Electronic Supplementary Information

For

Single source precursor route for the first graphene oxide-Pd$_6$P nanocomposite: Application in electrochemical hydrogen evolution reaction

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S1. Experimental Section

S1.1 Physical measurements

The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra were recorded on a JNM ECX−500 NMR spectrometer at 500, 125 and 202.46 MHz respectively. Single crystal X-ray diffraction studies were performed on Supernova X-ray diffractometer system at 150 K using Mo Kα radiation (0.710 Å). CrysalisPro Software (online version) was used for data collection. Mass spectrometric studies were done using Impact HD mass spectrometer operated at 50 Hz.

FEI Technai G2-F30 electron microscope has been used for TEM studies, operated at 200 kV. The specimen for TEM was prepared by dispersing the nanoparticles in methanol by ultrasonic treatment and further dropping the slurry onto a porous carbon film supported on a copper grid and then drying in air. Powder X-ray diffraction (PXRD) studies were carried out on Panalytical XPert diffractometer with Cu filtered radiaton using a scan speed of 2 degrees per minute an dscan step of 0.02 degree. EDX system FEI-Quanta FEG200F has been used for elemental composition studies of nanoparticles. The X-ray photoelectron spectroscopy data was collected on Thermofisher scientific Nexsa base photoelectron spectrometer. Raman spectroscopy was performed by raman optics using a microscope from Horiba lab RAM HR evolution. BET studies were carried out using Quantachrome Autosorb 1C system.

The electrochemical studies were performed in autolab instrument PGSTAT30. The electrochemical workstation comprises of three electrode system where 3 M Ag/AgCl is used as a reference electrode and a platinum wire is used as a counter electrode respectively. The electrochemistry has been performed by taking 0.5 M H_2SO_4 in 50 ml of deionized water in a glass cell. All the measurements has been carried out with reference to Ag/AgCl and then plotted against reversible hydrogen electrode (RHE). For measuring Hydrogen Evolution Reaction (HER) study, the Linear sweep voltammetry (LSV) measurement has been done at 5 mV/s scan rate in the potential window of 0 V to -0.60 V Vs RHE. The electrochemical impedance study and chronoamperometry study is carried out at -0.26 V Vs RHE respectively.

S1.2 Experimentation

9-Anthracene carboxaldehyde, sodiumtetrachloropalladate and Nafion were procured from Sigma Aldrich. 2-(diphenylphosphino)ethylamine has been synthesized via reported procedures [1]. H_2SO_4, acetone, ethanol, graphite powder all of analytical grade were procured from local suppliers and used without any further purification. Deionized water from a Milli−Q system was used for all syntheses, purification of electrocatalyst and electrochemical studies.

*Synthesis of ligand **L1**:*

9-Anthracenecarboxaldehyde (0.206 g, 1 mmol) was stirred in dry ethanol (20 mL) at room temperature for 0.5 h. Thereafter the solution of 2-(diphenylphosphino)ethylamine (0.229 g, 1 mmol) was added dropwise with stirring. The mixture was stirred further at room temperature for 6 h under ambient conditions. The solvent was evaporated off on a rotary evaporator resulting in a yellow precipitate of corresponding ligand **L1**.

L1. Yield: 0.899 g (89 %); yellow solid. ^1H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): δ (ppm): 2.70 (t, 2H, J = 5 Hz), 4.01−4.09 (m, 2H), 7.39−7.26 (m, 6H), 7.50−7.48 (m, 3H), 7.56−7.51 (m, 5H), 8.020 (d, 2H, J = 8 Hz), 8.50−8.52 (m, 3H), 9.40 (s, 1H). $^{13}C\{^1H\}$NMR (125 MHz, CDCl$_3$, 25 °C, TMS): δ (ppm): 30.2, 59.8, 124.9, 125.3, 126.8, 128.6, 128.7, 128.8, 128.9, 129.4, 130.6, 131.3, 132.8, 133.0, 160.8.

*Synthesis of palladium complex **1**:*

A solution of Na$_2$PdCl$_4$ (0.147 g, 0.5 mmol) (in 5mL of distilled water) was mixed with a solution of **L** (0.208 g, 0.5 mmol) in acetone (10 mL) with vigorous stirring. Complex **1** was obtained instantaneously in the form of orange precipitate which was filtered and dried.

1. Yield: 0.270 g (90%); orange solid. ^1H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): δ (ppm): 3.43−3.53 (m, 2H), 4.45−4.49 (m, 2H), 7.54−7.57 (m, 6H), 7.67−7.70 (m, 6H), 8.71 (s, 1H), 8.99 (d, 2H, J = 10 Hz), 11.54 (s, 1H). $^{13}C\{^1H\}$NMR (125 MHz, CDCl$_3$, 25 °C, TMS): δ (ppm): 30.9, 50.1, 123.6, 125.7, 126.1, 127.9, 128.2, 129.1, 129.3, 131.2, 132.2, 133.4, 135.2, 193.2. $^{31}P\{^1H\}$NMR (202.46 MHz, CDCl$_3$, 25 °C, TMS): δ (ppm): 50.185. HRMS, [M−Cl]$^+$ (m/z) = 560.02; calculated value for C$_{29}$H$_{24}$Cl$_2$NPPd = 560.04.

Synthesis of Pd$_6$P nanospheres:

In an oven dried round bottom flask, 0.5 mmol (0.297 g) of the Pd(II) complex **1** was added along with 10 mL of oleic acid−oleyl amine solution (5 mL/5mL) in presence of N$_2$ atmosphere with constant stirring for 2 h at 250 °C. The color of the mixture changed from orange to dark brown within the first 30 minutes and black−brown precipitate started appearing thereafter. The reaction mixture was cooled to room temperature and 20 mL of acetone was added into the flask in order to isolate the black precipitate which was further separated by centrifugation. The isolated precipitate was washed three to four times with methanol and dried in vacuo.

Synthesis of GO−Pd$_6$P nanocomposite:

Graphene oxide (GO) was synthesized from graphite powder by modified Hummers method [2]. The suspension of graphene oxide (GO) (100 mg) made in 20 mL of ethanol and nanoparticles of Pd$_6$P (50 mg) dispersed in 20 mL of ethanol were mixed. This reaction mixture was allowed to stirred at room temperature for 24 h. the resulting black colored dispersion was centrifuged and further washed three times with acetone and dried in vacuo.
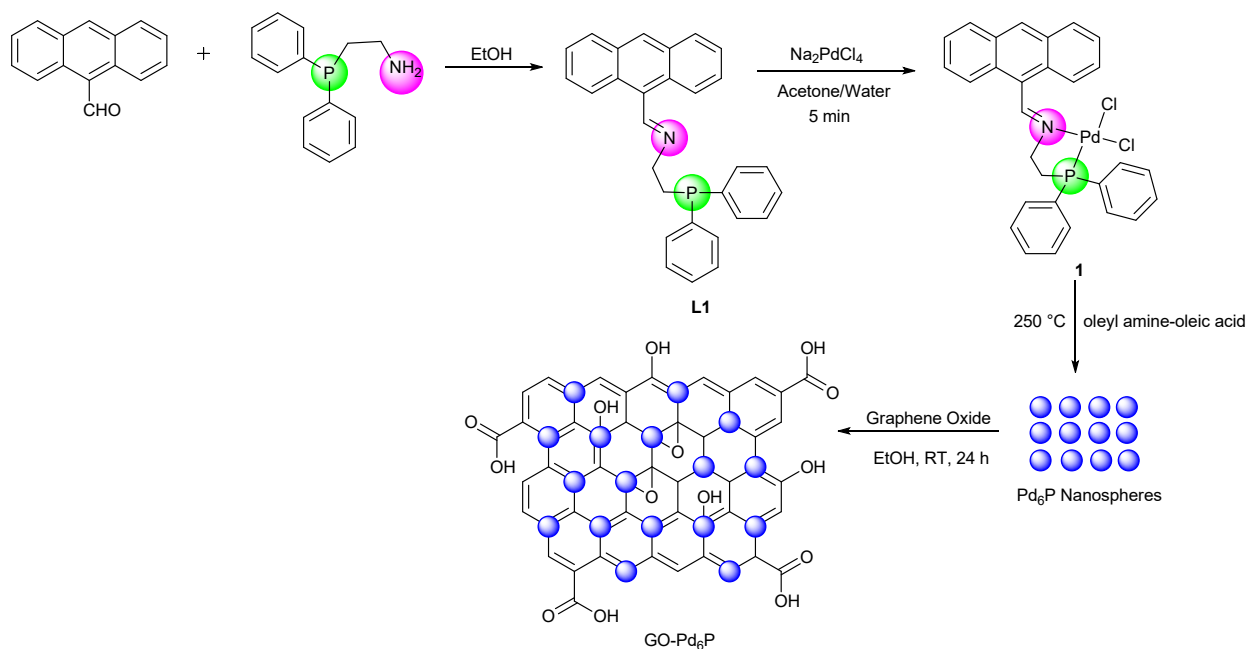
Scheme S1. Systematic synthesis of **L1**, **1**, Pd_6P nanospheres and GO-Pd_6P composite.

