Electronic Supplementary Information:

Architecturally designed Pt-MoS_2 and Pt-graphene composites for electrocatalytic methanol oxidation†

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By integrating the hydrogen adsorption/desorption curve in Fig. 8 (in manuscript) the Electro Chemical active Surface Areas (ECSA) were calculated. Following equation was used for the calculations. [S1-S3]

ECSA (cm^2Pt/gPt) = qPt / Γ*L

Where, qPt is the charge density,
Γ = 210 μC/cm^2 Pt the charge required to reduce a monolayer of protons on Pt, and
L = gPt/cm^2 the Pt content or loading in the electrode.

ECSA values were found to be 13.4, 13, 10.8 and 10.4 m^2/g, for Pt-MoS_2, Pt-GNS, Pt NPs thin film and Pt/C respectively. The lower values of ECSA can be attributed to resistance of FTO.

By using the ECSA values and the actual mass of Pt in the electrodes intensities for methanol oxidation (mA/cm2 and mA/mg) were calculated and are tabulated in following table.

Sr.No.	Sample	Intensities of Methanol oxidation peak calculated y considering **geometrical area of the electrode** (mA/cm^2) (Manuscript)	Intensities calculated by considering **ECSA** of electrodes. mA/cm^2	Intensities calculated by considering the **Pt mass** in active electrodes (mA/mg)
1	Pt-MoS_2	3.07	13.23	177.4
2	Pt-GNS	2.61	10.53	137.5
3	Pt-NPs thin film	0.977	5.13	55.51
4	PT/C	0.772	3.18	33.16

Table-S1 Comparative study between the intensities calculated from geometrical area of the electrodes, an ECSA of electrodes and by considering the Pt mass in active electrodes.

Sr. no.	Sample/Catalysts	mA/mg	Electrolyte	Reference
1	Pt/C E-TEK	95 ± 8	0.1 M $HClO_4$	Ref. S4
2	octahedral Pt_3Ni	440	0.1 M $HClO_4$	Ref. S5
3	Au/Pt_3Ni nanowires	479	0.1 M $HClO_4$	Ref. S6
4	GN-Pt_3Ni-IL	870	0.1 M $HClO_4$	Ref. S7
5	GN-Pt	39	0.5 M H_2SO_4	Ref. S8
6	Pt/Vulcan carbon	40	0.5 M H_2SO_4	Ref. S9
7	Pt/C E-TEK	31	0.5 M H_2SO_4	Ref. S8
8	Pt nanoflowers/RGO/CCE	133.43	0.5 M H_2SO_4	Ref. S10
9	Pt-MoS_2	177.4	0.5 M H_2SO_4	This work
10	Pt-GNS	137.5	0.5 M H_2SO_4	This work
11	Pt-NPs thin film	55.51	0.5 M H_2SO_4	This work
12	PT/C	33.16	0.5 M H_2SO_4	This work

Table-S2 Literature study of intensities calculated from an ECSA of electrodes and by considering the Pt mass in active electrodes.

