Supporting Information

Reaction of H_2 with Polyoxometalate supported Rhodium(0) and Iridium(0) Nanoparticles in aqueous suspensions: A kinetic Study

[a] Department of Chemical Sciences and The Radical Research Center
Ariel University, Ariel, Israel. E-mail:
[b] Chemistry Department
Ben-Gurion University, Beer-Sheva, Israel
[c] Department of Chemical Sciences
Ariel University, Ariel, Israel
[d] Department of Chemical Engineering and The Radical Research Center
Ariel University, Ariel, Israel.
E-mail: yaelyt@ariel.ac.il

Table of contents

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

The Rh^0 NPs, Rh^0-POM, Ir^0 NPs, and Ir^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 synthesized 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 the air before the measurement was done.

NMR Spectroscopy

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

^{1}H NMR spectra were measured 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**.** ([Rh] and [Ir] = 0.25 mM)

^{31}P{^{1}H} NMR spectra were measured 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. ([Rh] and [Ir] = 0.125 mM, [POM] = 10.0 mM)

Calculations for the number of Rh and Ir atoms on the surface

[NP] = C/ n, where C = Concentration of M^0 (Rh^0 and Ir^0), based on the metal precursors, n = number of M atoms per particle

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

For Rh,

$\rho_{Rh} = 12.41\ g/cm^3$

M.W. = 102.90 g/mol

Diameter of Rh nanoparticle = 2.4 nm $r = 1.20\ nm = 1.20 \times 10^{-7}\ cm$

From the calculations,

n = 525.0 Rh atoms/ Rh NPs

Therefore,

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

$n_s = n[\frac{r^3-(r-2r_{(Rh)})^3}{r^3}]$ r_{Rh} = 1.34 Å = 1.34 × 10^{-8} cm   r = 1.20 × 10^{-9} m = 1.20 ×10^{-7} cm

n_s = 279 Number of Rh atoms on the surface of one NP.

For Ir

ρ_{Ir} = 22.56 g/cm^3, M.W. = 192.21 g/mol and r = 1.25 nm

From the calculations,

n= 578 Ir atoms per Ir particle and **n_s** = **298** atoms/particle

^{1}H NMR

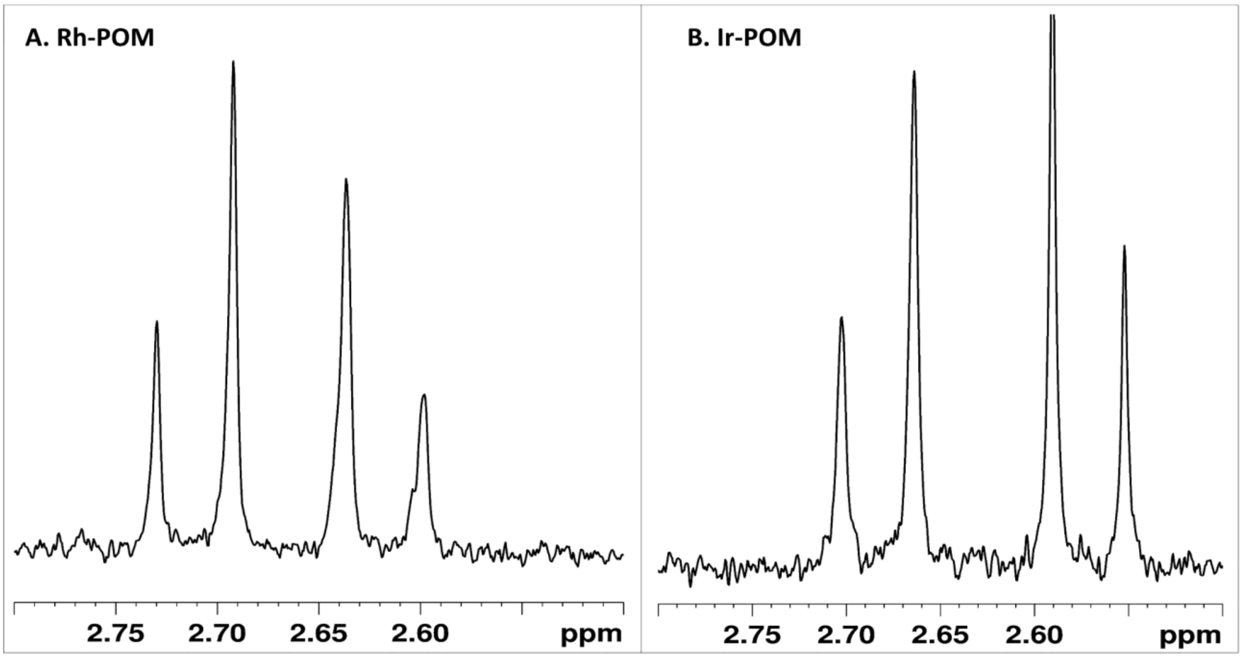

Figure S1. ^{1}H NMR (400 MHz, 90 % H_2O/10 % D_2O, 300 K) spectrum of synthesized Rh and Ir nanoparticles (0.125 mM). The peaks show the presence of citrate.

