

Electronic Supplementary Information

**Palladium-phosphorous/sulfur nanoparticles(NPs) decorated on graphene oxide: synthesis using the same precursor for NPs and catalytic applications in Suzuki-Miyaura coupling**

Hemant Joshi, Kamal Nayan Sharma, Alpesh K. Sharma and Ajai Kumar Singh\*

Department of Chemistry, Indian Institute of Technology Delhi, New Delhi 110016, India.

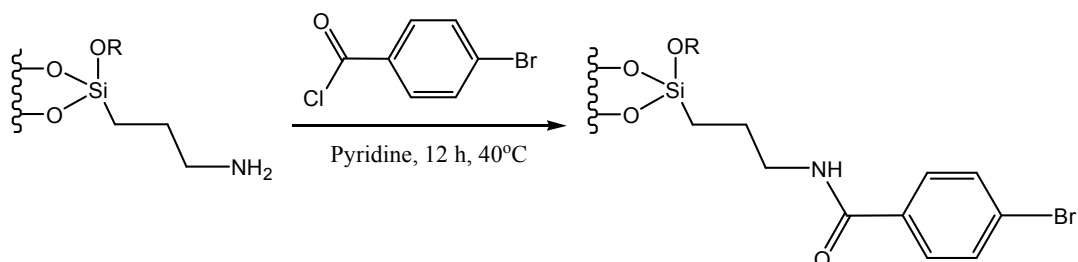
### Filtration experiment

In a oven dried flask ethanol (2 mL) and water (2 mL) were added to the GO-PdP<sub>2</sub> (0.5 mol %), potassium carbonate (0.276 g, 2 eq.), phenylboronic acid (0.158 g, 1.3 eq.) and 4-bromoacetophenone (0.199 g, 1.0 mmol). Afterwards, the suspension was stirred at 80 °C. After 10 min the reaction was stopped and the catalyst settled down and the reaction mixture turned clear. Half portion of the liquid reaction mixture was taken into another reaction flask under same conditions. After that both reactions proceed for another 1 hour, and conversion calculated by using <sup>1</sup>H NMR spectroscopy.

### Two Phase Test:

#### Immobilization of 4-Bromobenzoic Acid on Silica<sup>1</sup>

4-Bromobenzoic acid (1.99 g, 10 mmol) was refluxed with dry SOCl<sub>2</sub> (20 mL) for 3 h. The solution was cooled and thionyl chloride was distilled off to give 4-bromobenzoyl chloride. 3-Aminopropyl trimethoxysilane-modified silica (1.00 g, Aldrich), pyridine (0.404 mL), dry THF (10 mL) and 4-bromobenzoyl chloride (1.150 g, 5.25 mmol) (synthesis described above), were stirred in a round bottom flask under a N<sub>2</sub> atmosphere at 40 °C for 12 h. The suspension was filtered through G-4 crucible and washed with 5% (v/v) HCl (3 × 20 mL) followed by 0.02 M aqueous K<sub>2</sub>CO<sub>3</sub> (2 × 20 mL) and rinsed with distilled water (40 mL) and ethanol (40 mL). The resulting solid was washed with excess dichloromethane and dried at room temperature in air, yielding a white powder.