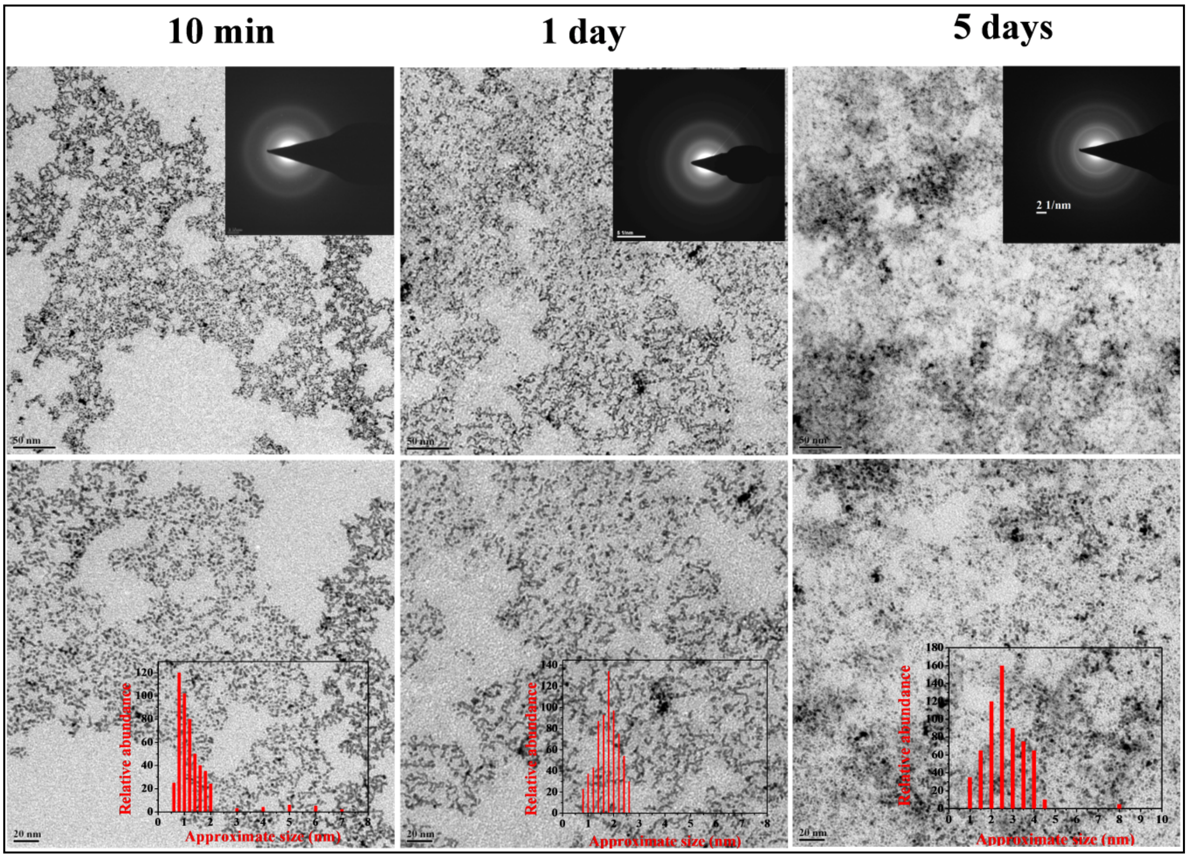

Fig. S1: Kinetic study of growth of Pt NPs with respect to the reaction time.

Inset shows respective electron diffractions and size distribution histograms.

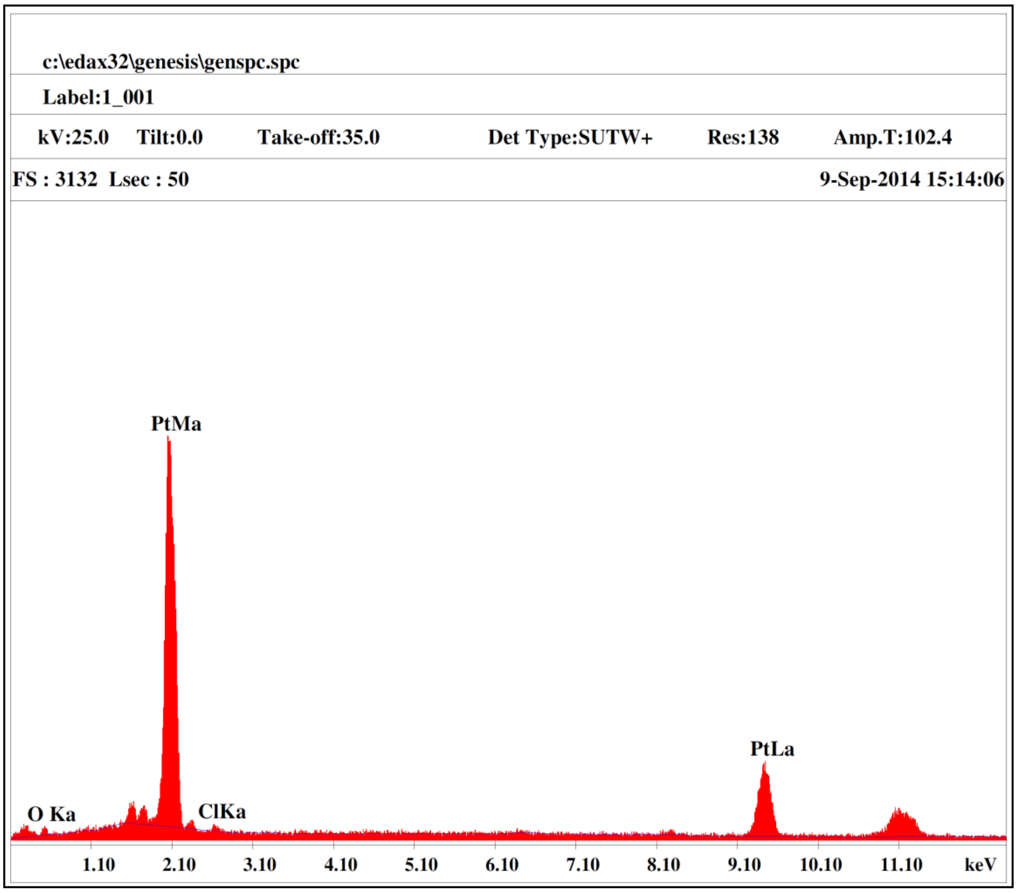

Fig. S2 EDS for Pt NPs thin film over silicon wafer.