^{31}P NMR

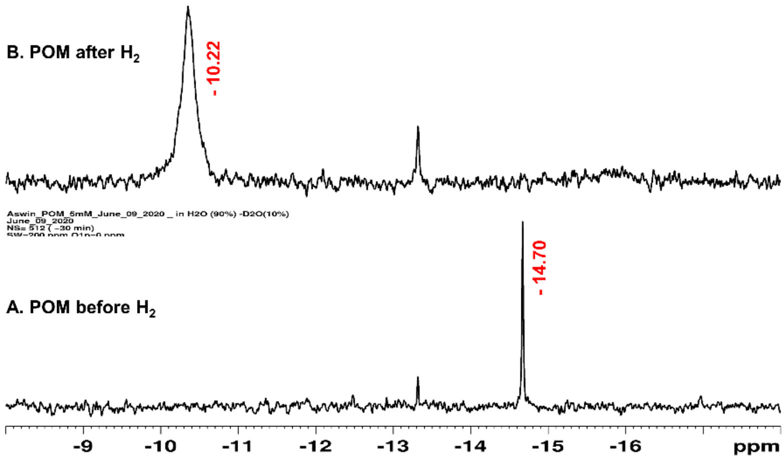

Figure S2. ^{31}P NMR (162 MHz, 90% H_2O/10% D_2O, 300 K) spectra of bare POM (**A**) Before H_2 and (**B**) After H_2.

Kinetics of bare POM with H_2

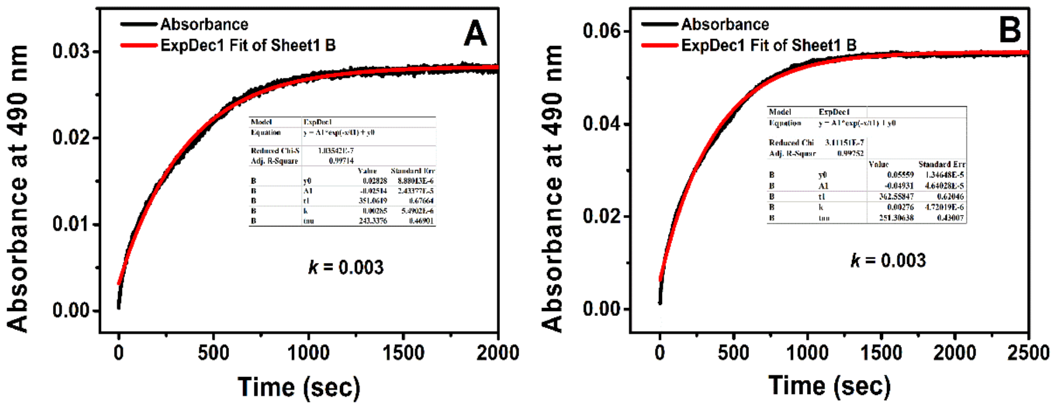

Figure S3. Typical kinetic curves of the reaction of $PW_{12}O_{40}^{3-}$ with H_2 (**A**) 1.0×10^{-4} M POM and (**B**) 2.0×10^{-4} M POM.

$Rh^0NP@POM-H_2$ (2.40 nm Rh)