Electrochemical measurement:

The electrochemical studies were carried out using Autolab (PGSTAT30) instrument with catalyst coated glassy carbon electrode (GCE) as working electrode, platinum wire as counter electrode and Ag/AgCl (saturated KCl) as refrence electrode. A mixture of ethanol (200 µL) and Nafion (10% v/v) was used to disperse the catalyst (5 mg) for preparing the catalyst ink. A 60 µL drop of ink was transferred to GCE (area = 0.07 cm^2). In this way 1.5 mg/cm^2 of catalyst was placed on electrode. All the three electrodes were fixed in the cell consisting 0.5 M H_2SO_4 solution (electrolyte). All the measurements has been carried out with reference to Ag/AgCl and then plotted against reversible hydrogen electrode (RHE). For measuring Hydrogen Evolution Reaction (HER) study, the Linear sweep voltammetry (LSV) measurement has been done at 5 mV/s scan rate in the potential window of 0 V to -0.60 V Vs RHE. The electrochemical impedance study and chronoamperometry study is carried out at -0.26 V Vs RHE respectively.

Fabrication of electrode

For the preparation of the working electrode, 5 mg of GO-Pd_6P nanoparticles were dispersed in a 200 µL ethanol. The sample is ultrasonicated for 45 min. at room temperature in order to achieve a dispersion. Afterwards, a nafion resin solution (10 % v/v) is added as a binder followed by 15 min of ultrasonication. The as-obtained dispersion (60 µl) was drop cast onto glassy carbon electrode (GCE) that have a 0.07 cm^2 geometric surface area (S_g). Further, the Go-Pd_6P@GCE has been used effectively as a working electrode with the calculated mass loading of 1.5 mg.

Electrochemical measurements

The hydrogen evolution study for GO-Pd$_6$P nanoparticles was recorded in 50 ml of 0.5 M H$_2$SO$_4$ (*p*H=0.60) electrolyte solution on a three electrode based electrochemical workstation. Prior to the electrochemical measurement the eletrolyte solution was saturated with inert gas (N$_2$) for at least 30 min to remove the dissolved gases. The platinum wire was used as a counter electrode and Ag/AgCl in 3 M saturated KCl was used as a reference electrode. The current measured is normalized to S$_g$ (geometric surface area of glassy carbon electrode) and the potential window in Ag/AgCl is converted to RHE using Nernst equation (eq. 1) as follows.

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + E^0_{Ag/AgCl} \qquad (1)$$

where, $E°\frac{Ag}{AgCl}$ is the standard electrode potential equals to 0.197 V at 25°C

The kinetics of the catalyst was determined by evaluating the Tafel slope. The Tafel slope shows how fast the current is varied against overpotential for H$_2$ evolution and is measured from eq. 2

$$\eta = b \log j + x \qquad (2)$$

where η gives over potential, b is the Tafel slope, j is the current density and x is constant. Further, to know the intrinsic mechanistic behaviour of the electrocatalyst, electrochemical impedance spectroscopy (EIS) has been done. The nyquist plot is obtained from EIS study at a frequency range of 0.01 Hz – 100 kHz that gives Ohmic resistance (R$_\Omega$) and charge transfer resistance (R$_{ct}$) respectively. The spectrum fitting was done with FRA software (Nova 1.1) Additionally, the cyclic voltammetry (CV) scan was performed in the non-faradic region at 10, 20, 40, 60, 80 and 100 mV/s varying scan rates to calculate charge double-layer (C$_{dl}$) value. The value of the slope gives the C$_{dl}$ value, the slope was evaluated from the graph between current density and scan rate at a fixed potential of 0.9 V. The electrochemically active surface area (ECSA) that signifies the electrode area readily available for catalysis was calculated from C$_{dl}$ value. Further, the roughness factor was calculated from the ECSA value using eq. 3.

$$R_f = \frac{ECSA}{area\ of\ electrode} \qquad (3)$$

TOF values have been calculated by following the exact method as demonstrated by T. F. Jaramillo and coworkers using eq. 4.

For the calculation of the TOF of the GO-Pd$_6$P we used the following formula

$$TOF = \frac{3.12 \times 10^{15} \left(\frac{\frac{H2}{S}}{cm^2} per \frac{mA}{cm^2} \right) \times |j|}{\#surface\ sites \times A_{ECSA}}$$

$$\text{Number of surface active sites in Pd}_6\text{P} = \left(\frac{24 \; atoms/unit \; cell}{433.7 \text{Å}^3/unit \; cell}\right)^{\frac{2}{3}} = 1.45 \times 10^{15} \text{ cm}^{-2}{}_{real}$$

$$TOF = \frac{3.12 \times 10^{15}\left(\dfrac{\dfrac{H2}{S}}{cm^2} \; per \; \dfrac{mA}{cm^2}\right) \times |j|}{1.45 \times 10^{15}\dfrac{atoms}{cm^2} \times A_{ECSA}}$$

(4)