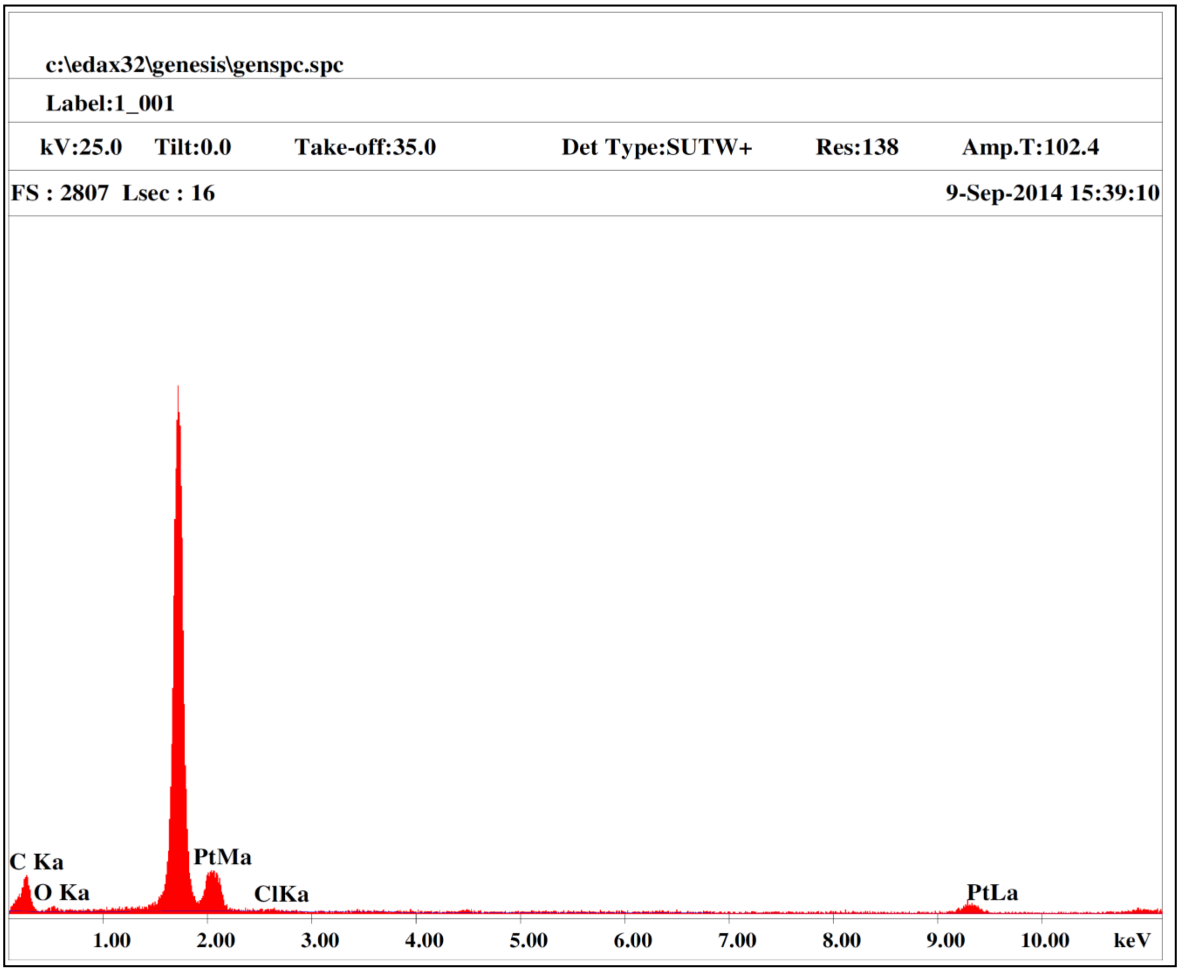

Fig. S3 EDS for Pt-GNS composite over silicon wafer.