POM dependence

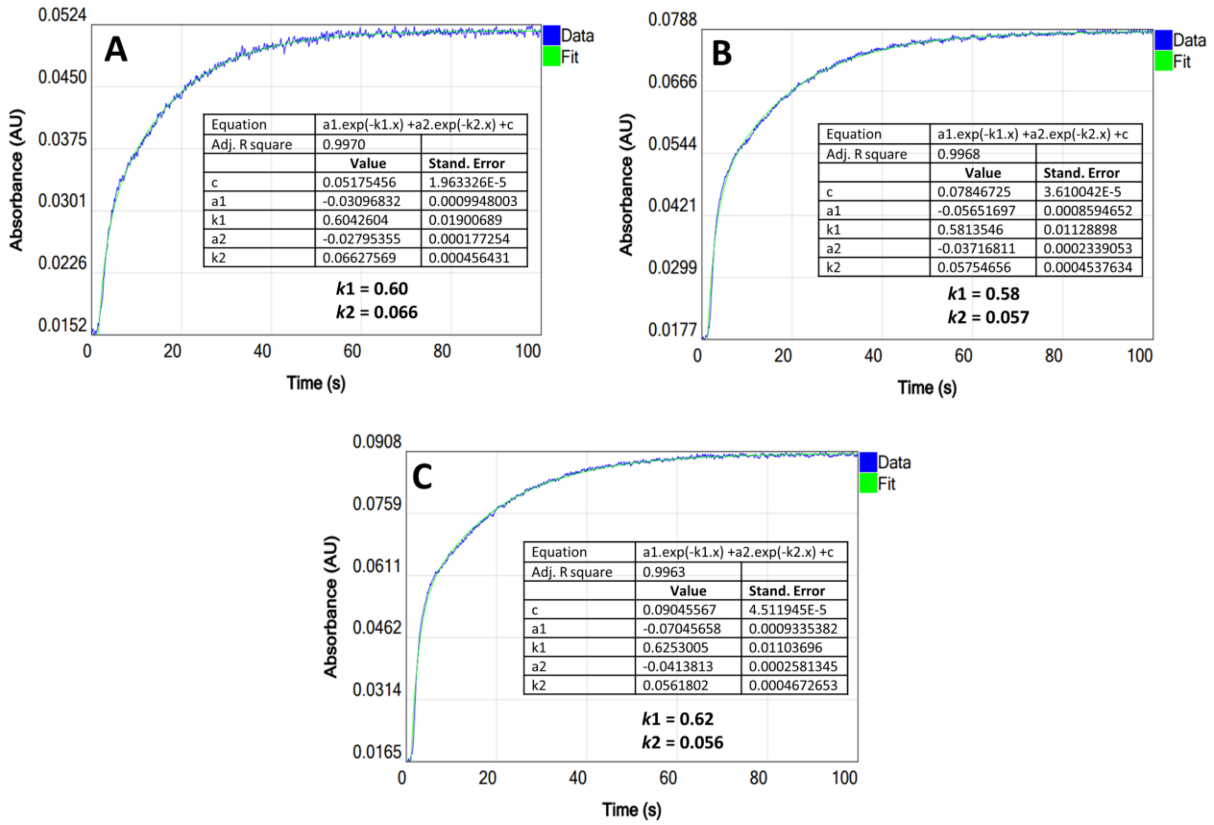

Figure S4. Typical kinetic curves of the reaction of Rh^0-NP@$PW_{12}O_{40}^{3-}$ with three different concentrations of $PW_{12}O_{40}^{3-}$ with H_2 saturated water (pH – 1.5) at 490 nm.

Table S1. The k_{obs} values and the ratio of their absorbance for three different concentrations of $PW_{12}O_{40}^{3-}$ (0.0001, 0.0002, and 0.0003 mol/L) by maintaining a constant concentration of surface Rh atoms (3.32×10^{-5} mol/L) and H_2 (0.00040 mol/L).

Concentration of $H_3PW_{12}O_{40}$ (mol/L)	k_{obs} s^{-1} in Rh^0-POM *k1*	k_{obs} s^{-1} in Rh^0-POM *k2*	Ratio of Absorbance A1/A2
0.00010	0.60	0.066	1.10
0.00020	0.58	0.057	1.50
0.00030	0.62	0.056	1.70

Rh dependence

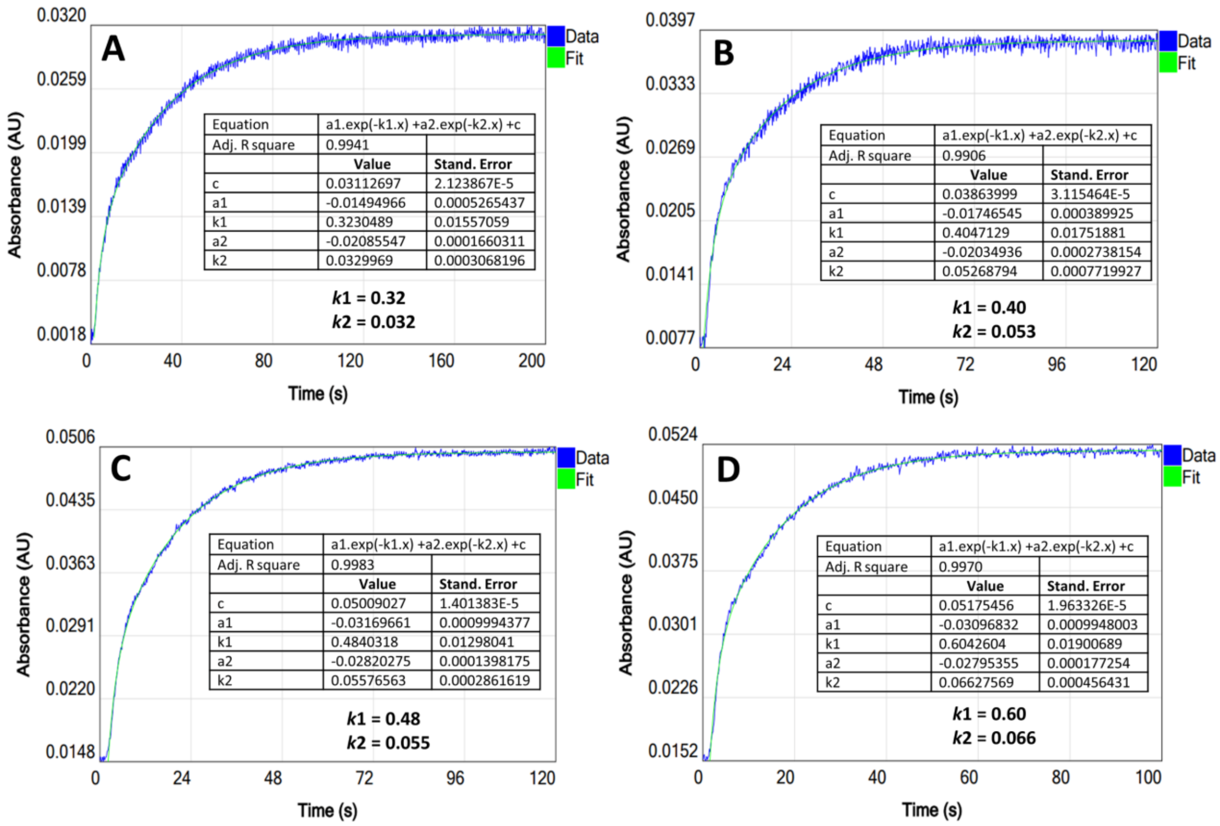

Figure S5. A typical kinetic curve of the reaction of Rh^0-NP@$PW_{12}O_{40}^{3-}$ with four different concentrations of surface Rh atoms with H_2 saturated water (pH – 1.6) at 490 nm.