S2. Characterization
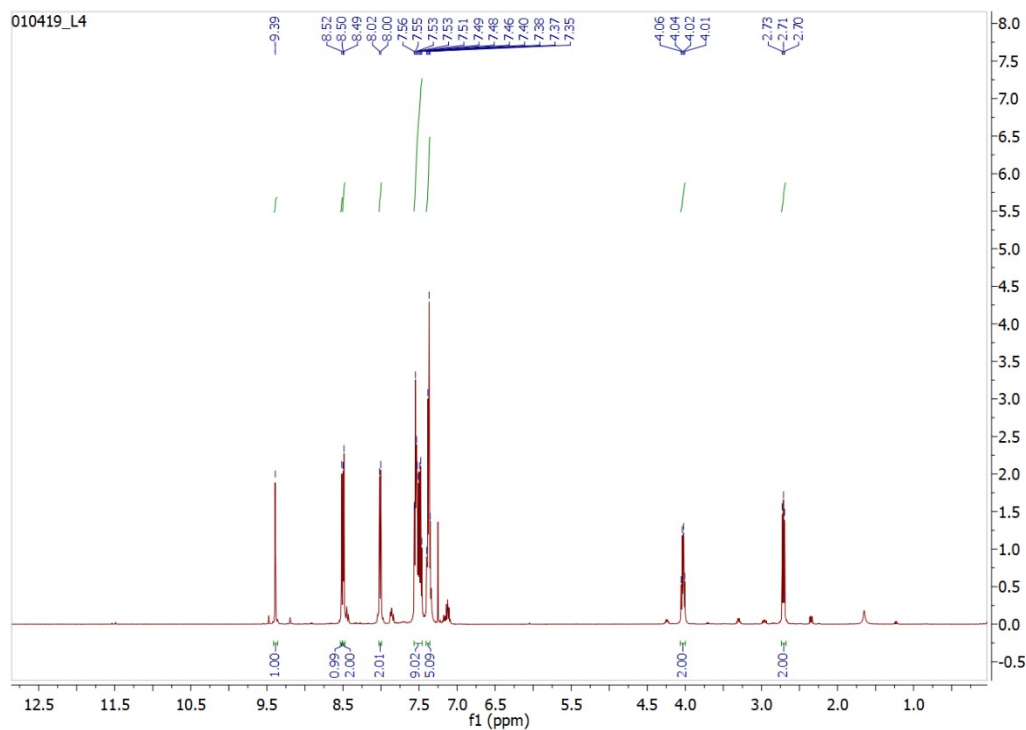
Fig. S1. ^{1}H NMR spectra of **L1**
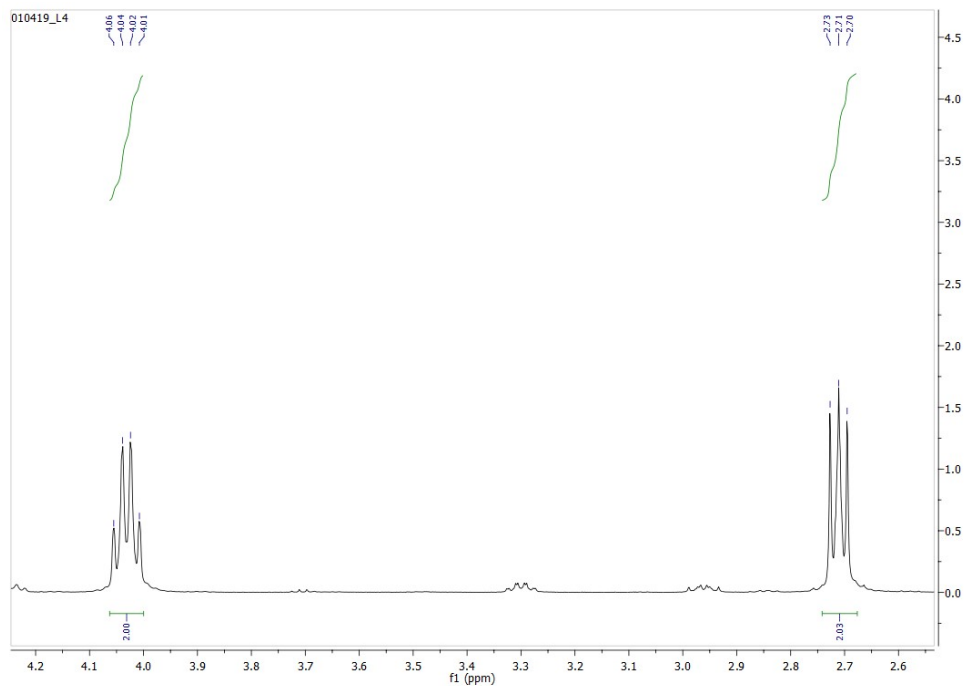
Fig. S2. ^{1}H NMR spectra of **L1** (aliphatic region)
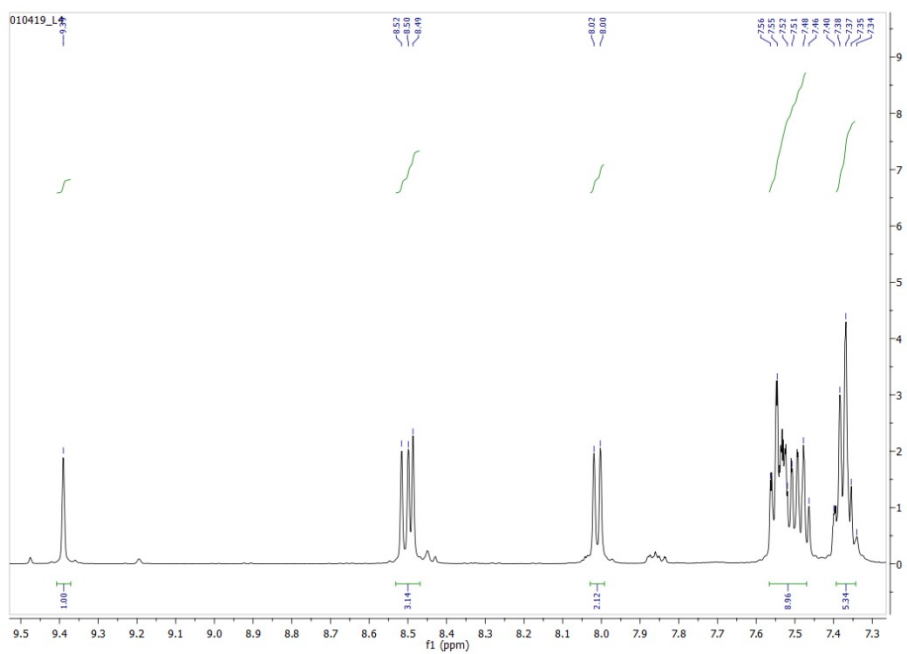
Fig. S3. ^{1}H NMR spectra of **L1** (aromatic region)
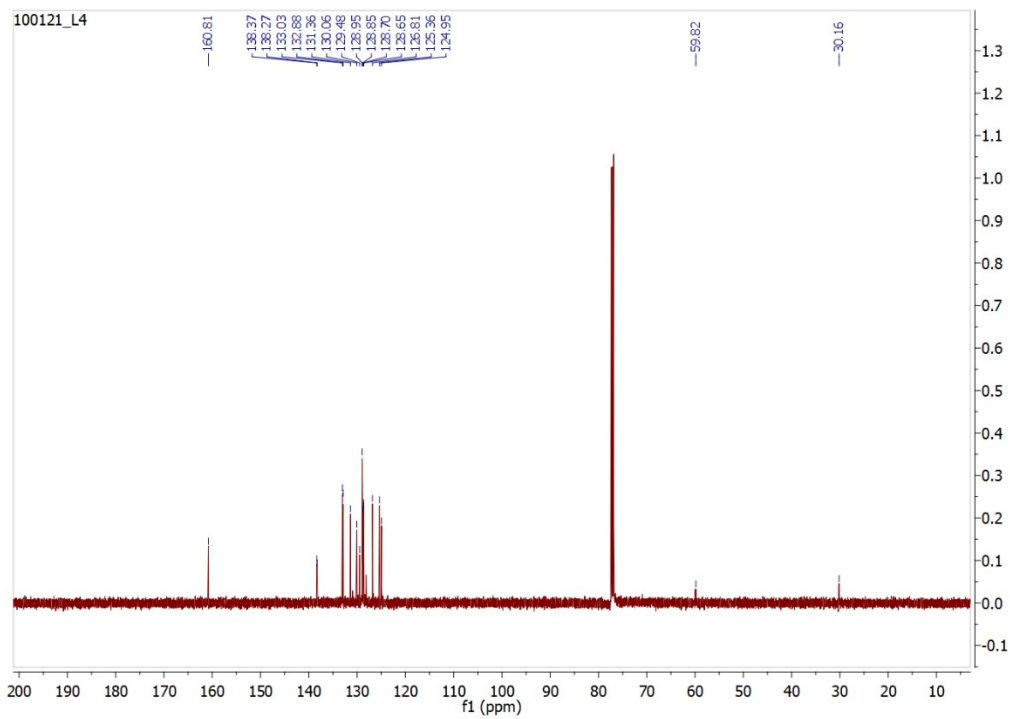
Fig. S4. $^{13}C\{^1H\}$ NMR spectra of **L1**
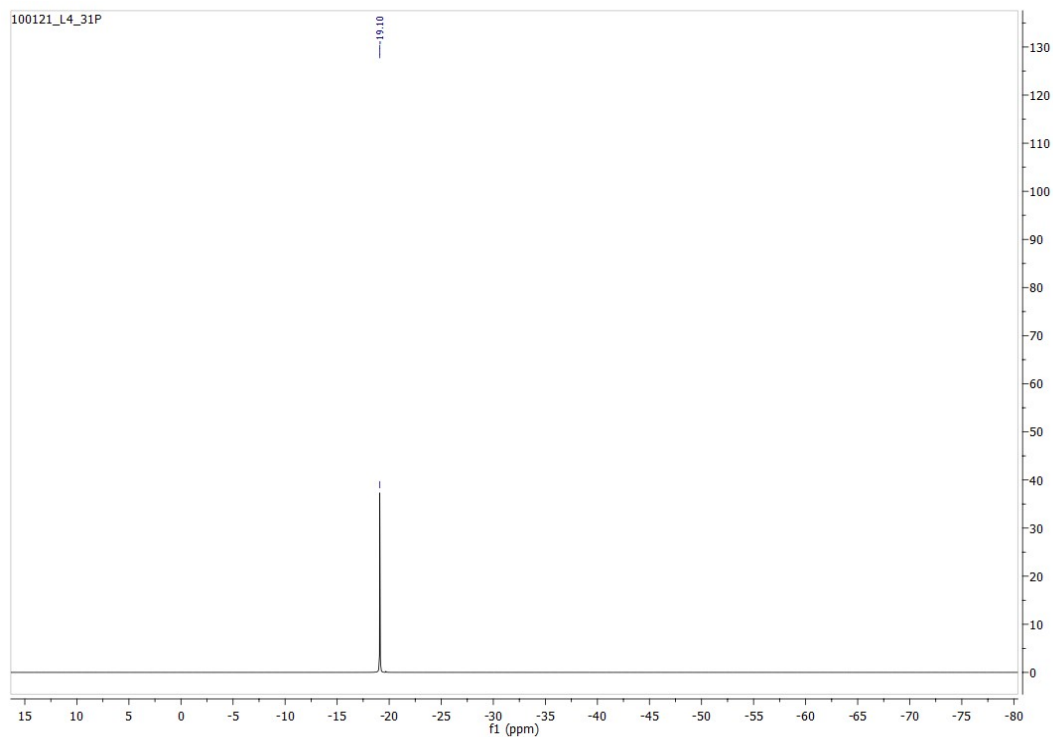
