}$ (0.00005, 0.0001, and 0.00015 mol/L) by maintaining a constant concentration of surface Pt atoms (6.14 × 10^{-5} mol/L) and H_2 (0.00040 mol/L).

Concentration of $H_3PW_{12}O_{40}$ (mol/L)	k_{obs} s^{-1} in Pt^0-POM *k*1	k_{obs} s^{-1} in Pt^0-POM *k*2	Ratio of Absorbance A1/A2
0.000050	0.82	0.19	9.69
0.00010	0.86	0.17	33.20
0.00015	0.77	0.16	42.0

Pt dependence

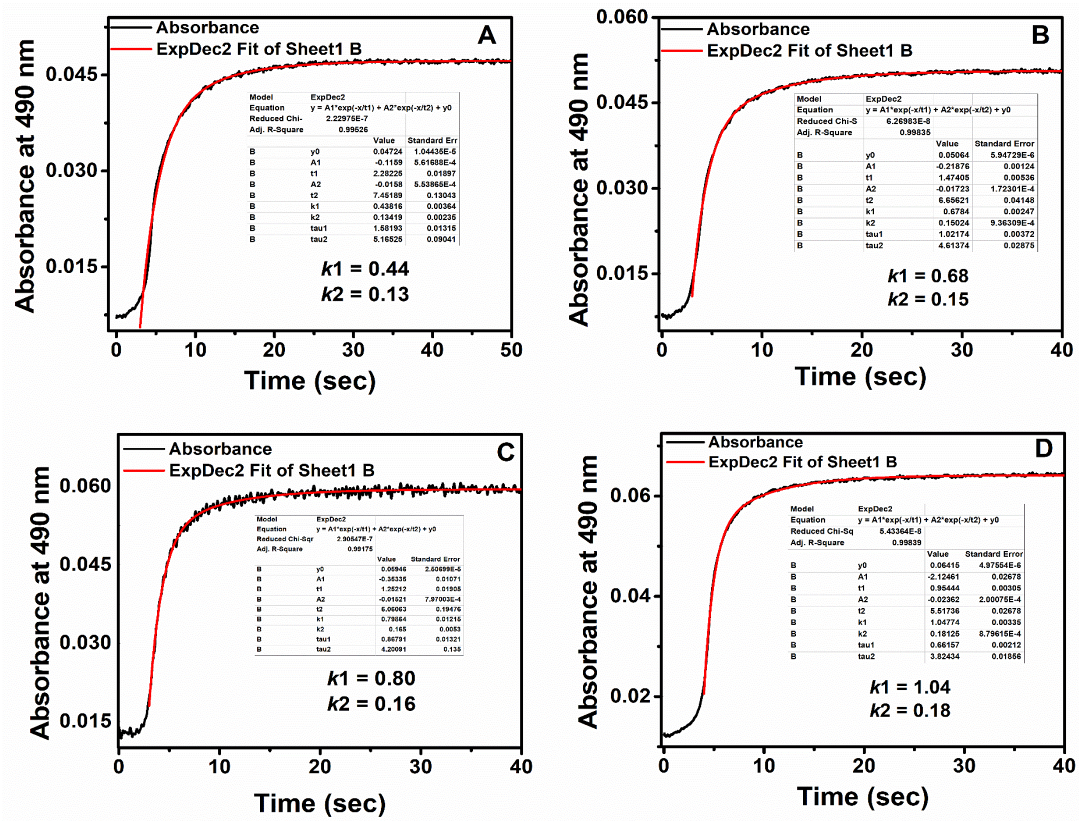

Figure S5. A typical kinetic curve of the reaction of Pt°-NP@$PW_{12}O_{40}^{3-}$ with four different concentrations of surface Pt atoms with H_2 saturated water (pH – 1.6) at 490 nm.

Table S2. The k_{obs} values and the ratio of their absorbance for four different concentrations of surface Pt atoms by maintaining a constant concentration of $PW_{12}O_{40}^{3-}$ (0.00010 mol/L) and H_2 (0.00040 mol/L).