Table S2. The k_{obs} values and the ratio of their absorbance for four different concentrations of surface Rh 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 Rh atoms on the surface (mol/L)	k_{obs} s^{-1} in Rh^0-POM *k1*	k_{obs} s^{-1} in Rh^0-POM *k2*	Ratio of Absorbance A1/A2
5.31×10^{-6}	0.32	0.032	0.70
1.32×10^{-5}	0.40	0.053	0.81
2.65×10^{-5}	0.48	0.055	1.0
3.32×10^{-5}	0.60	0.066	1.10

H_2 dependence

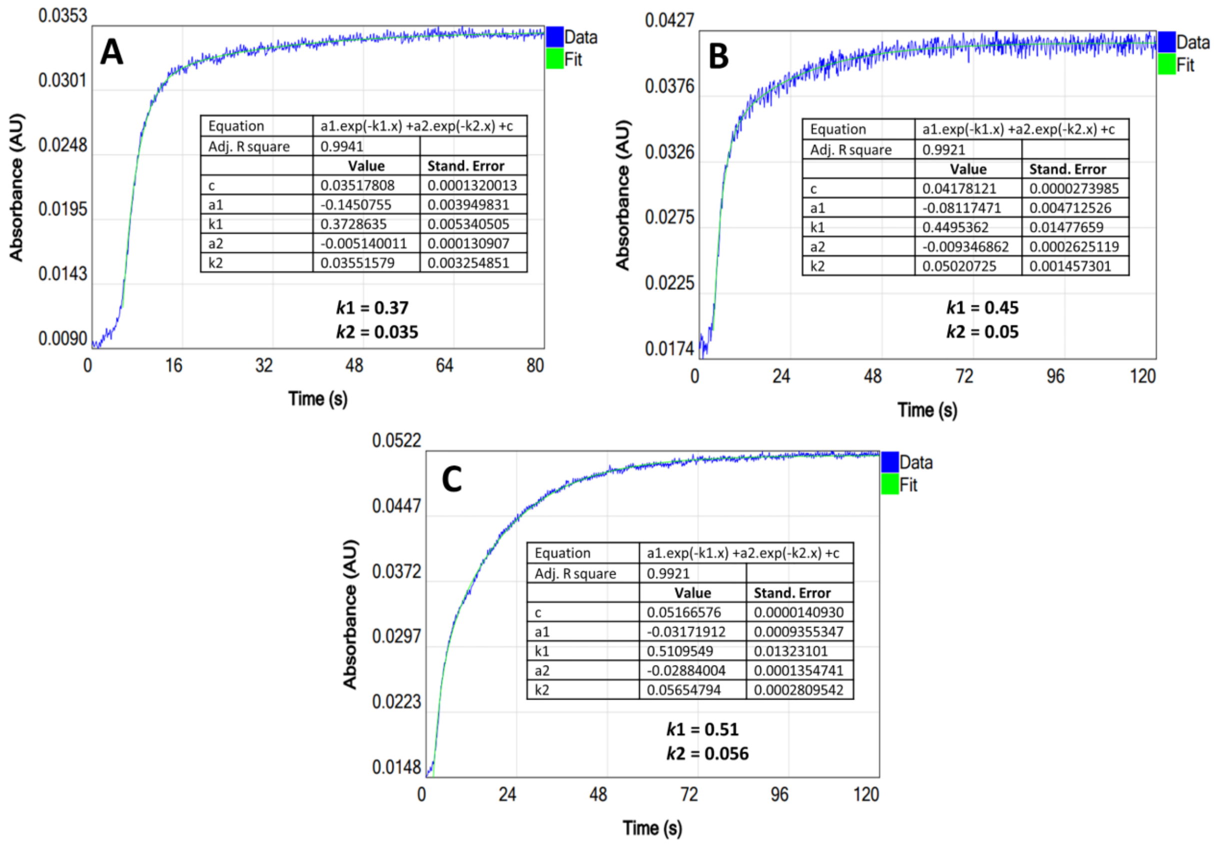

Figure S6. A typical kinetic curve of the reaction Rh^0-NP@$PW_{12}O_{40}^{3-}$ with three different concentrations of H_2 saturated water (pH 1.5) at 490 nm.

Table S3. The k_{obs} values and the 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 Ir atoms (3.32×10^{-5} mol/L).