Fig. S5. $^{31}P\{^1H\}$ NMR spectra of **L1**
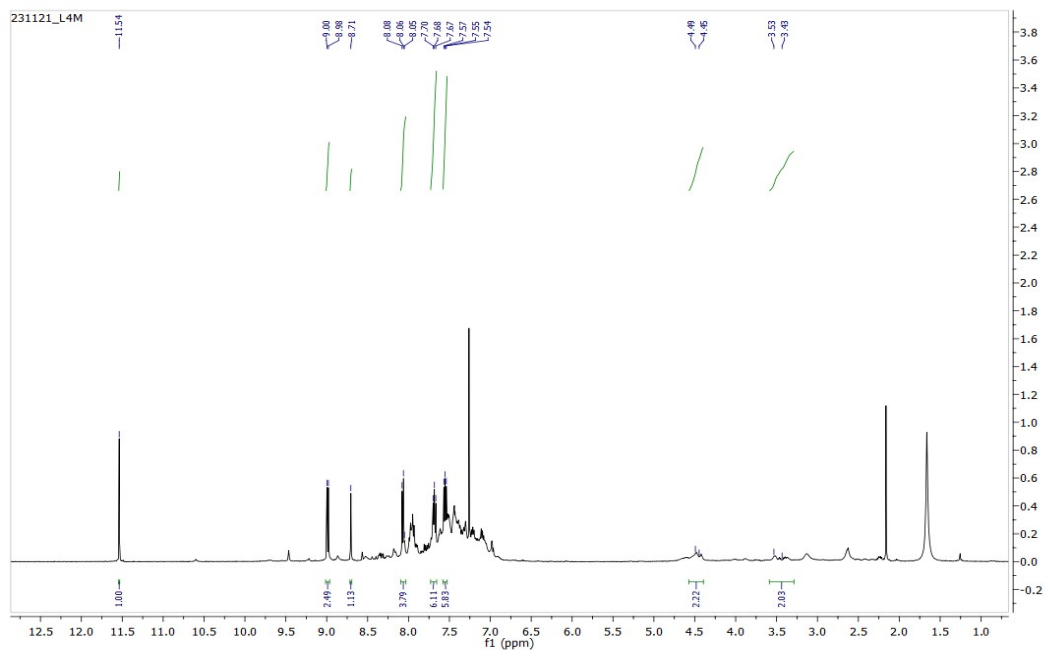
Fig. S6. ^{1}H NMR spectra of **1**
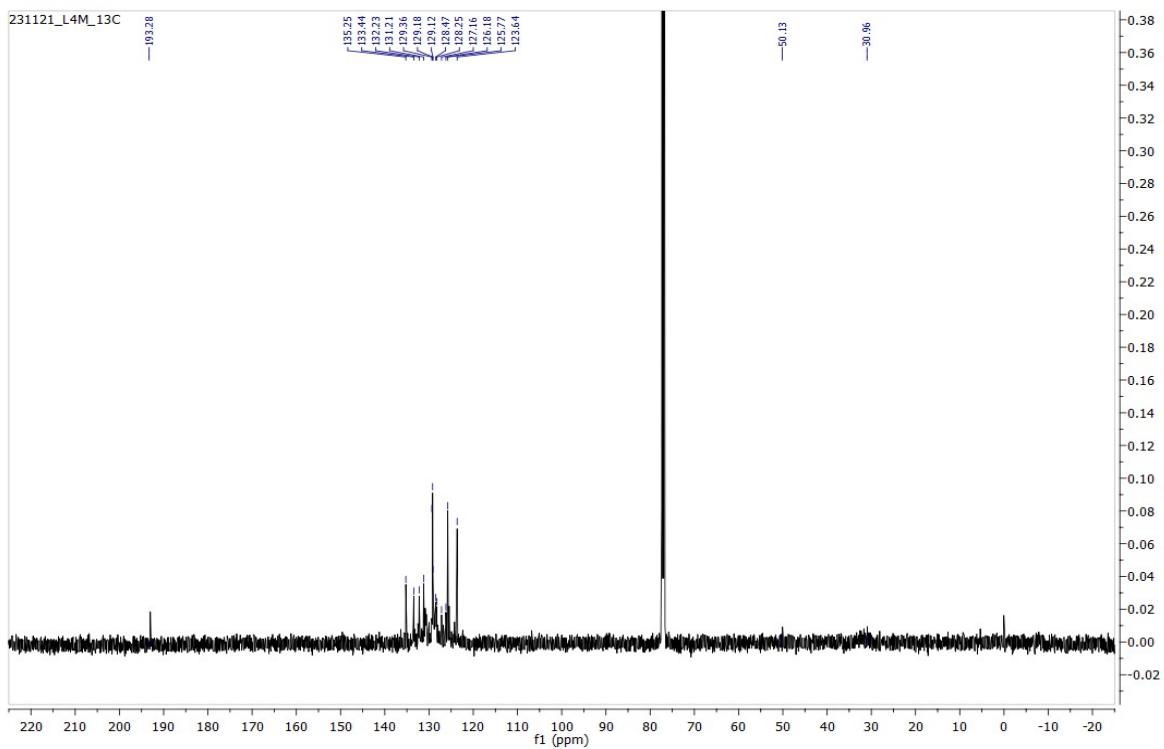
Fig. S7. ^{13}C{^{1}H} NMR spectra of **1**
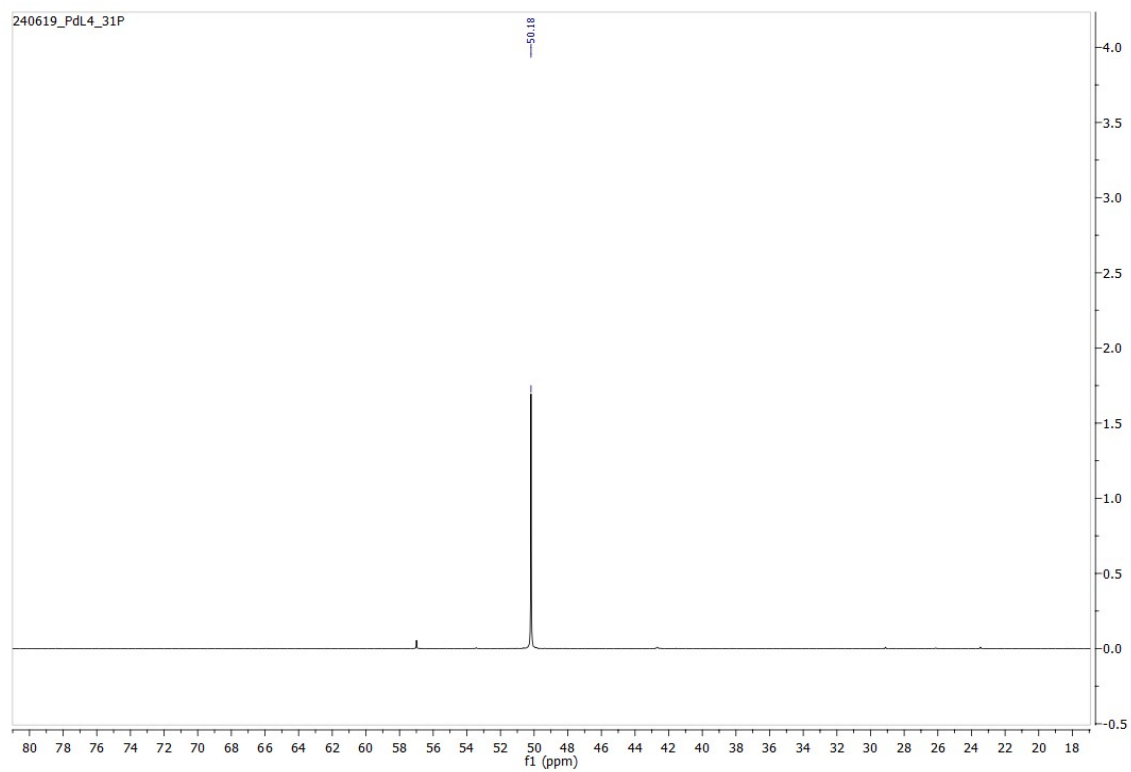
Fig. S8. $^{31}P\{^1H\}$ NMR spectra of **1**
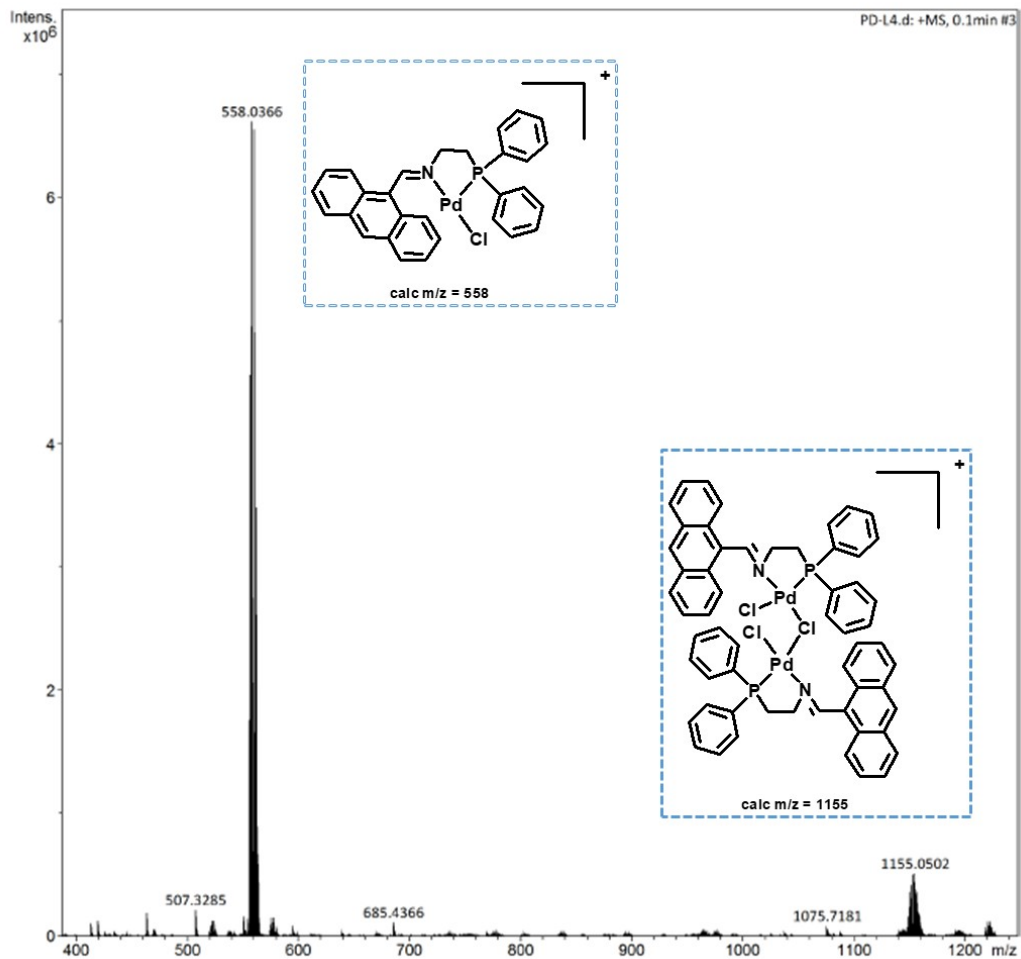
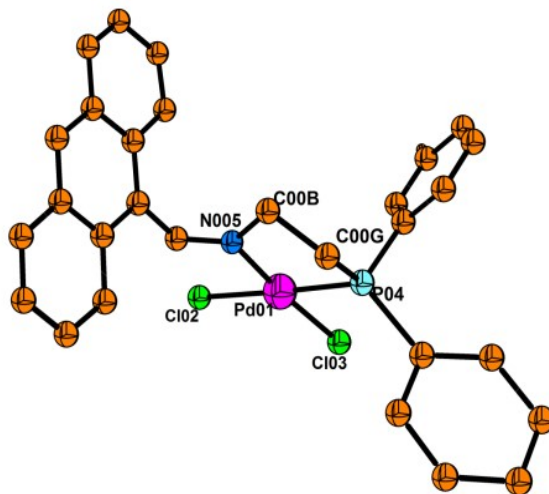**Fig. S9.** Mass Spectra of **1**