## Scheme S1. Immobilization of 4-Bromobenzoic Acid on Silica.

### NMR Spectra

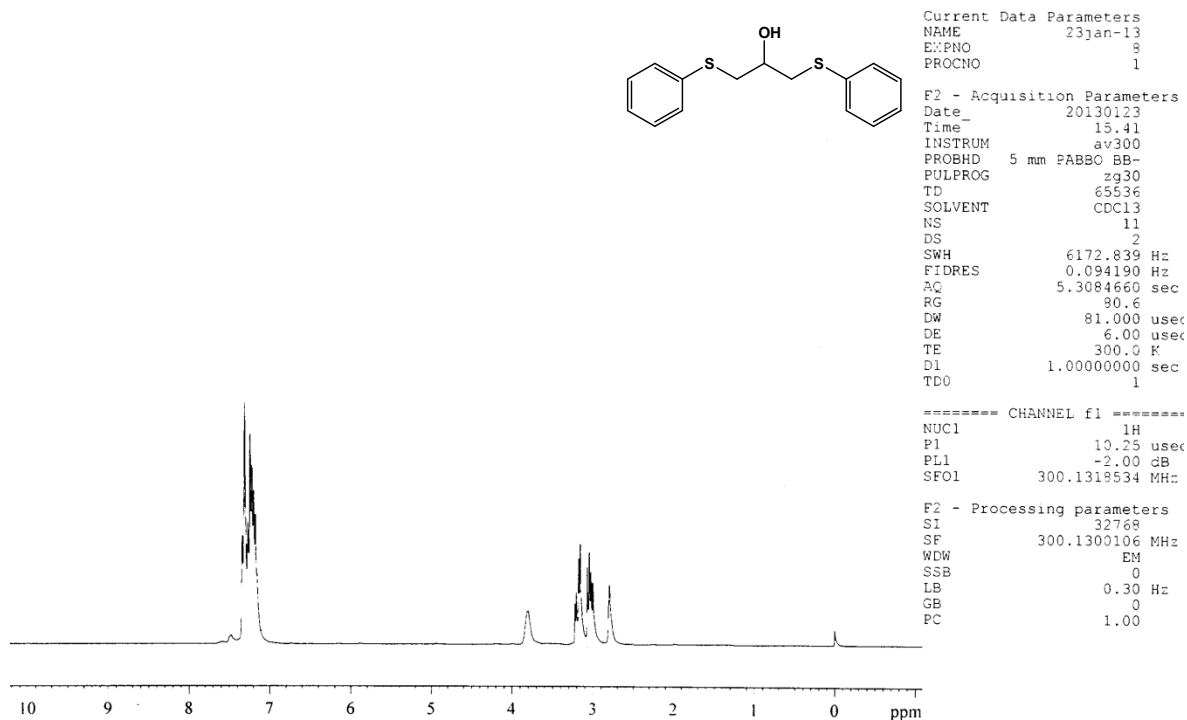


Figure S1. <sup>1</sup>H NMR of Ligand L

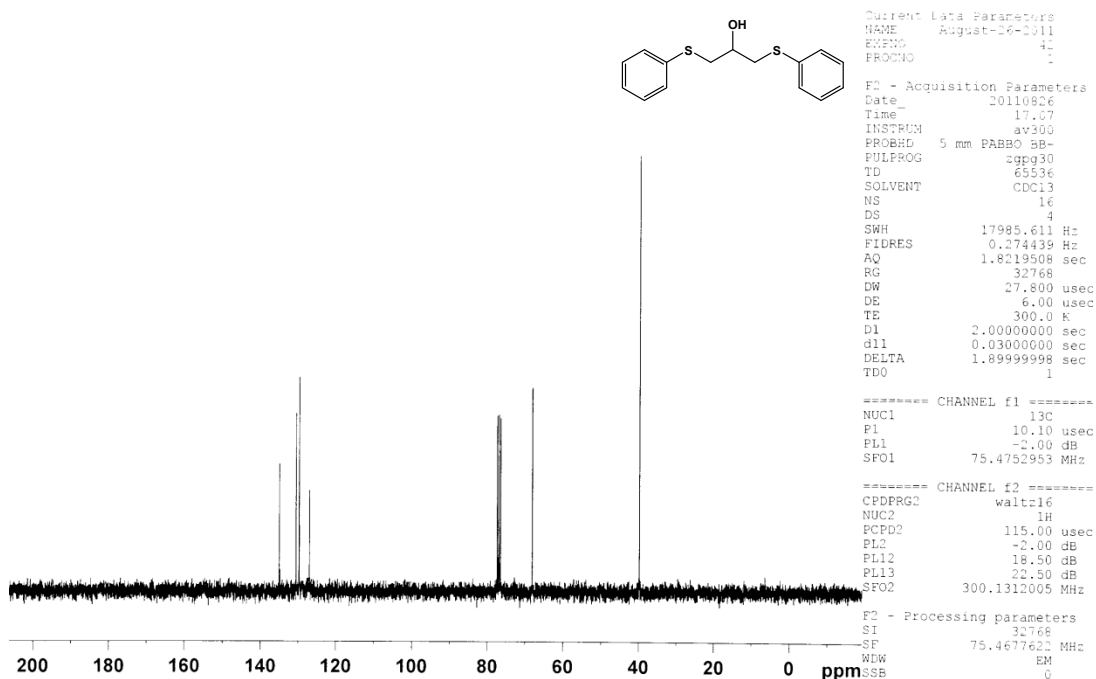


Figure S2.  $^{13}\text{C}\{^1\text{H}\}$  NMR of Ligand L

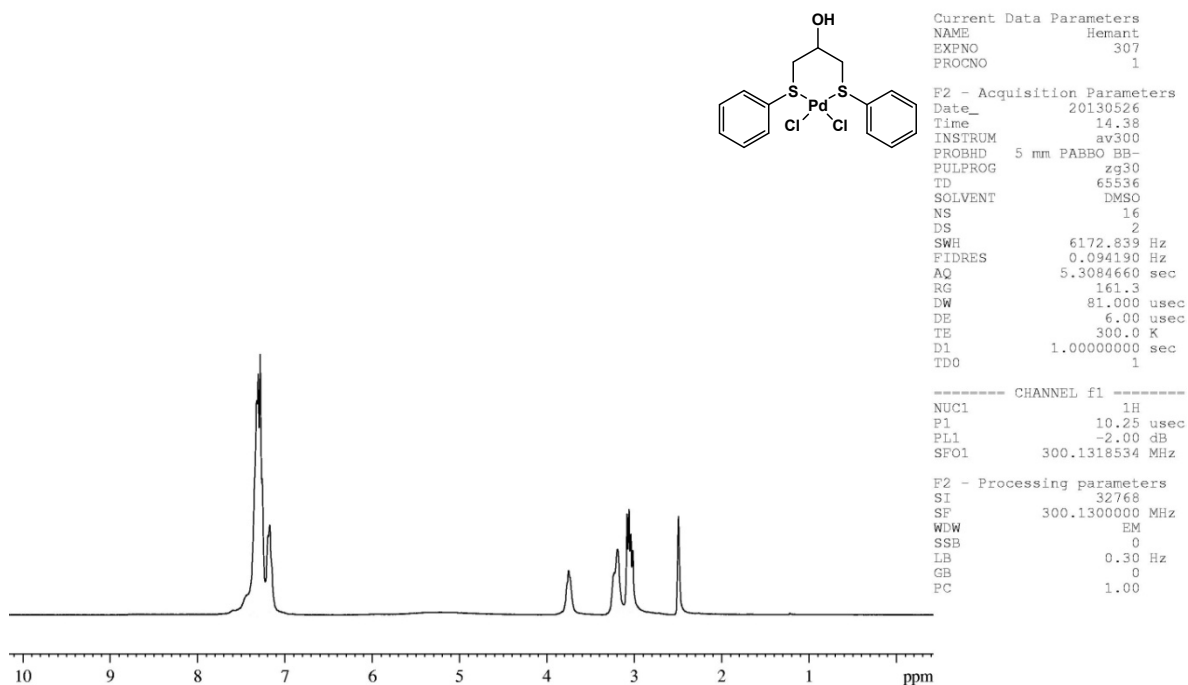


Figure S3.  $^1\text{H}$  NMR of Complex 1

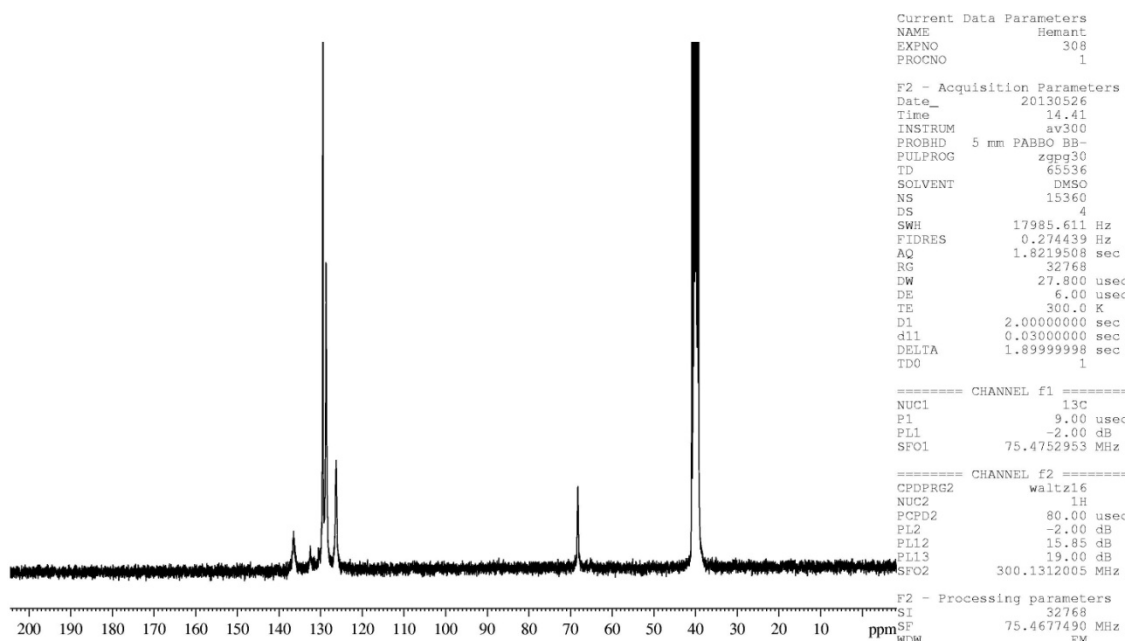


Figure S4.  $^{13}\text{C}\{^1\text{H}\}$  NMR of Complex 1

**Table S1.** Crystal data and structural refinement parameters

Compounds	<b>1</b>
Empirical formula	C <sub>15</sub> H <sub>16</sub> Cl <sub>2</sub> O Pd S <sub>2</sub>
Formula wt.	453.72
Crystal size [mm]	0.32×0.26×0.21
Crystal system	Orthorhombic
Space group	<i>P b c a</i>