Concentration of H_2 (mol/L)	**k_{obs} s^{-1} in Ir^0-POM $k1$**	**k_{obs} s^{-1} in Ir^0-POM $k2$**	**Ratio of Absorbance A1/A2**
0.00020	0.39	0.03	32.0
0.00030	0.45	0.05	9.0
0.00040	0.50	0.056	1.10

$Ir^0NP@POM-H_2$ (2.50 nm Ir)

POM dependence

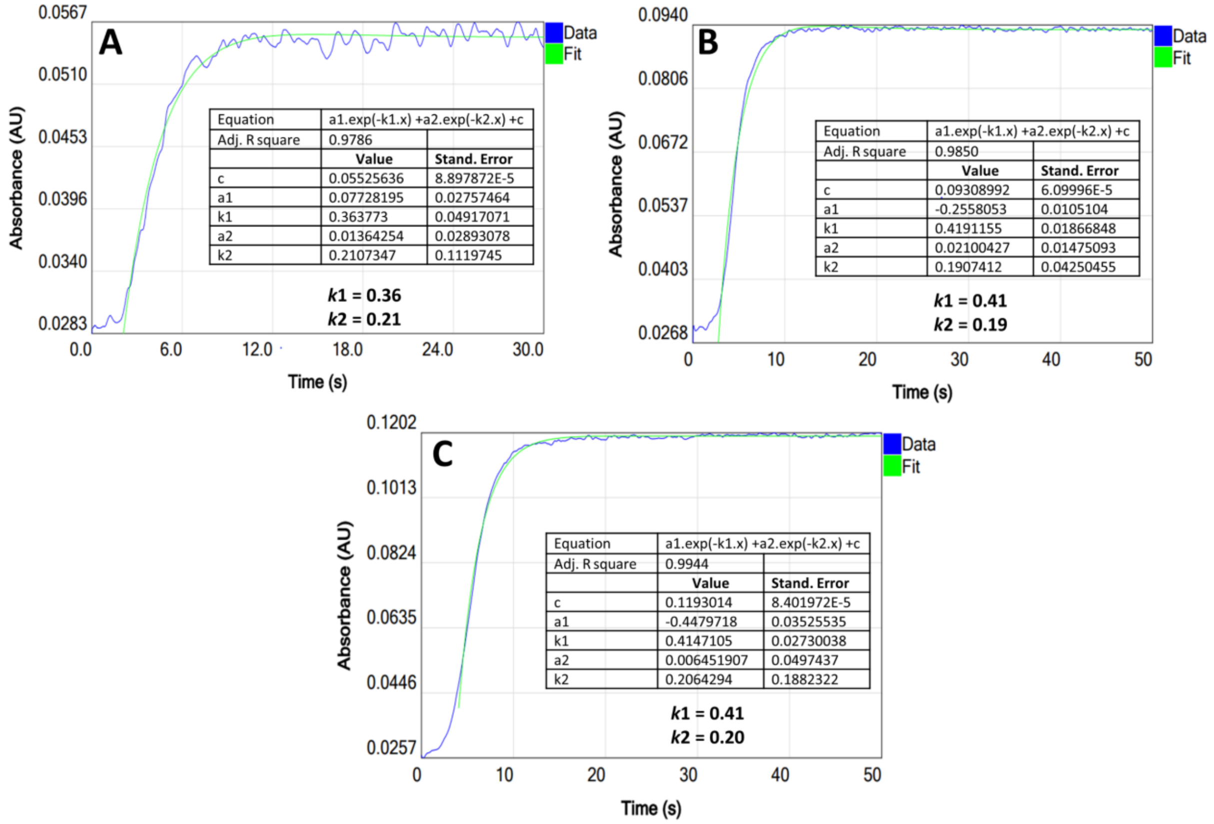

Figure S7. Typical kinetic curves of the reaction of Ir^0-NP@$PW_{12}O_{40}^{3-}$ with three different concentrations of $PW_{12}O_{40}^{3-}$ with H_2 saturated water (pH – 1.5) at 490 nm.

Table S4. The k_{obs} values and the ratio of their absorbance for three different concentrations of $PW_{12}O_{40}^{3-}$ (0.0001, 0.0002, and 0.0003 mol/L) by maintaining a constant concentration of surface Ir atoms (5.15×10^{-5} mol/L) and H_2 (0.00040 mol/L).

Concentration of $H_3PW_{12}O_{40}$ (mol/L)	k_{obs} s^{-1} in Ir^0-POM *k1*	k_{obs} s^{-1} in Ir^0-POM *k2*	Ratio of Absorbance A1/A2
0.00010	0.36	0.21	5.92
0.00020	0.41	0.19	12.14
0.00030	0.41	0.20	74.0