Fig. S10. ORTEP diagram of complex **1**.

Table S1. Crystal data and structural refinements for Pd(II) complex 1.

Parameters	Pd(II) complex 1
Formula	$C_{29}H_{24}C_{12}PNPd$
Formula Weight (g mol^{-3})	1247.58
Temperature/K	293(2)
Space Group	P-1
Crystal System	Triclinic
a(Å)	8.1929(6)
b(Å)	9.3335(6)
c(Å)	18.8176(9)
α(°)	79.704(5)
β(°)	84.877(5)
γ(°)	74.6.38(6)
V(Å^3)	1363.86(15)
Z	2
Density (g cm^{-3})	1.448
F(000)	600.0
Theta range for data collection	2.202<θ<28.223
Index ranges	-8 < h < 10
	-11 < k < 10
	-9 < I < 11
Reflections Collected	4928
Independent Reflection	5863
GOF on F^2	.994
R1 ($I > 2\sigma(I)$)	0.0754
R1 (all data)	0.0872
w R2 ($I > 2\sigma(I)$)	0.2292
w R2 (all data)	0.2435
CCDC	2124189

Table S2. Selected bond lengths and bond angles of 1

Bond lengths (Å)	
Pd01−P04	2.2155(18)
Pd01−N005	2.073(5)
Pd01−Cl02	2.3748(18)
Pd01−Cl03	2.2997(17)
Bond angles (°)	
N005−Pd01−Cl02	93.41(15)
N005−Pd01−Cl03	174.34(16)
P04−Pd01−Cl02	177.92(6)
P04−Pd01−Cl03	89.90(7)
N005−Pd01−P04	84.57(15)

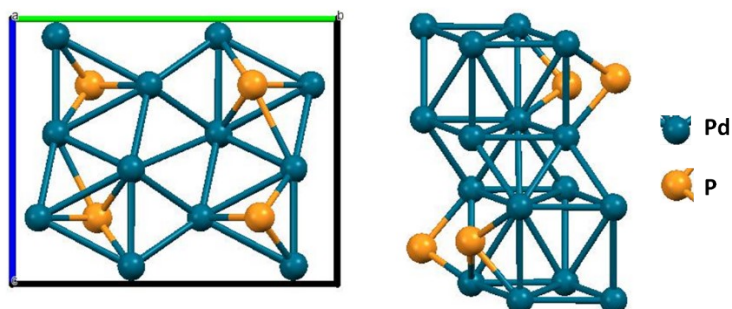| Cl02−Pd01−Cl03	92.11(7)

Fig. S11. Schematic representation of Pd$_6$P crystal.

Table S3. Binding energies of corresponding core levels of Pd$_6$P and GO-Pd$_6$P and the observed shift values

XPS core level	Binding energy Pd$_6$P (eV)	Binding energy GO-Pd$_6$P (eV)	Observed shift (eV)
Pd 3d$_{5/2}$	336.2	335.7	0.5±0.1
	338.1	337.4	0.7±0.1
Pd 3d$_{3/2}$	341.6	341.0	0.6±0.1
	342.4	341.9	0.5±0.1
P 2P$_{1/2}$	134.4	133.9	0.5±0.1
P 2P$_{3/2}$	130.6	130.0	0.6±0.1
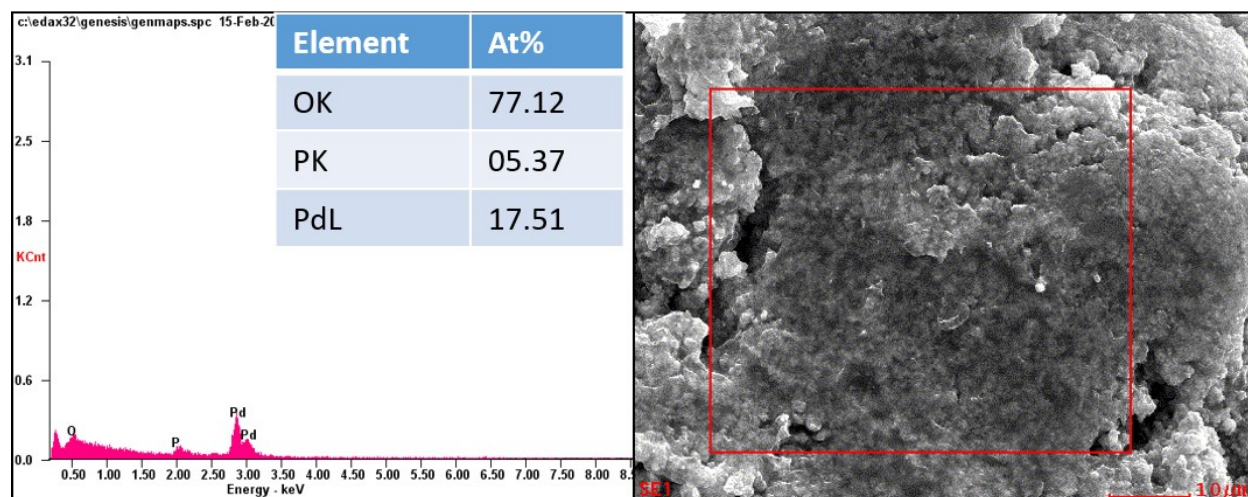
Fig S12. SEM-EDX spectrum of Pd$_6$P