Unit Cell dimension	$a = 08.117 (3)\text{Å}$ $b = 20.123(8)\text{Å}$ $c = 20.541 (8)\text{Å}$ $\alpha = 90.00^\circ$ $\beta = 90.00^\circ$ $\gamma = 90.00^\circ$
Volume [Å <sup>3</sup> ]	3355(2)
<i>Z</i>	8
Density (Calc.) [Mg·m <sup>-3</sup> ]	1.796
Absorption coeff. [mm <sup>-1</sup> ]	1.668
<i>F</i> (000)	1808.0
$\theta$ range [°]	2.25–27.33
Index ranges	$-09 \leq h \leq 09$ $-23 \leq k \leq 23$ $-24 \leq l \leq 24$
Reflections collected	28910
Independent reflections ( <i>R</i> <sub>int</sub> ·)	2959 (0.0254)
Max./min. Transmission	0.707/0.597
Data/restraints/parameters	2959/0/191
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.068
Final R indices	$R_I = 0.0426$ ,

[ $I > 2\sigma(I)$ ]	$wR_2 = 0.1124$
R indices (all data)	$R_1 = 0.0547,$ $wR_2 = 0.1191$
Largest diff. peak/hole [ $e.\text{\AA}^{-3}$ ]	1.476/−0.639