Concentration of Pt atoms on the surface (mol/L)	**k_{obs} s^{-1} in Pt^0-POM *k*1**	**k_{obs} s^{-1} in Pt^0-POM *k*2**	**Ratio of Absorbance A1/A2**
3.07×10^{-5}	0.44	0.13	7.33
4.91×10^{-5}	0.68	0.15	13.0
6.14×10^{-5}	0.80	0.16	23.23
7.67×10^{-5}	1.04	0.18	90.0

H_2 dependence

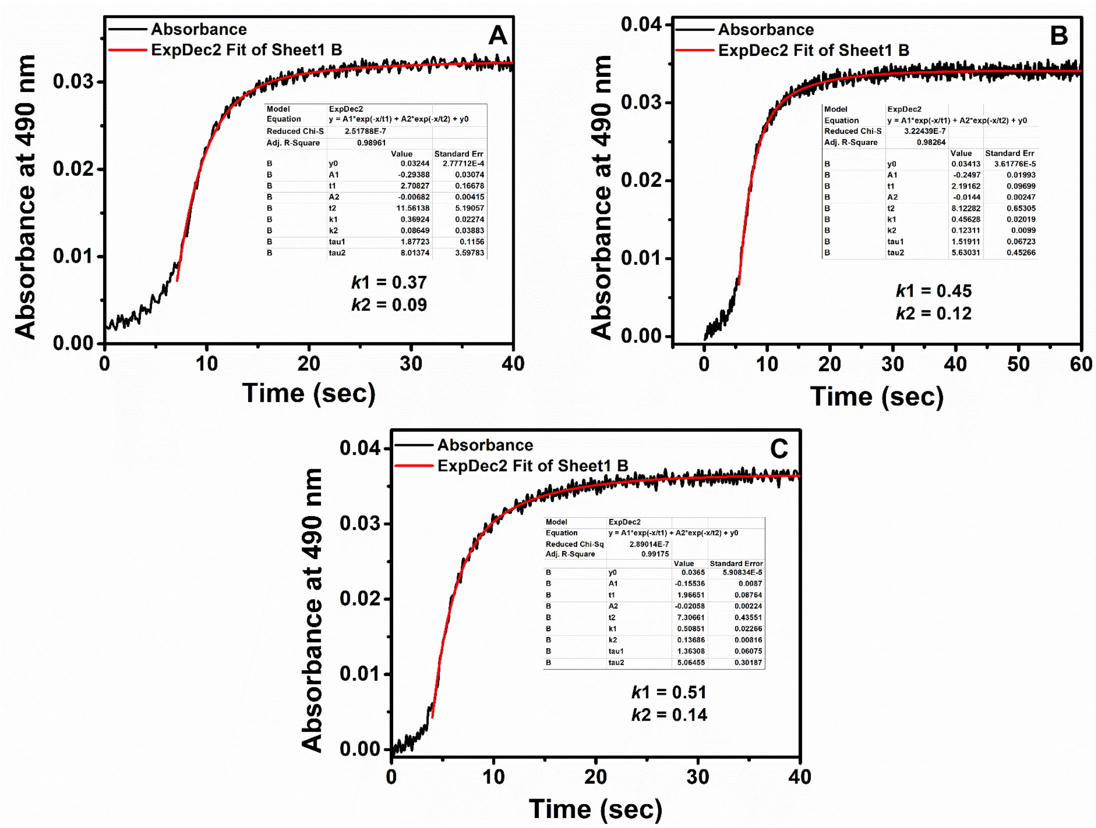

Figure S6. A typical kinetic curve of the reaction Pt°-NP@$PW_{12}O_{40}^{3-}$ with three different concentrations of H_2 saturated water (pH 1.5) at 490 nm.

Table S3. The k_{obs} values and ratio of their absorbance for four different concentrations of H_2 by maintaining a constant concentration of $PW_{12}O_{40}^{3-}$ (0.00010 mol/L) and surface Pt atoms (7.68 ×10^{-6} mol/L).