Element	At%
CK	57.27
OK	38.74
PK	01.25
PdL	02.75
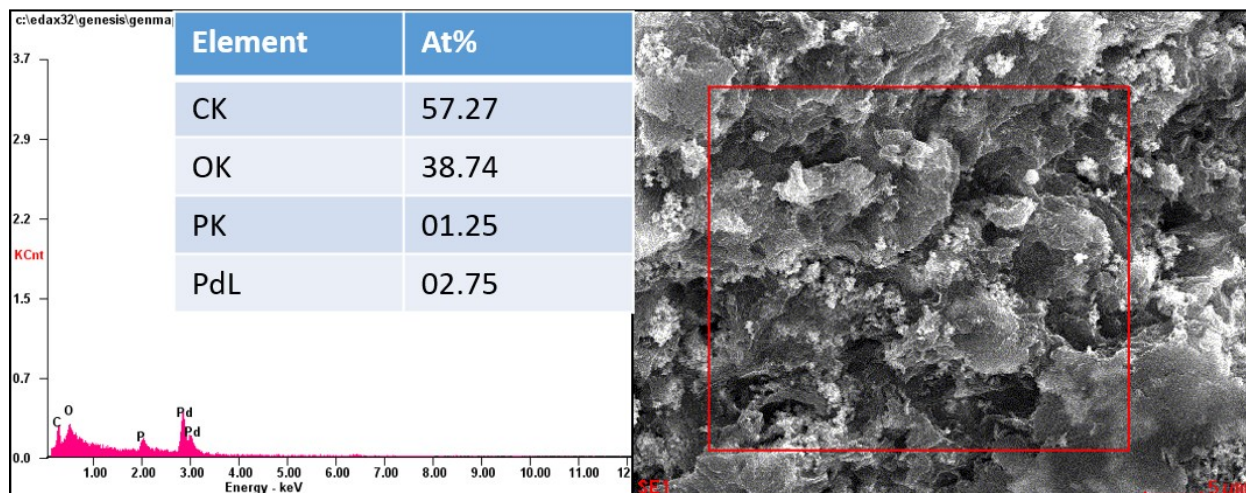
Fig S13. SEM-EDX spectrum of GO-Pd$_6$P
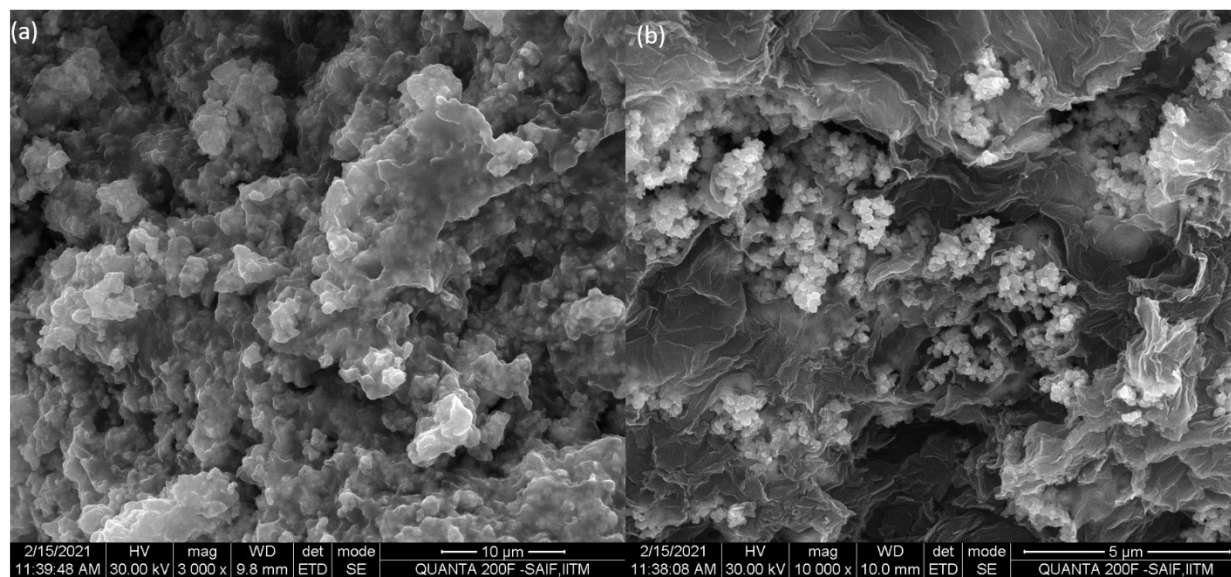
Fig S14. SEM images of (a) Pd$_6$P; (b) GO-Pd$_6$P.
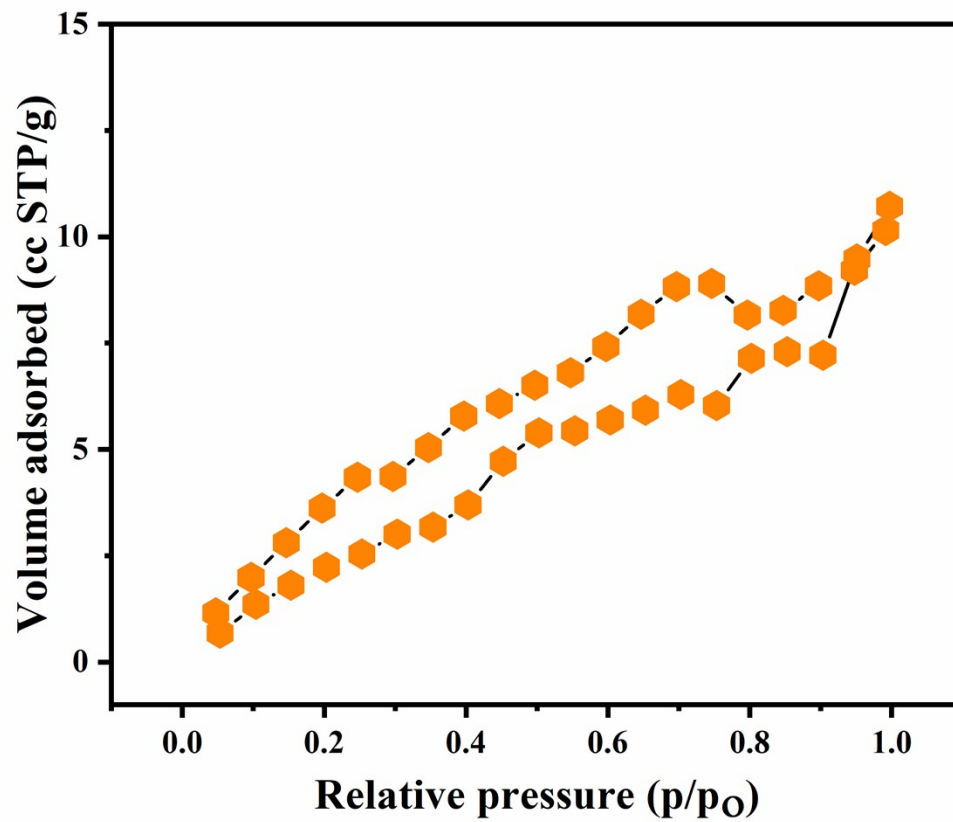
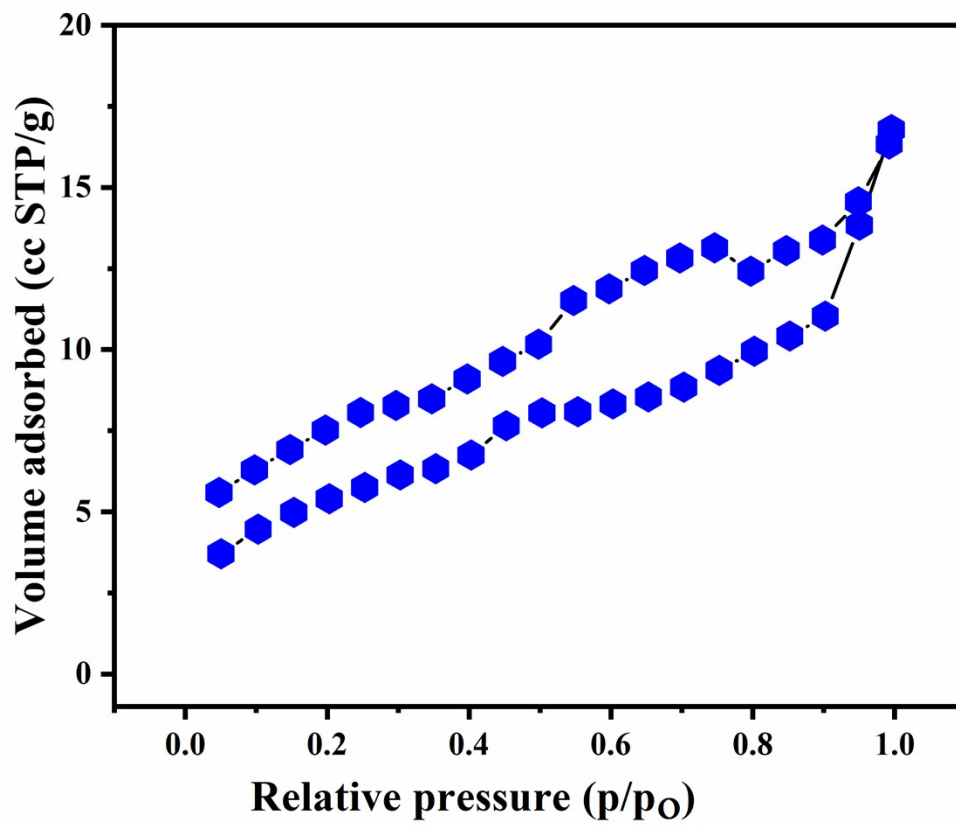**Fig S15.** BET analysis of Pd_6P