**Table S2.** Selected bond lengths [ $\text{\AA}$ ] and bond angles [ $^\circ$ ]

Bond length [ $\text{\AA}$ ]	Bond angle [ $^\circ$ ]
Pd(1)—S(1) 2.277(15)	S(1)—Pd(1)—S(2) 100.41(5)
Pd(1)—S(2) 2.279(14)	S(1)—Pd(1)—Cl(1) 84.08(6)
Pd(1)—Cl(1) 2.317(16)	S(1)—Pd(1)—Cl(2) 174.40(6)
Pd(1)—Cl(2) 2.310 (15)	S(2)—Pd(1)—Cl(1) 175.22(5)
O(1)—C(8) 1.387(7)	S(2)—Pd(1)—Cl(2) 84.12(6)
S(1)—C(1) 1.782(5)	Cl(1)—Pd(1)—Cl(2) 91.30(7)
S(1)—C(7) 1.821(6)	C(7)—C(8)—O(1) 108.9(4)
S(2)—C(9) 1.825(6)	C(9)—C(8)—O(1) 107.9(5)
S(2)—C(10) 1.794(5)	C(1)—S(1)—C(7) 100.8(2)
C(7)—C(8) 1.540(7)	C(9)—S(2)—C(10) 101.2(2)
C(8)—C(9) 1.514(8)	C(1)—C(6)—S(1) 123.7(4)
	C(11)—C(10)—S(2) 116.0(4)

**Table S3.** Distances [ $\text{\AA}$ ] of inter and intra-molecular interactions for complex **1**

<b>1</b>	
C(7)—H(7A)⋯Cl(1) (inter-molecular)	2.961(2)
C(6)—H(6)⋯Cl(2) (inter-molecular)	3.043(2)
C(9)—H(9B)⋯Cl(2) (inter-molecular)	3.170(2)
C(4)—H(4)⋯Cl(2) (inter-molecular)	3.089(2)
C(3)—H(3)⋯Cl(2) (inter-molecular)	2.949(2)
C(12)—H(12)⋯Cl(1) (inter-molecular)	3.071(2)
C(4)—H(4)⋯Cl(1) (inter-molecular)	3.064(2)

# Mass Spetra

## Mass Spectrum SmartFormula Report

### Analysis Info

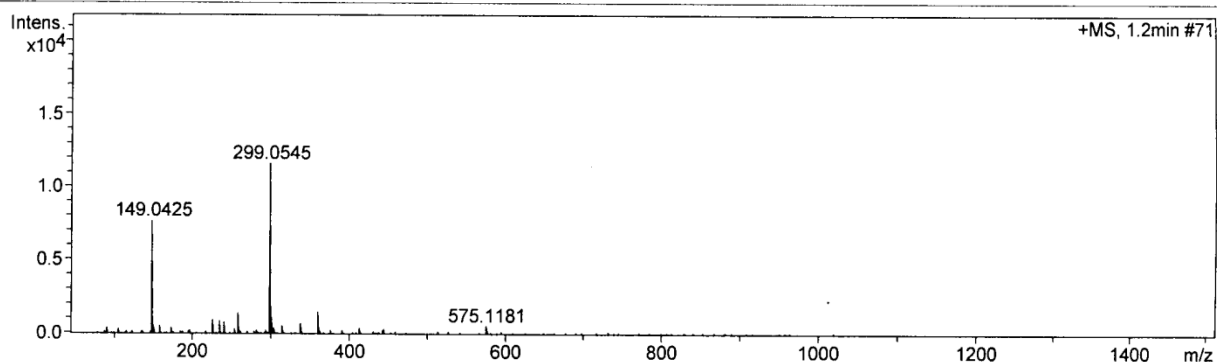
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Sample Name  
Comment

Acquisition Date 4/27/2012 11:54:35 AM

Operator C/A  
Instrument / Ser# micrOTOF-Q II 10262

### Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	N-Rule
299.0545	1	C 15 H 16 Na O S 2	100.00	299.0535	-1.0	-3.3	5.1	7.5	even	ok

Figure S5. Mass Spectrum of L.



## Mass Spectrum SmartFormula Report

**Analysis Info**

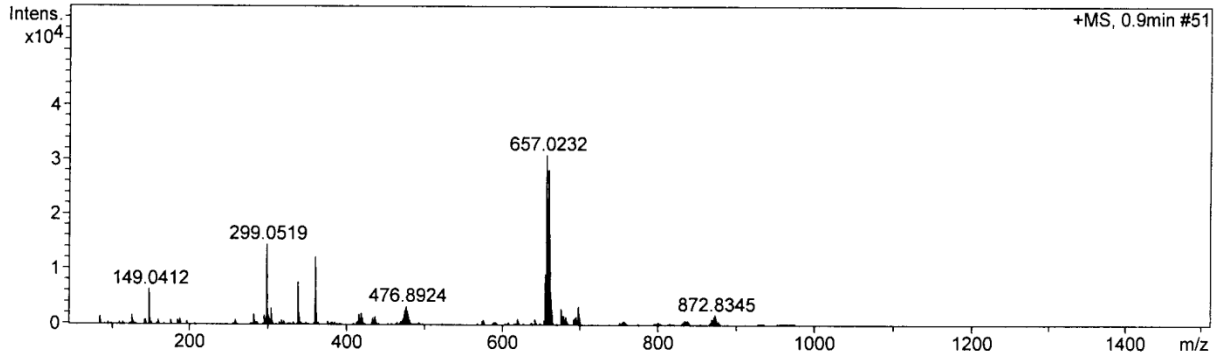
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**Acquisition Parameter**