Concentration of H_2 (mol/L)	k_{obs} s^{-1} in Pt^0-POM *k1*	k_{obs} s^{-1} in Pt^0-POM *k2*	Ratio of Absorbance A1/A2
0.00030	0.37	0.09	43.10
0.00036	0.45	0.12	17.25
0.00040	0.51	0.14	7.50

Pt-H_2-POM (2 nm Pt)

POM dependence

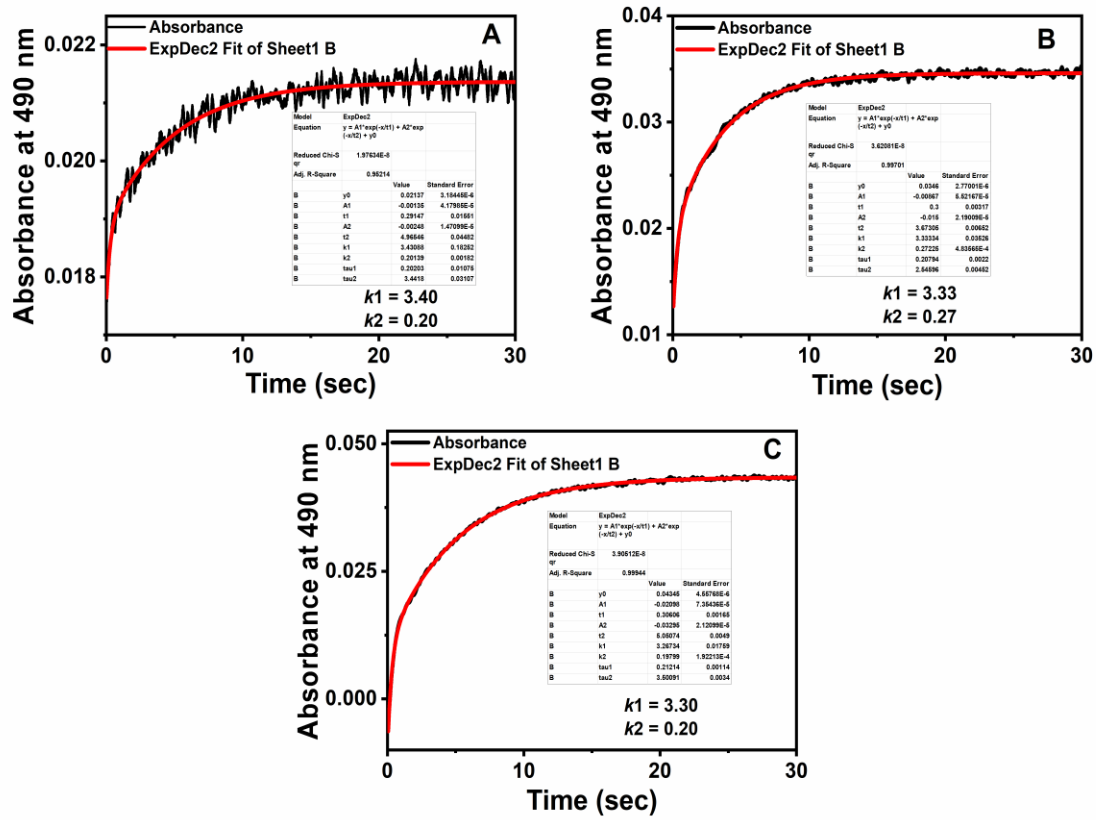

Figure S7. A typical kinetic curve of the reaction of Pt°-NP-H_2 with three different concentrations of $PW_{12}O_{40}^{3-}$ at 490 nm.