Fig S16. BET analysis of GO-Pd$_6$P
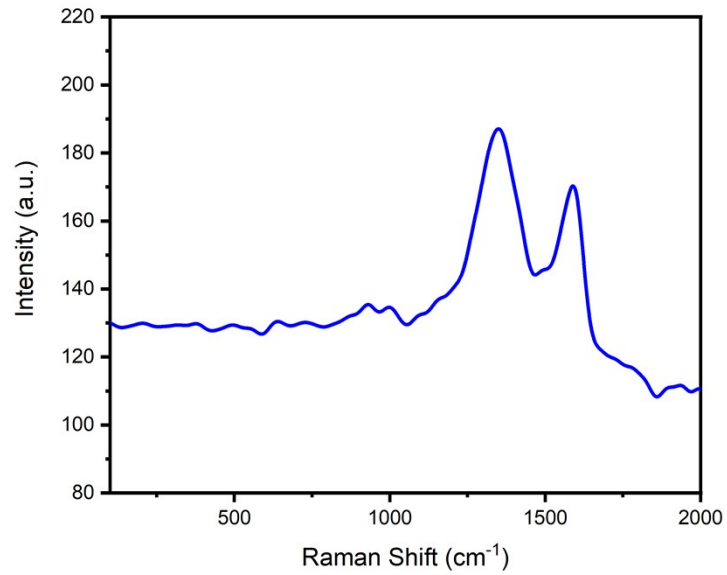
Fig S17. Raman spectra of GO-Pd$_6$P
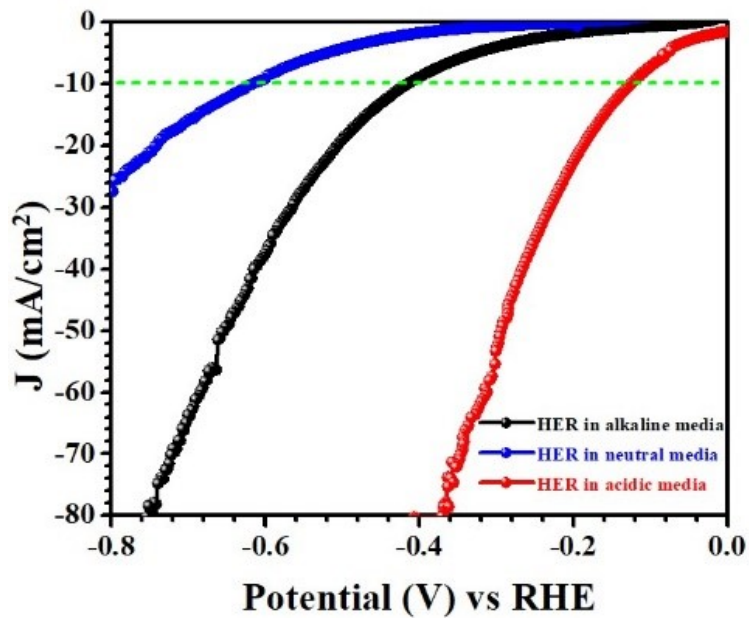

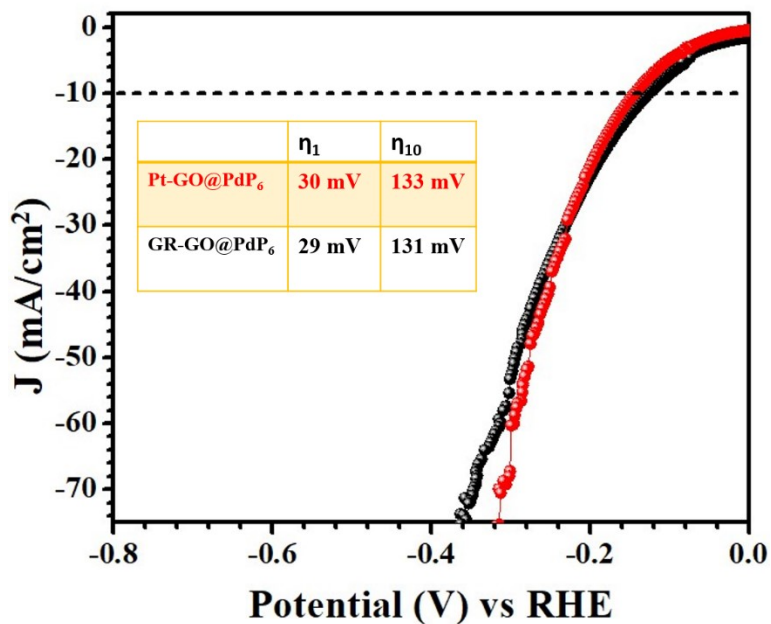**Fig S18.** LSV results in alkaline, neutral and acidic media

Fig S19. LSV results using Graphite rod as counter electrode

Table S4. Electrocatalytic parameters for hydrogen evolution reaction

Materials	Onset potential at 1 mA/cm² (mV)	Over potential (mV) 10mA/cm²	Tafel slope	Charge transfer resistance (R_{ct})
GO- Pd_6P @GCE	30	133	60	120
Pd_6P@ GCE	54	312	159	232
Bare GCE	183	506	194	1424

Table S5. Results of the electrochemically active surface area (ECSA) from C_{dl} and roughness factor (R_f) for each of the electrocatalysts prepared in 0.5 M H_2SO_4 hydrogen evolution reaction

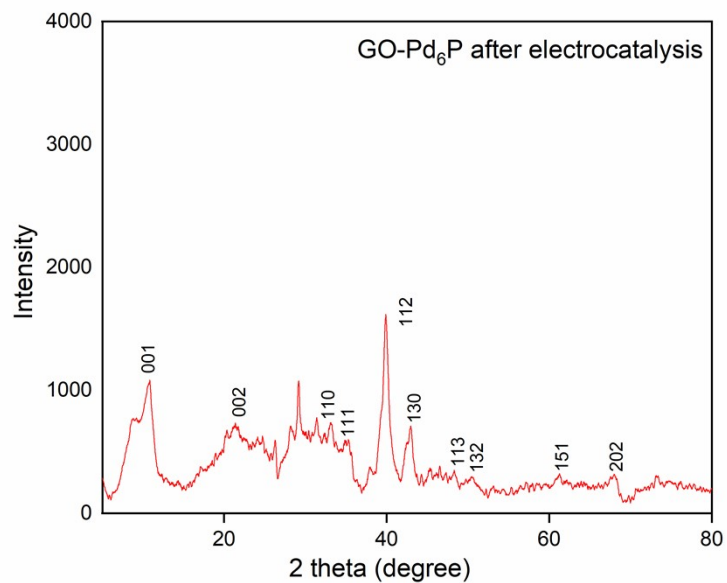| Materials	GO- Pd_6P @GCE
C_{dl} ($\mu F/cm^2$)	474
ECSA (cm^2/mg)	135
R_f	1928

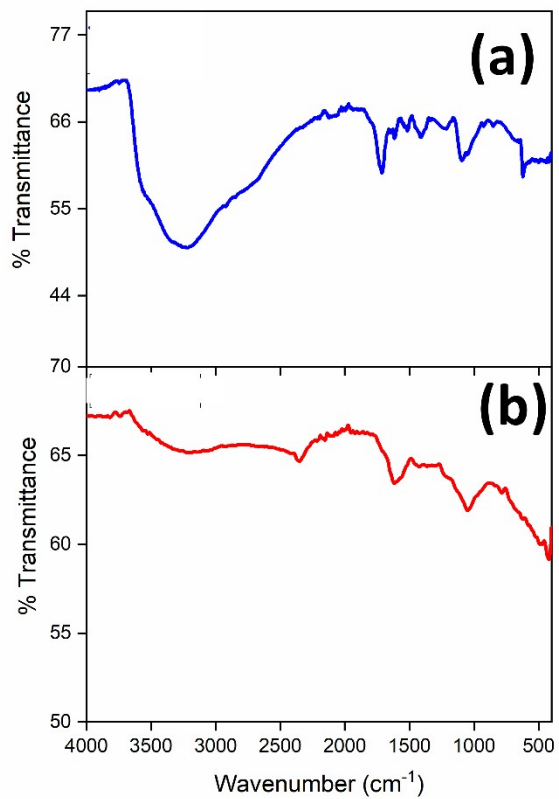**Fig S20.** PXRD of GO-Pd$_6$P (post-electrocatalysis)