Ir dependence

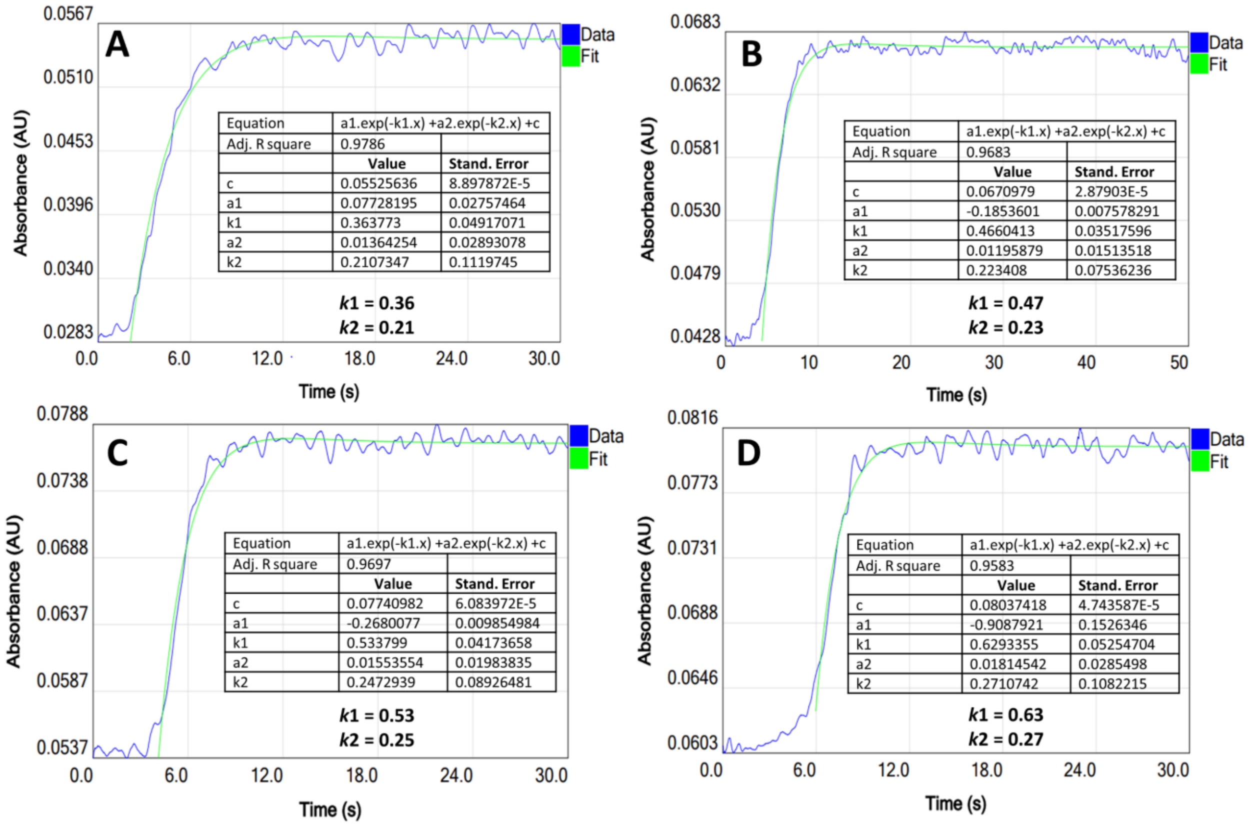

Figure S8. A typical kinetic curve of the reaction of Ir^0-NP@$PW_{12}O_{40}^{3-}$ with four different concentrations of surface Ir atoms with H_2 saturated water (pH – 1.6) at 490 nm.

Table S5. The k_{obs} values and the ratio of their absorbance for four different concentrations of surface Ir 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 Ir atoms on the surface (mol/L)	k_{obs} s^{-1} in Ir^0-POM *k1*	k_{obs} s^{-1} in Ir^0-POM *k2*	Ratio of Absorbance A1/A2
5.15×10^{-5}	0.36	0.21	5.92
7.73×10^{-5}	0.47	0.23	16.50
1.03×10^{-4}	0.53	0.25	17.30
1.28×10^{-4}	0.63	0.27	50.16