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Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSig	rdb	e <sup>-</sup> Conf	N-R ule
474.8945	1	C <sub>15</sub> H <sub>16</sub> Cl <sub>2</sub> NaOPdS <sub>2</sub>	100.00	474.8946	0.2	0.3	31.5	6.5	even	ok

**Figure S6.** Mass Spectrum of Complex 1.

## Powder XRD patterns

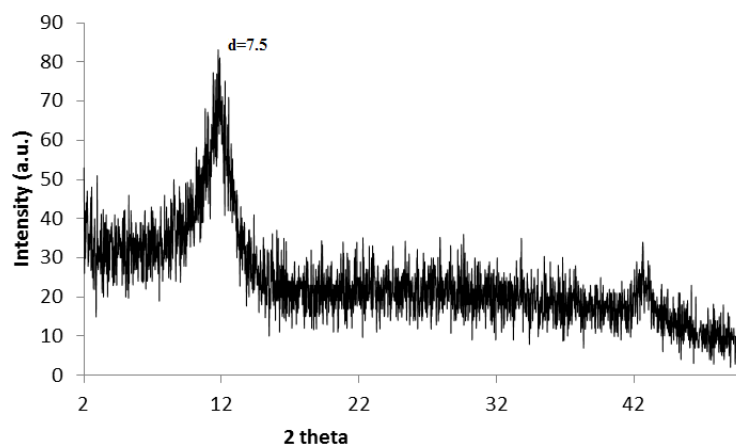