Fig S21. FTIR of GO-Pd$_6$P (a) before electrocatalysis (b) post-electrocatalysis
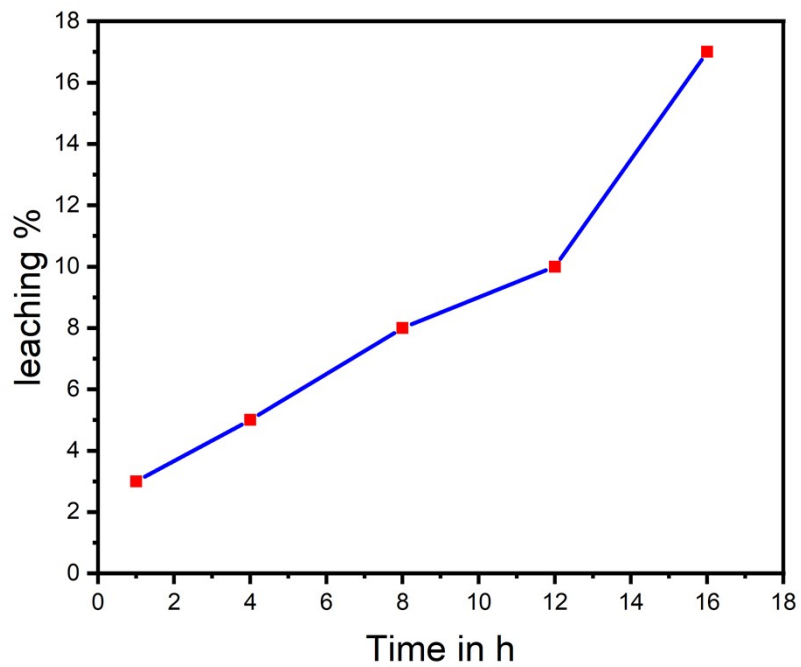
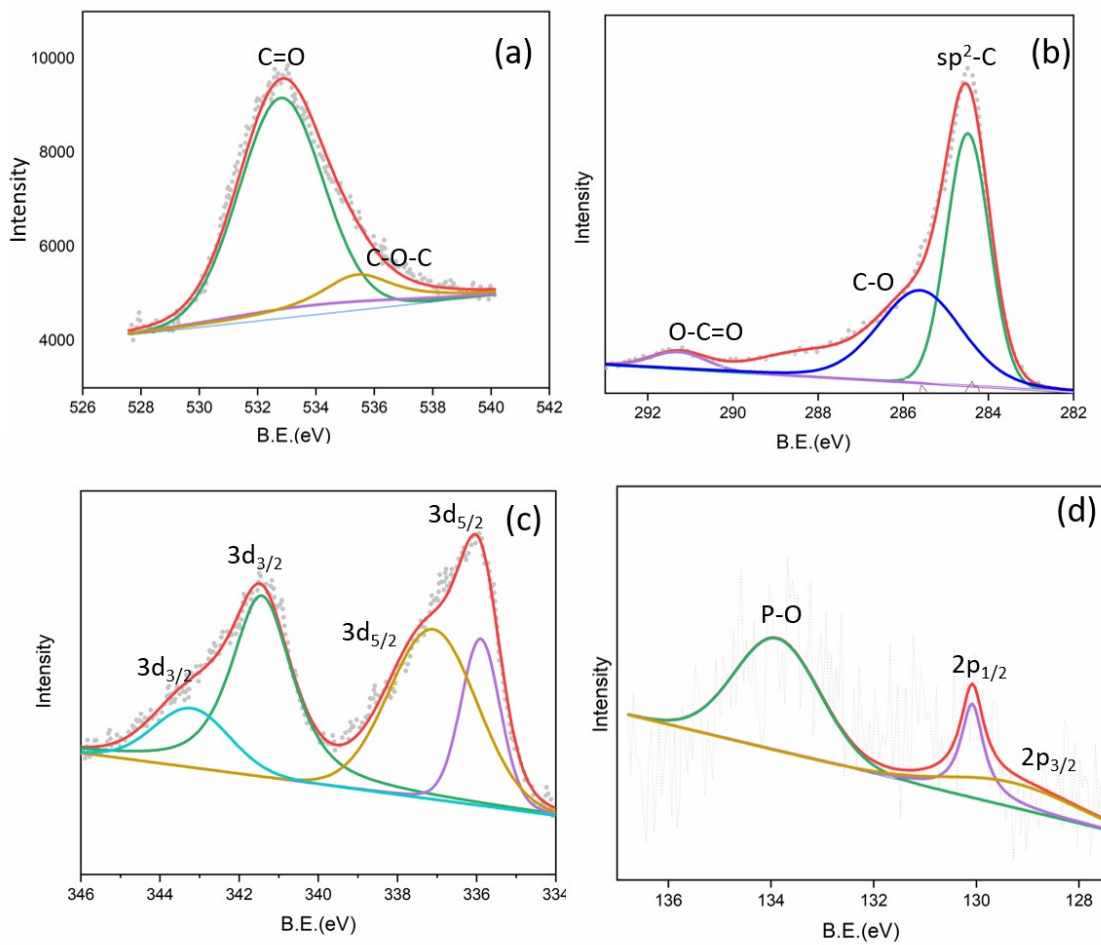**Fig S22.** ICP results for leaching of Pd upto 16 hours

Fig S23. XPS Spectra (a) O1s, (b) C1s, (c) Pd3d (d) P2p of GO- Pd_6P (post-electrocatalysis)
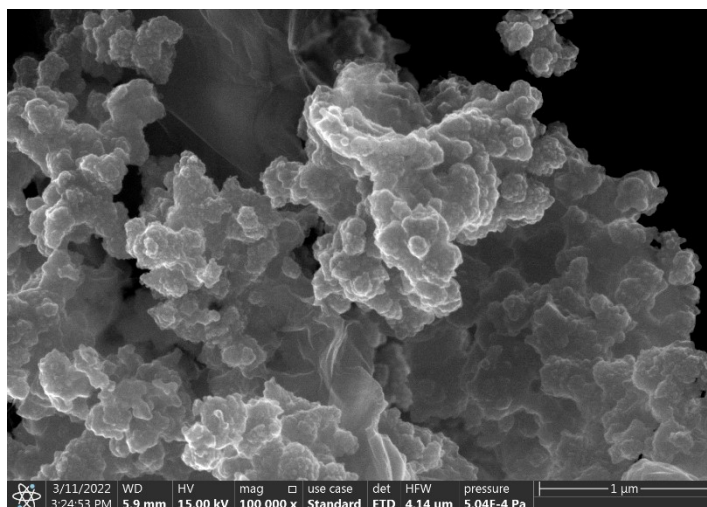
Fig S24. SEM image of GO-Pd$_6$P (post-electrocatalysis)

Table S6. Comparison of HER performance of some transition metal based catalytic system with present system:

S. No.	Material	η_{100} (mV)	Tafel Slope (mV/dec)	Exchange current Density (mA cm^{-2})	Mass loading (mg/cm^2)	Reference
1.	GO-Pd$_6$P	133	60	10	1.5	This report
2.	MoP	271	54	0.086	0.36	3
3.	Ni$_2$P@Ti	180	46	3.3	1	4
4.	CoP-CC	204	51	0.288	0.92	5
5.	Go-Co$_2$P	137	83	3.48	1.33	6
6.	CoSe$_2$NP@CP	181	40	0.049	2.8	7
7.	NiSe$_2$	358	72.1	-	0.4	8
8.	NiSe	331	28.6	-	0.4	8
9.	Pd-graphene nanocomposite	-	46	-	0.02	9
10.	Pd$_{3.02}$Te NWs/rGO	355	90	1.807	-	10
11.	Pd$_4$Se	180 (η_{10})	57	0.23	-	11
12.	Pd$_{17}$Se$_{15}$	162 (η_{10})	56	0.006	-	11
13.	Pd$_7$Se$_4$	94 (η_{10})	50	0.025	-	11
14.	Pd nanoparticle Assemblies	80	30	-	0.28	12

15.	PdPS@rGO	~90(η10)	46	0.14	-	13
16.	PtPd on WC/C		21	-	0.05	14

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