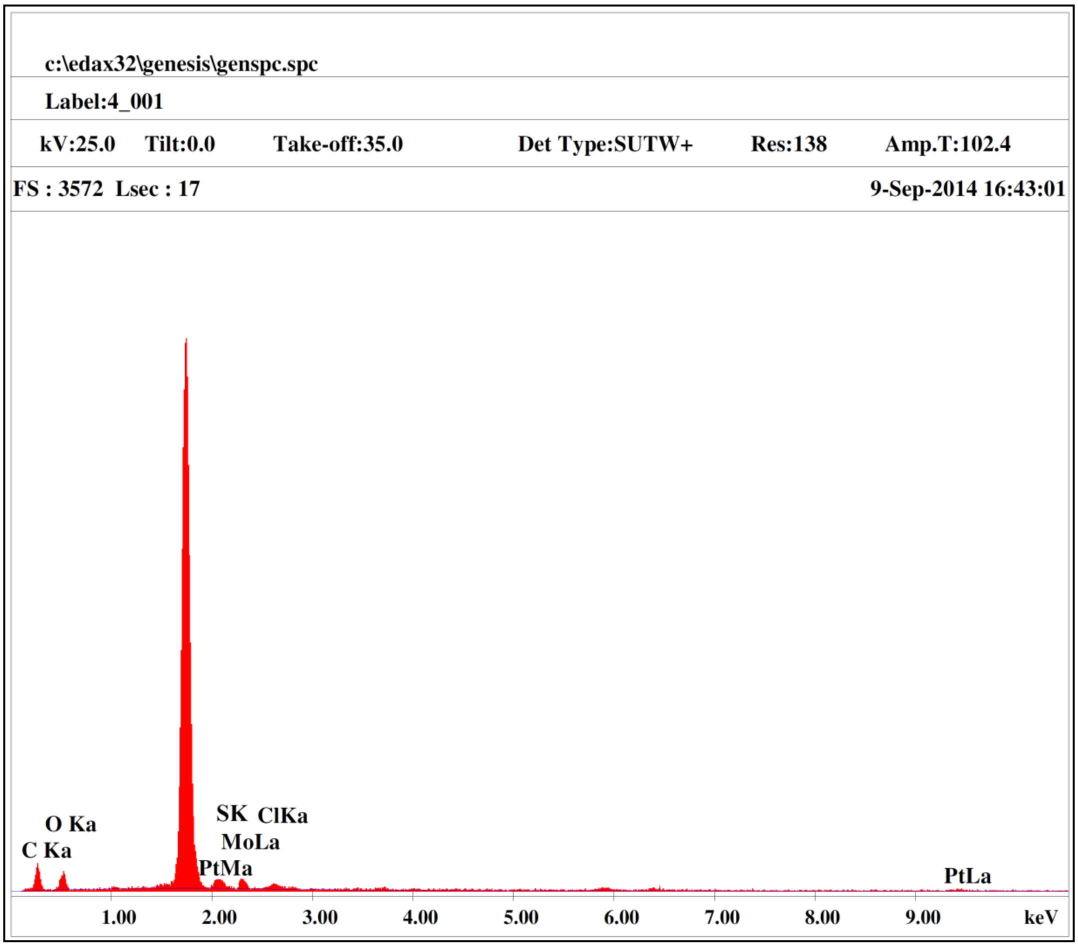

Fig. S4 EDS for Pt-MoS_2 composite over silicon wafer.

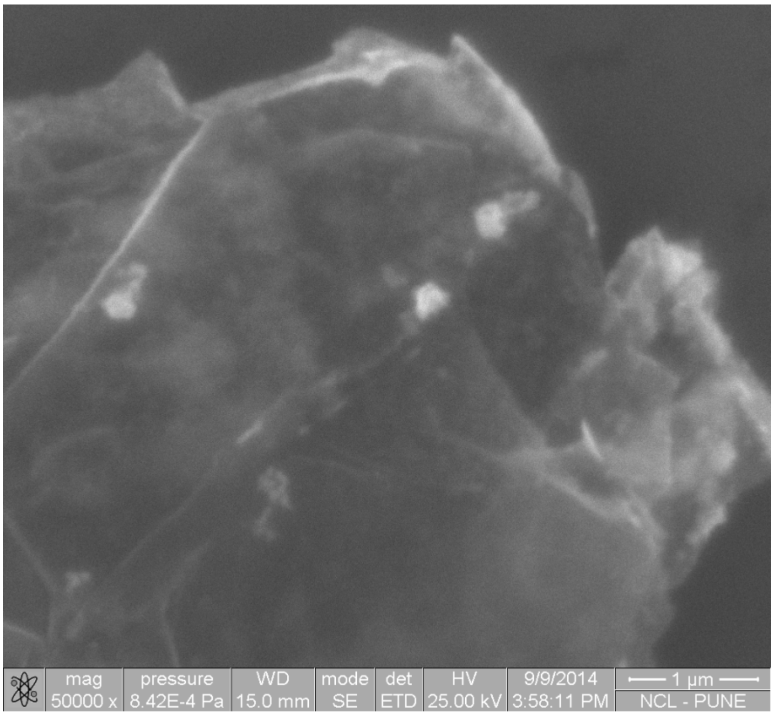

Fig. S5 SEM image for Pt-GNS composite before electrochemical measurements.

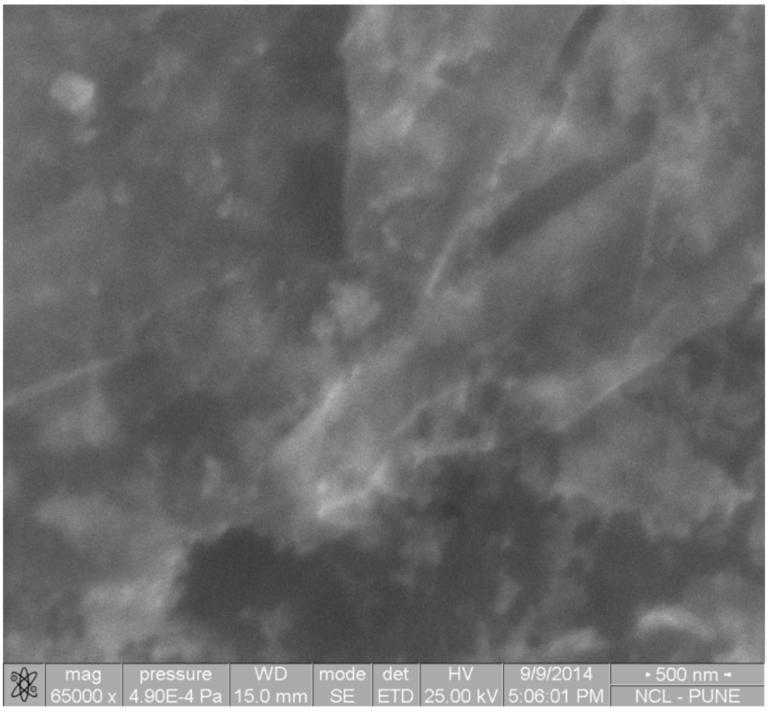

Fig. S6 SEM image of Pt-MoS_2 before the electrochemical experiment.