Table S4. The k_{obs} values and the ratio of their absorbance for three different concentrations of $PW_{12}O_{40}^{3-}$ by maintaining a constant concentration of surface Pt^0 atoms (3.07×10^{-5} mol/L) and H_2 (0.00040 mol/L)

Concentration of $H_3PW_{12}O_{40}$ (mol/L)	k_{obs} s^{-1} in Pt^0-POM *k*1	k_{obs} s^{-1} in Pt^0-POM *k*2	Ratio of Absorbance A1/A2
0.000010	3.40	0.20	0.50
0.000080	3.33	0.27	0.54
0.00015	3.30	0.20	0.64

Pt dependence

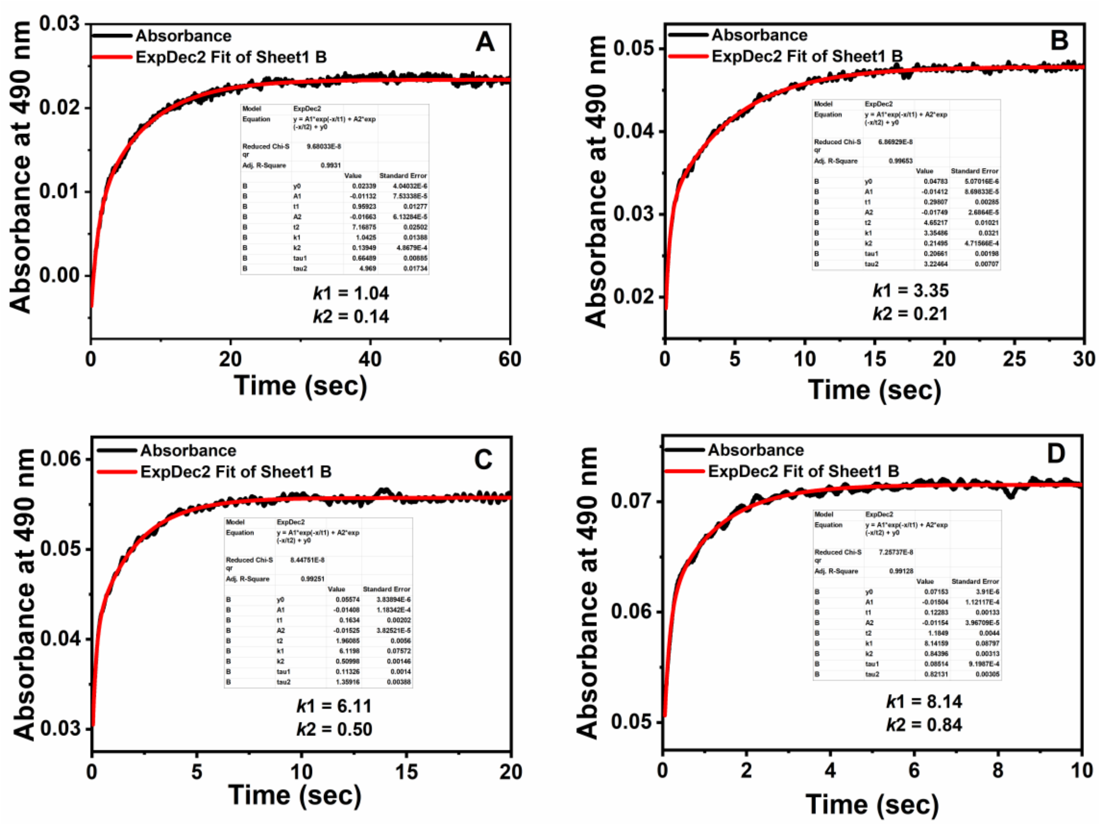

Figure S8. A typical kinetic curve of the reaction of Pt°-NP-H_2 with four different concentrations of surface Pt atoms at 490 nm.

Table S5. The k_{obs} values and the ratio of their absorbance for four different concentrations of surface Pt atoms by maintaining a constant concentration of $PW_{12}O_{40}^{3-}$ (0.00010 mol/L) and H_2 (0.00040 mol/L).