Fig. S7 PXRD of Graphene oxide

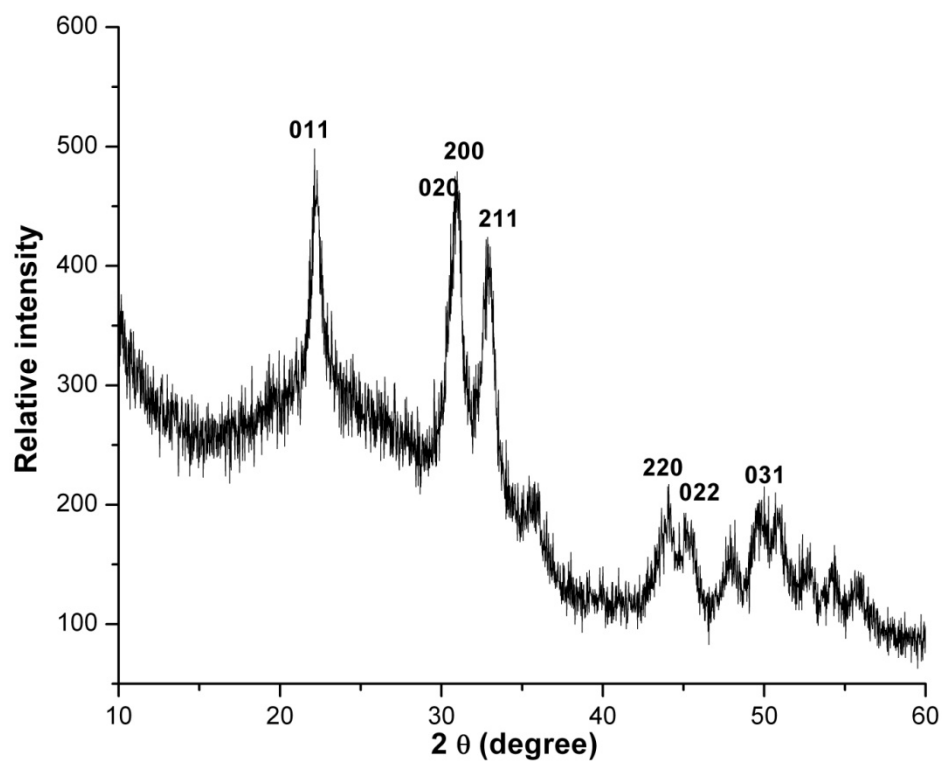
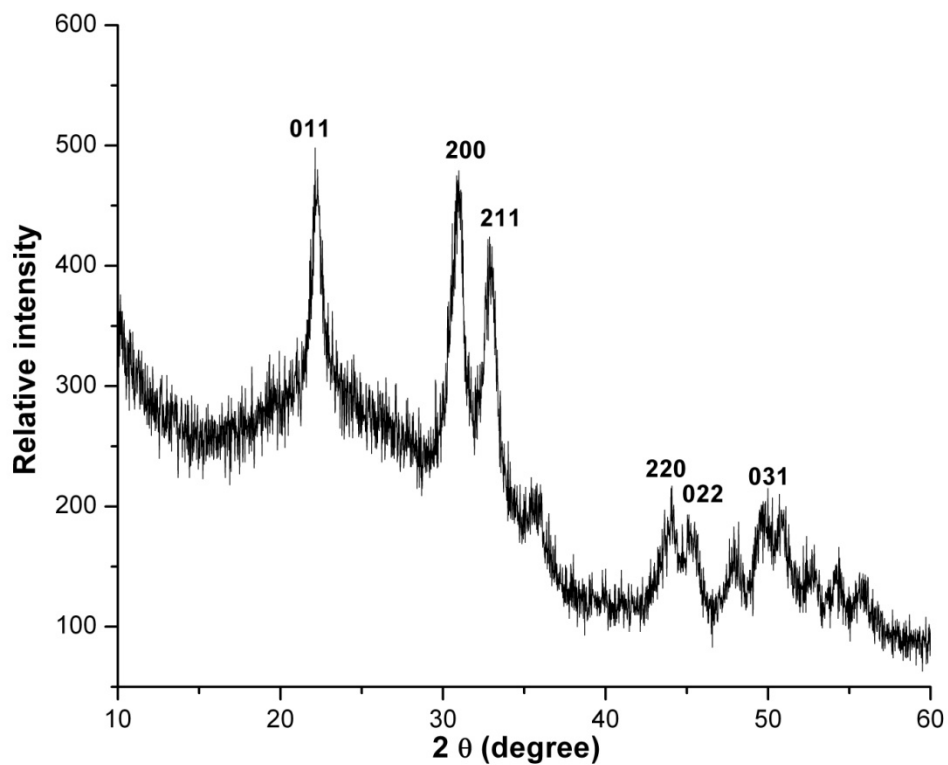
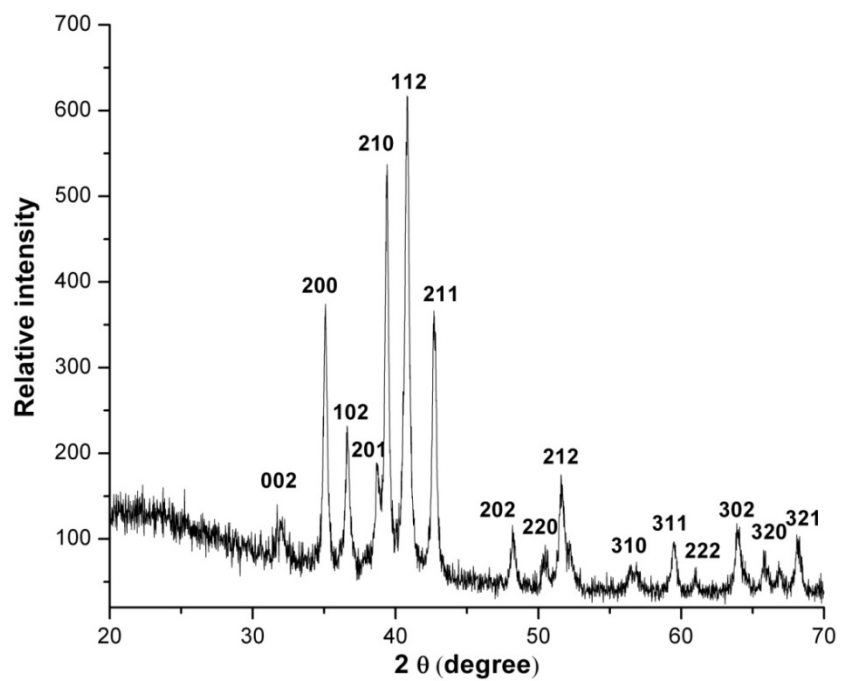


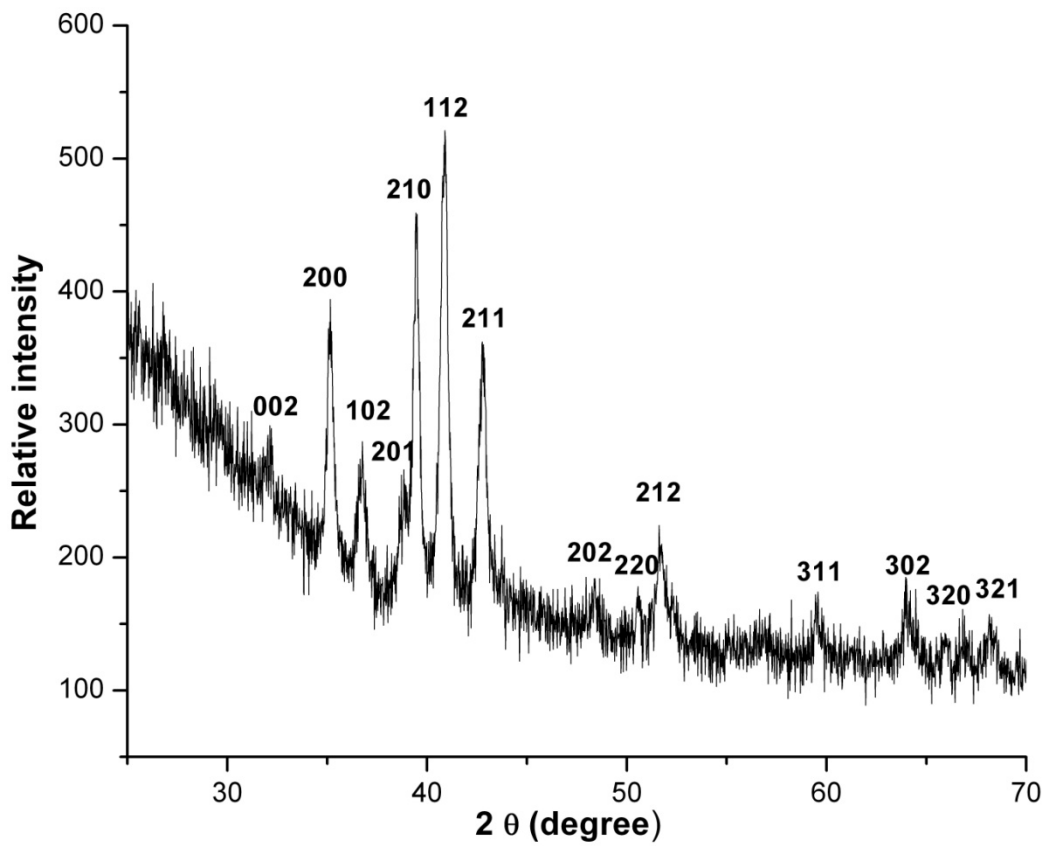
Figure S8. Powder XRD pattern of PdP<sub>2</sub> (JCPDS No 77-1421) nano-particles.