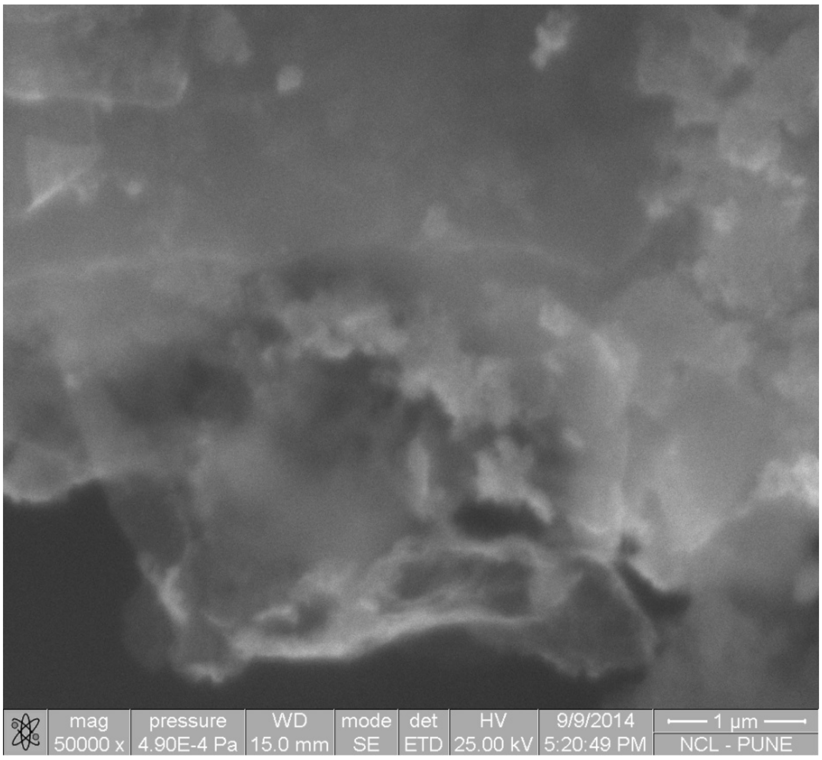

Fig. S7 SEM image of Pt-GNS after the electrocatalytic experiment in 0.5 M $HClO_4$ + 2M methanol at a scan rate of 500 mV/s after the chronoamperometry study for 3600s.

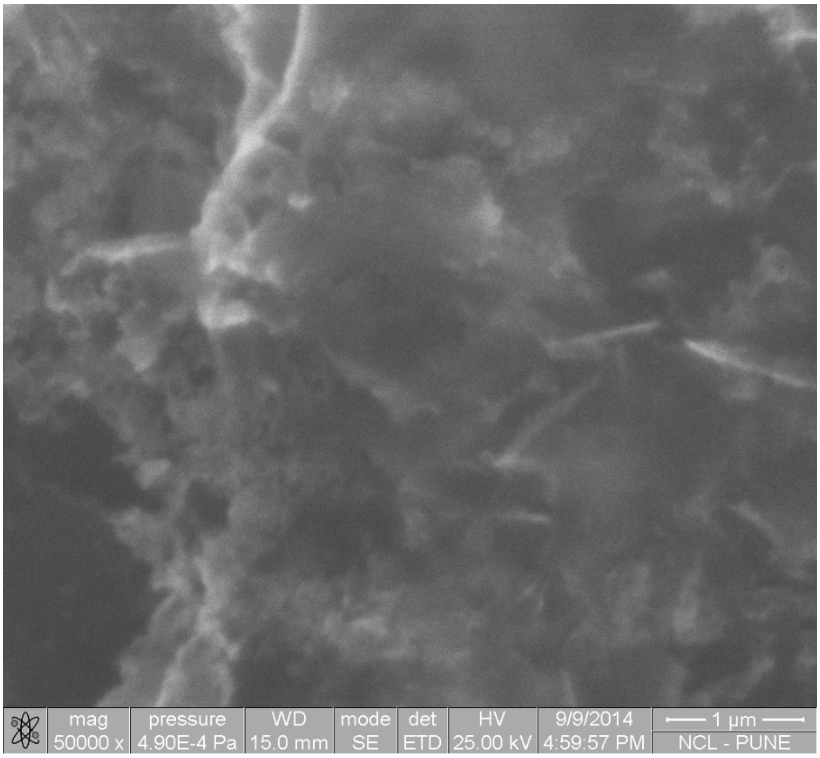

Fig. S8 SEM image of Pt-MoS_2 after the electrocatalytic experiment in 0.5 M $HClO_4$ + 2M methanol at a scan rate of 500 mV/s after the chronoamperometry study for 3600s.