Concentration of Pt atoms on the surface (mol/L)	k_{obs} s^{-1} in Pt^0-POM k1	k_{obs} s^{-1} in Pt^0-POM k2	Ratio of Absorbance A1/A2
6.14×10^{-6}	1.04	0.14	0.68
3.07×10^{-5}	3.35	0.21	0.80
6.14×10^{-5}	6.11	0.50	0.92
9.21×10^{-5}	8.14	0.84	1.30

Pt°NP@POM-H_2 (4 nm Pt)

Pt dependence

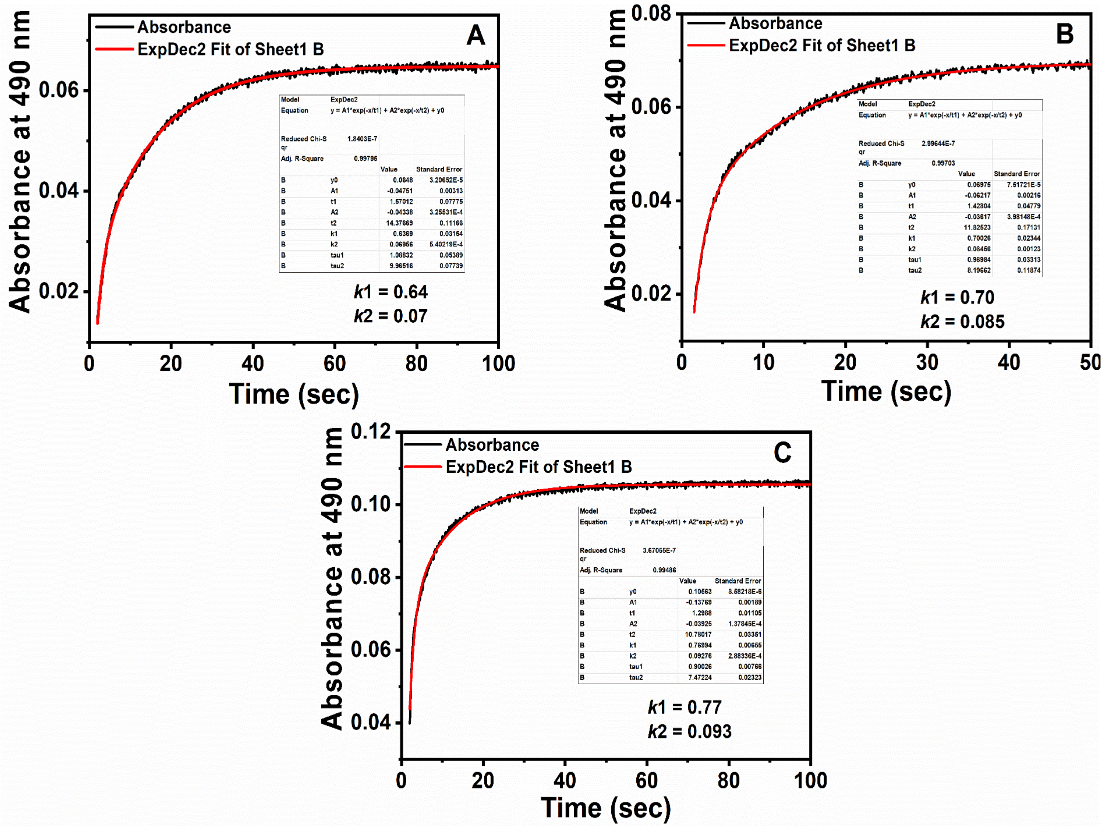

Figure S9. A typical kinetic curve of the reaction of Pt°-NP@$PW_{12}O_{40}^{3-}$ with three different concentrations of surface Pt atoms (Pt = 4nm) with H_2 saturated water (pH – 1.6) at 490 nm.

Table S6. The k_{obs} values and the ratio of their absorbance for three different concentrations of surface Pt atoms by maintaining a constant concentration of $PW_{12}O_{40}^{3-}$ (0.00020 mol/L) and H_2 (0.00040 mol/L).