**Figure S9.** Powder XRD pattern of GO-PdP<sub>2</sub> (JCPDS No 77-1421) nano-particles.

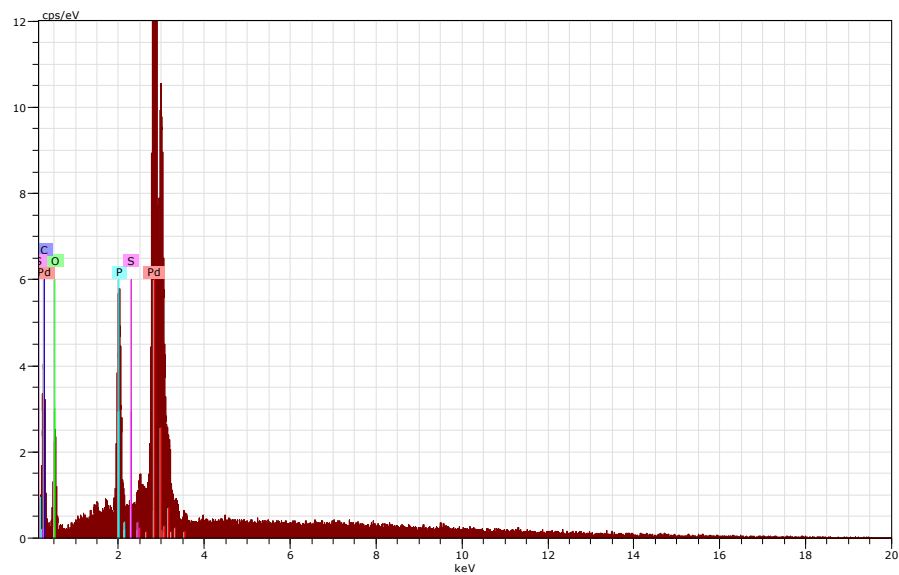


**Figure S10.** Powder XRD pattern of Pd<sub>4</sub>S (JCPDS No 73-1387) nano-particles.

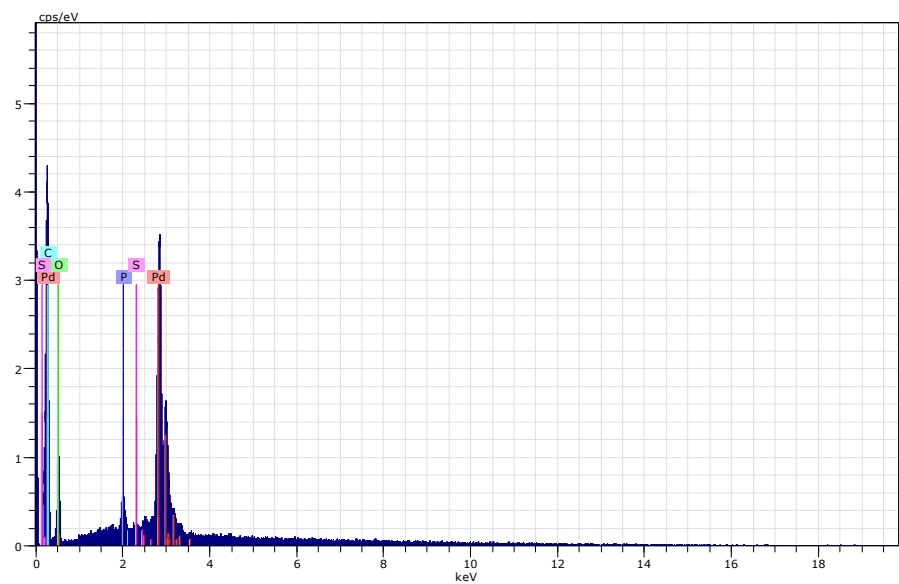


**Figure S11.** Powder XRD pattern of GO-Pd<sub>4</sub>S (JCPDS No 73-1387) nano-particles.

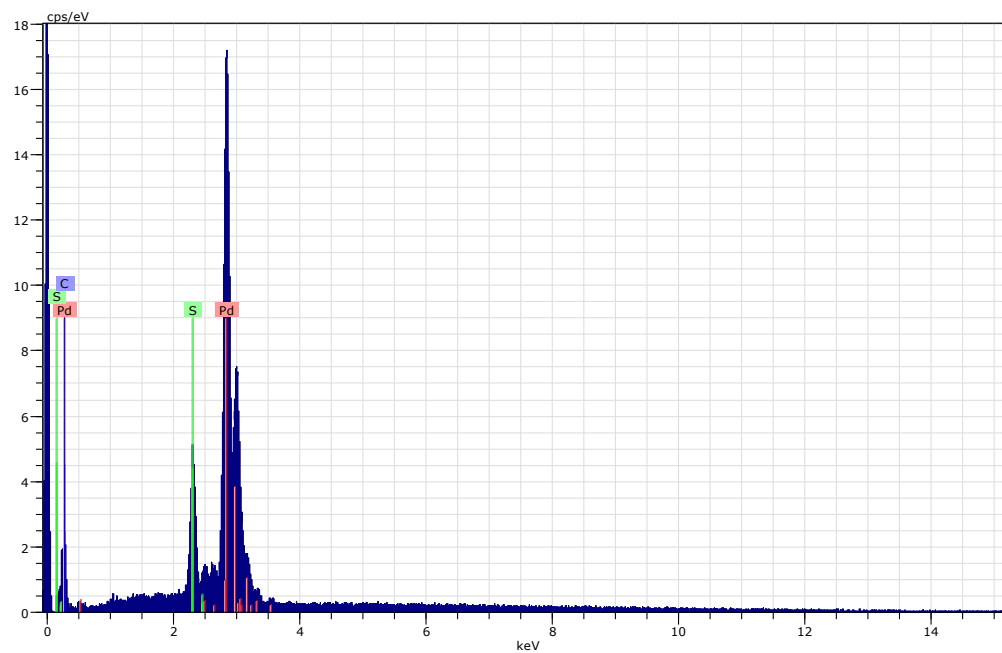