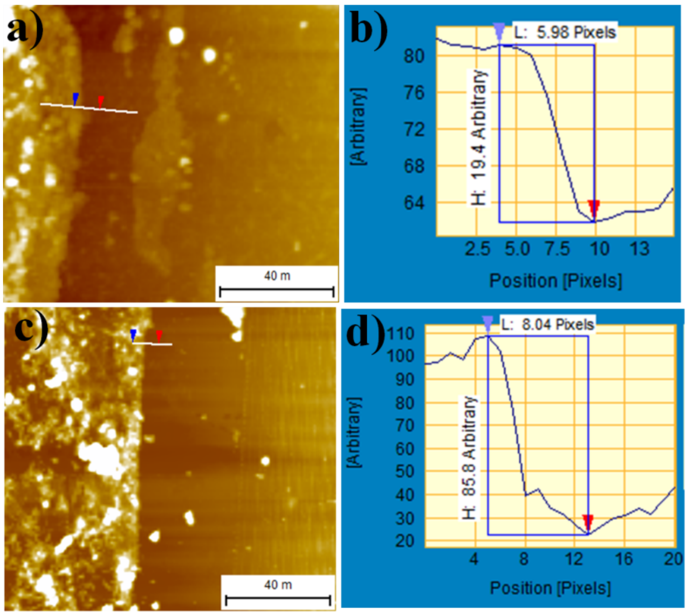

Fig. S9 (a&c) Atomic force microscopy (AFM) images for the 20 dips coated graphene nanosheets (GNS) and 20-20 alternate Pt-GNS coated LbL composite, (b&d) height profile for a and b.

To see actual thickness of the thin film and effect of LbL deposition on interlayer spacing of GNS, an AFM study was employed. The samples were coated over the cleaned Si-wafer by using dip coating method described in manuscript. For an example 20 dips of GNS were coated over one Si wafer and 20-20 alternated dips of GNS and Pt over another Si wafer. The height profile in AFM gives the thickness of the film. The height for the 20 dips of GNS is 19.4 nm which gives the average thickness of 0.9 nm for each GNS layer. On the other hand the thickness for Pt-GNS LbL composite of 20-20 alternate dips is 85.8 nm which means the average separation between two graphene layers is 3 nm. Thus, Interlayer spacing has increased.

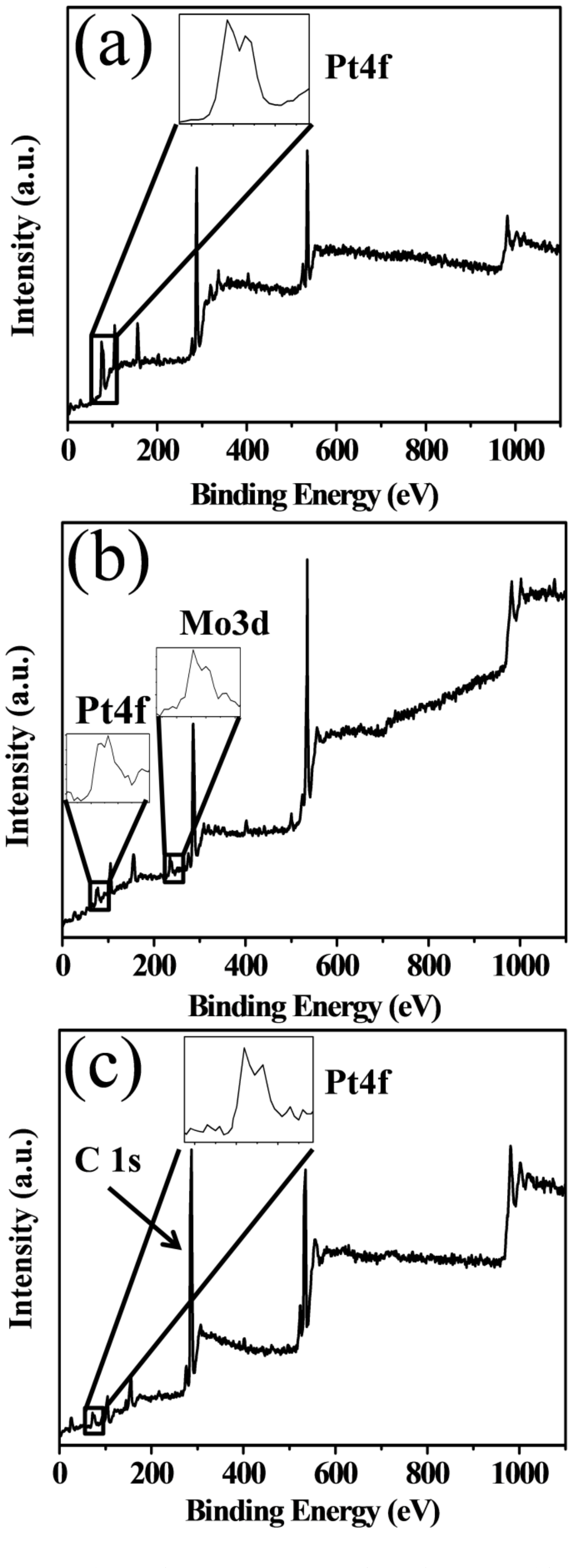

Fig. S10 General XPS spectra for a) bare Pt NPs catalyst, inset Pt4f b) Pt-MoS_2 catalyst inset Pt 4f, Mo 3d and c) Pt-GNS catalyst.