H_2 dependence

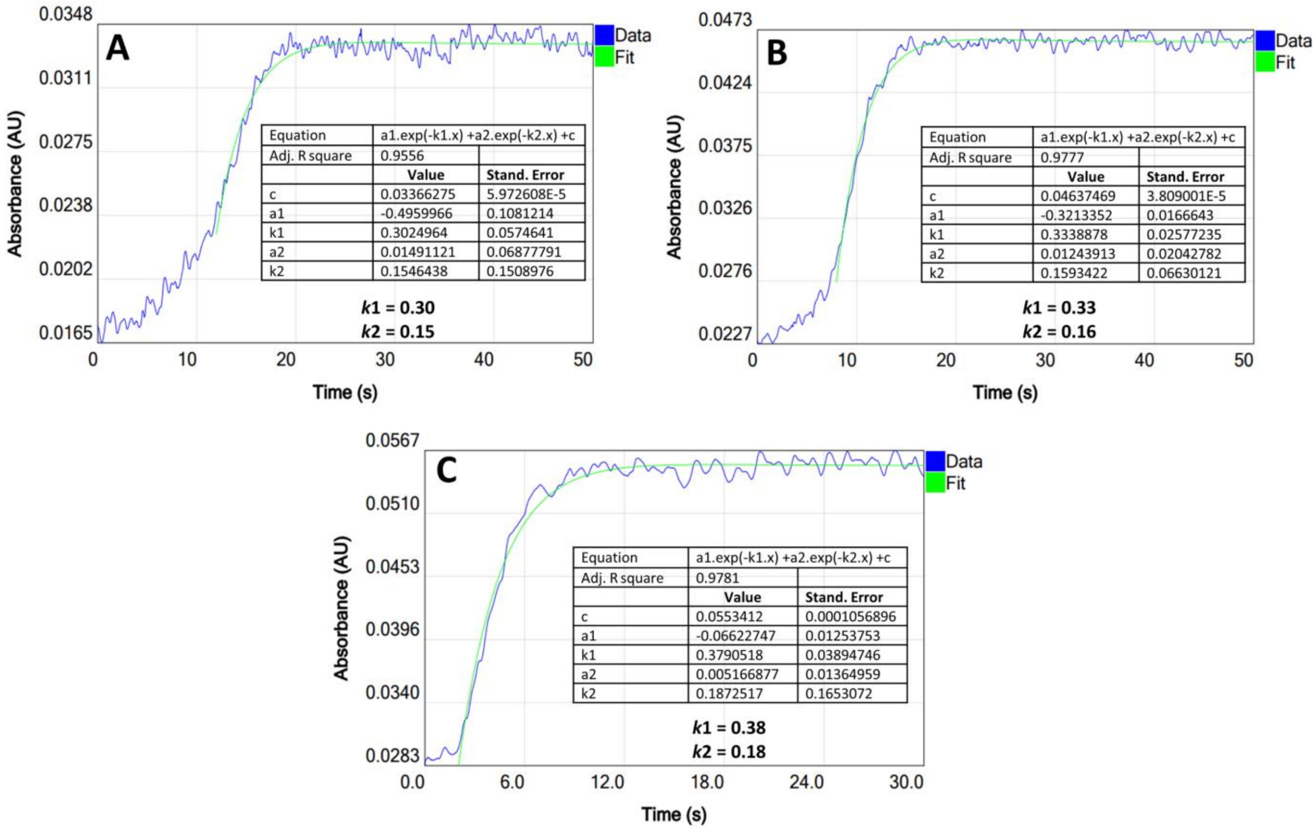

Figure S9. A typical kinetic curve of the reaction Ir^0-NP@$PW_{12}O_{40}^{3-}$ with three different concentrations of H_2 saturated water (pH 1.5) at 490 nm.

Table S6. The k_{obs} values and the 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 Ir atoms (5.15×10^{-5}mol/L).

Concentration of H_2 (mol/L)	**k_{obs} s^{-1} in Ir^0-POM *k*1**	**k_{obs} s^{-1} in Ir^0-POM *k*2**	**Ratio of Absorbance A1/A2**
0.00020	0.30	0.15	32.88
0.00036	0.33	0.16	25.88
0.00040	0.38	0.18	13.20

Rh-H_2-POM

Rh dependence

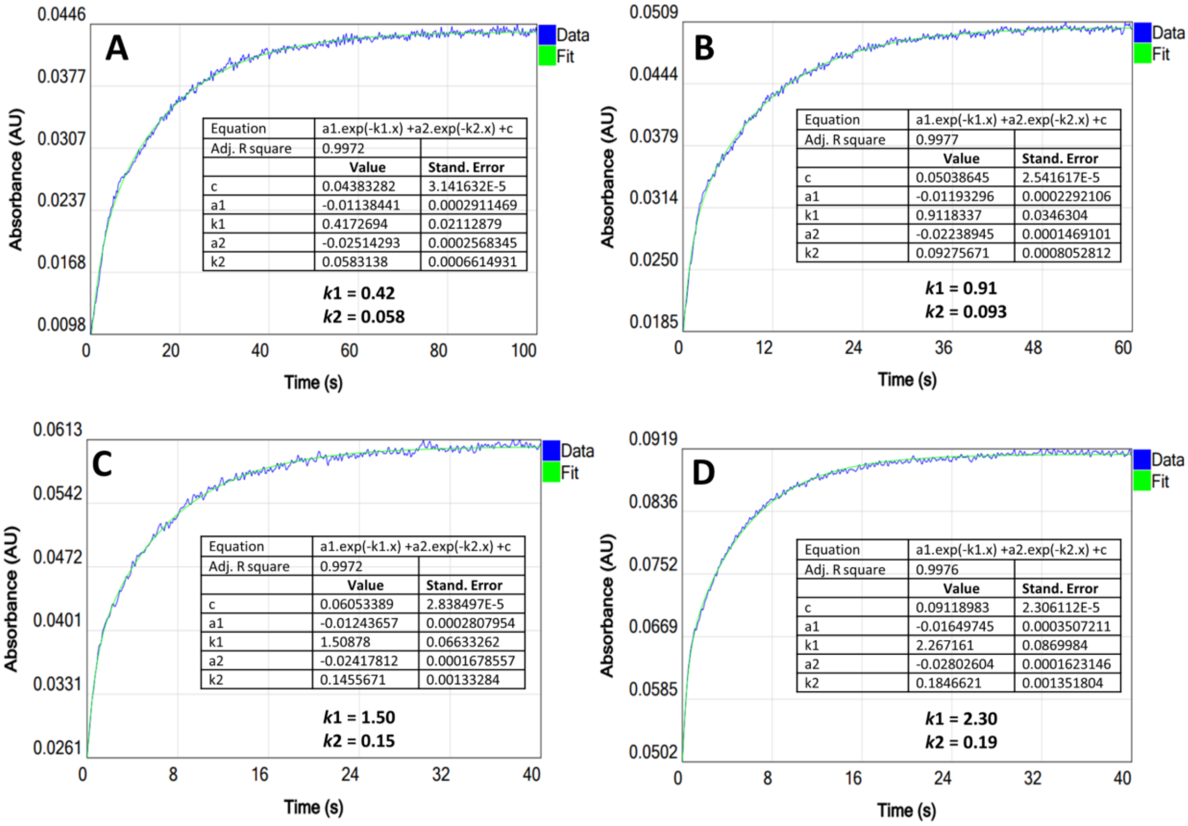

Figure S10. A typical kinetic curve of the reaction of Rh^0-NP-H_2 with four different concentrations of surface Rh atoms at 490 nm.