## SEM-EDX Data of NPs



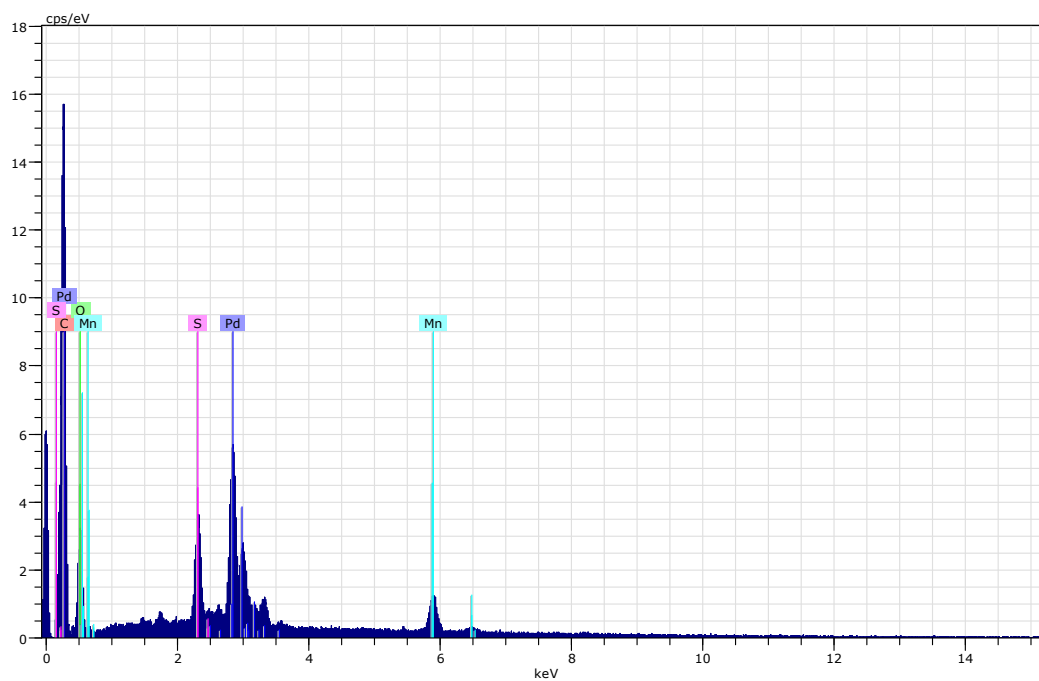
**Figure S12.** SEM-EDX of PdP<sub>2</sub> Nano-particles.



**Figure S13.** SEM-EDX of GO-PdP<sub>2</sub> Nano-particles.



**Figure S14.** SEM-EDX of Pd<sub>4</sub>S Nano-particles.



**Figure S15.** SEM-EDX of GO-Pd<sub>4</sub>S Nano-particles.