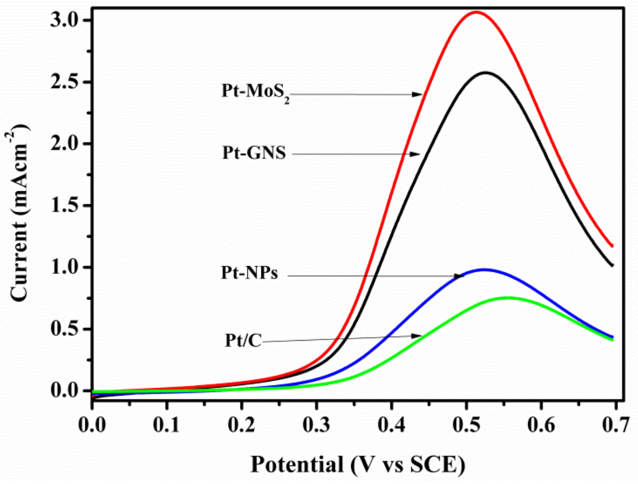

Fig. S11 Linear sweep voltamogram (LSV) for Pt-MoS2, Pt-GNS, Pt NPs thin film and commercial Pt/C catalyst for the electrocatalytic oxidation of 0.1 M methanol in 0.5 M H_2SO_4 solution vs SCE.

From Figure S10 it is seen that the Pt-MoS_2 electrode has lower onset potential (0.17V) as compare to rest of the catalysts namely Pt-GNS (0.25V), Pt NPs thin film (0.31V) and Commercial Pt/C catalyst (0.35V).

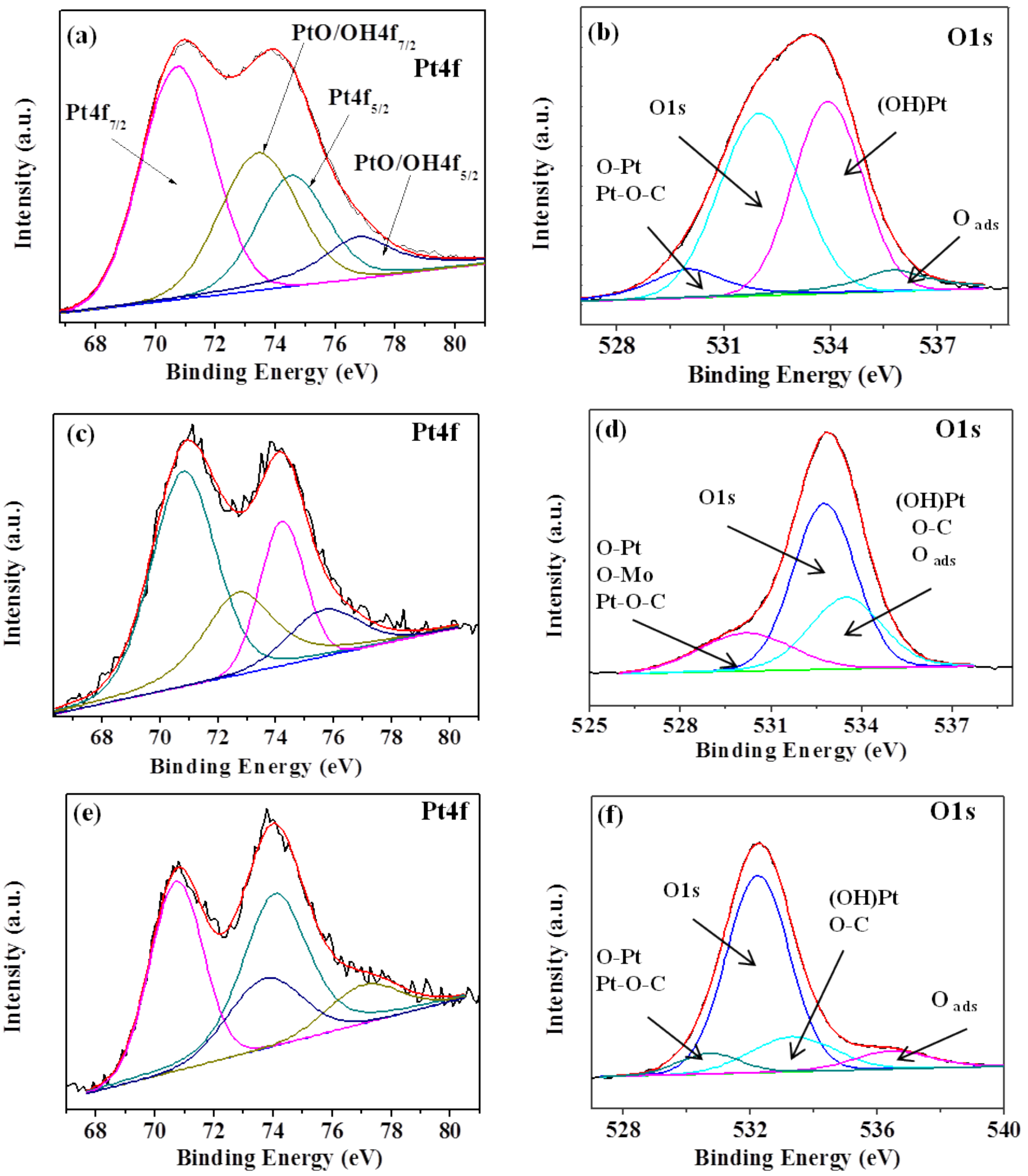

Fig. S12: Pt4f and O1s respectively in (a,b) PtNPs, (c,d) Pt-MoS_2 (e,f) Pt-GNS, after the electrochemical reaction.