Table S7. The k_{obs} values and the ratio of their absorbance for four different concentrations of surface Rh 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 Rh atoms on the surface (mol/L)	k_{obs} s^{-1} in Rh^0-POM k1	k_{obs} s^{-1} in Rh^0-POM k2	Ratio of Absorbance A1/A2
1.32×10^{-5}	0.42	0.058	0.44
2.65×10^{-5}	0.91	0.093	0.50
3.32×10^{-5}	1.50	0.150	0.52
6.64×10^{-5}	2.30	0.190	

Ir-H_2-POM

Ir dependence

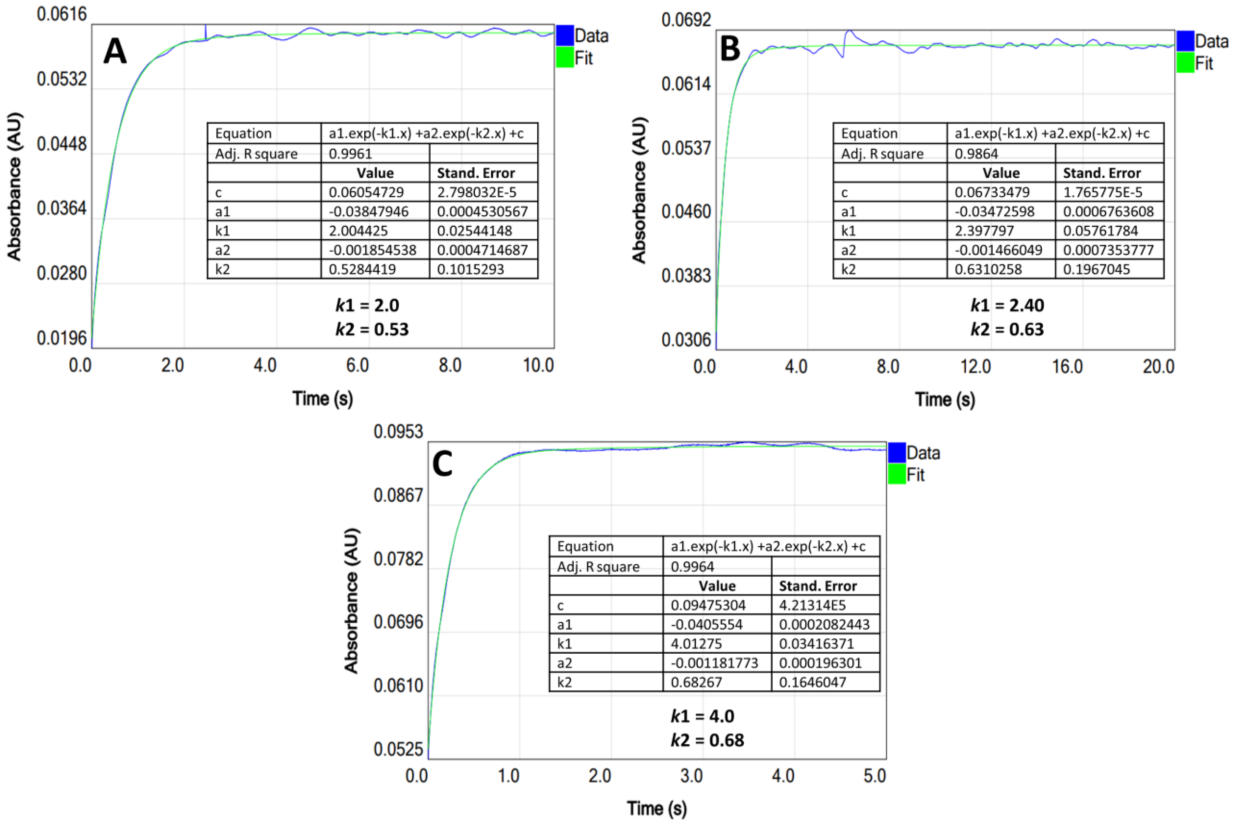

Figure S11. A typical kinetic curve of the reaction of Ir^0-NP-H_2 with four different concentrations of surface Ir atoms at 490 nm.

Table S8. The k_{obs} values and the ratio of their absorbance for four different concentrations of surface Ir 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 Ir atoms on the surface (mol/L)	k_{obs} s^{-1} in Ir^0-POM k1	k_{obs} s^{-1} in Ir^0-POM k2	Ratio of Absorbance A1/A2
5.15×10^{-5}	2.0	0.53	21.33
7.73×10^{-5}	2.40	0.63	25.0
1.28×10^{-4}	4.0	0.68	36.36