Concentration of Pt atoms on the surface (mol/L)	k_{obs} s^{-1} in Pt^0-POM *k*1	k_{obs} s^{-1} in Pt^0-POM *k*2	Ratio of Absorbance A1/A2
6.78×10^{-6}	0.64	0.07	1.10
1.80×10^{-5}	0.70	0.085	1.71
2.71×10^{-5}	0.77	0.093	3.50

Pt-H_2-POM (4 nm Pt)

Pt dependence

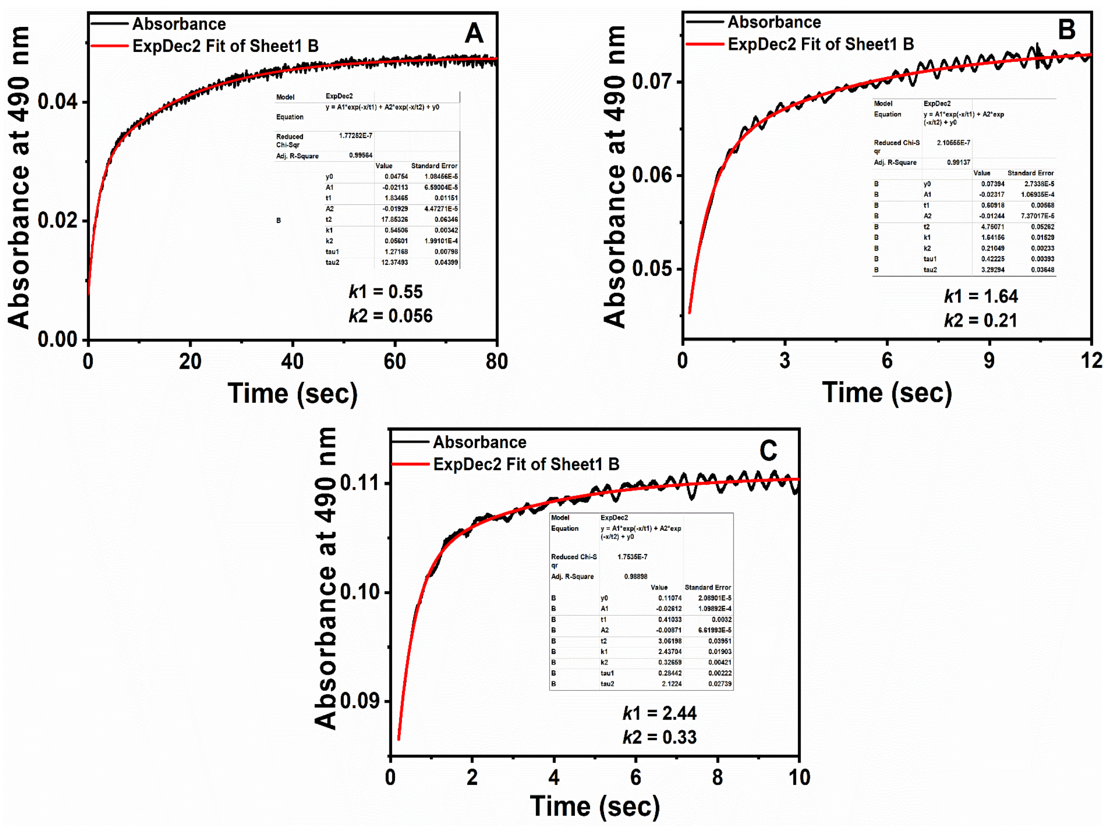

Figure S10. A typical kinetic curve of the reaction of Pt°-NP-H_2 with three different concentrations of surface Pt atoms (Pt =4nm) at 490 nm.

Table S7. The k_{obs} values and the ratio of their absorbance for three different concentrations of surface Pt atoms by maintaining a constant concentration of $PW_{12}O_{40}^{3-}$ (0.00020 mol/L) and H_2 (0.00040 mol/L).

Concentration of Pt atoms on the surface (mol/L)	k_{obs} s^{-1} in Pt^0-POM *k*1	k_{obs} s^{-1} in Pt^0-POM *k*2	Ratio of Absorbance A1/A2
6.78×10^{-6}	0.55	0.056	1.10
2.71×10^{-5}	1.64	0.21	1.90
5.42×10^{-5}	2.44	0.33	3.0