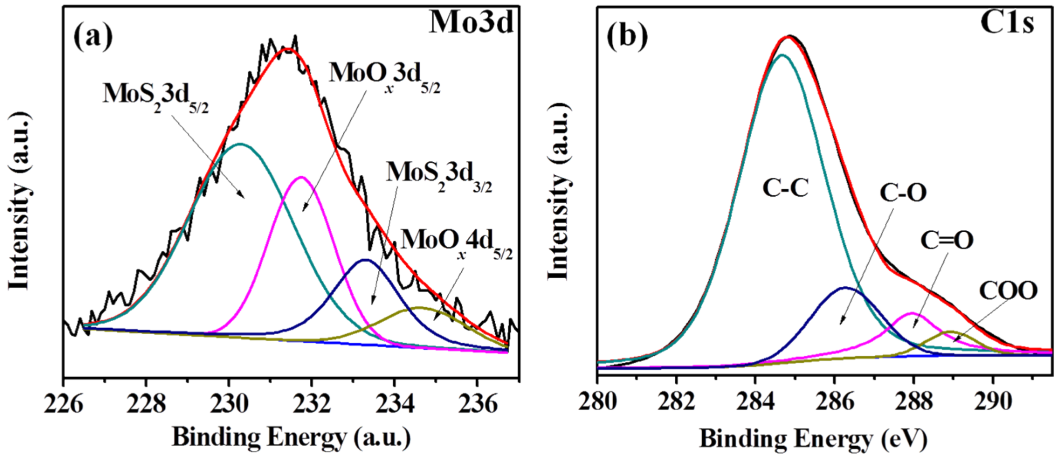

Fig. S13 a) Mo3d and b) C1s in MoS2 and GNS respectively after the electrocatalytic oxidation of methanol and chronoamperometry study.

The quantitative estimation of elemental composition and different species formed at surfaces is rather very important factor in catalyst performance therefore XPS spectra were deconvoluted and evaluated for the quantity of different species present at the surface. Following table shows the detailed analysis of all the catalyst electrodes before and after the electrocatalytic reactions.

Sample	**Main peak**	**Deconvoluted peak(s)**	**Binding energy position (in eV)**	**Atomic %**	**FWHM**	**Species/ moiety**
Pt NPs (before ECE)	Pt4f	$4f_{7/2}$	70.70	93.6	2.36	Pt^0
		$4f_{5/2}$	74.01		2.31	
		$4f_{7/2}$	72.73	6.4	1.82	Pt-O*x*
		$4f_{5/2}$	75.99		1.75	
Pt NPs (After ECE)	Pt4f	$4f_{7/2}$	70.87	65.5	2.36	Pt^0
		$4f_{5/2}$	75.09		3.03	
		$4f_{7/2}$	73.55	34.5	2.30	Pt-O*x*
		$4f_{5/2}$	77.32		3.08	
C in GNS	C1s	C1s	284.46	75.5	2.59	C-C
		C1s	287.75	9.1	1.68	C-O
		C1s	288.73	3.1	1.49	C=O
		C1s	286.07	12.4	2.09	COO
C in Pt-GNS (Before ECE)	C1s	C1s	284.6	86	1.90	C-C
		C1s	285.62	7.5	1.89	C-O
		C1s	286.89	4.4	1.89	C=O
		C1s	288.28	1.5	1.62	COO
C in Pt-GNS (after ECE)	C1s	C1s	284.61	83.8	2.83	C-C
		C1s	287.35	12.7	2.55	C=O
		C1s	288.96	3.3	1.60	COO
Pt in Pt-GNS (Before ECE)	Pt4f	$4f_{7/2}$	70.70	90.6	2.35	Pt^0
		$4f_{5/2}$	74.15		2.31	
		$4f_{7/2}$	72.73	9.4	1.82	Pt-O*x*
		$4f_{5/2}$	75.99		1.75	
Pt in Pt-GNS (After ECE)	Pt4f	$4f_{7/2}$	70.8	71.9	2.62	Pt^0
		$4f_{5/2}$	74.20		1.83	
		$4f_{7/2}$	72.71	28.1	2.88	Pt-O*x*
		$4f_{5/2}$	75.65		2.88	
Mo in MoS_2(Before ECE)	Mo3d	$3d_{5/2}$	230.14	99.9	1.51	Mo-S-Mo
		$3d_{3/2}$	233.29		1.78	
Mo in MoS_2(After ECE)	Mo3d	$3d_{5/2}$	230.29	66.2	2.98	Mo-S-Mo
		$3d_{3/2}$	231.74		1.86	
		$3d_{5/2}$	234.69	33.78	2.48	Mo-O*x*
		$3d_{3/2}$	233.31		1.90	
Pt in Pt-MoS_2 (Before ECE)	Pt 4f	$4f_{7/2}$	70.47	86.78	2.94	Pt^0
		$4f_{5/2}$	73.73		2.45	
		$4f_{7/2}$	73.42	13.21	1.59	Pt-O*x*
		$4f_{5/2}$	76.73		2.75	
Pt in Pt-MoS_2 (After ECE)	Pt 4f	$4f_{7/2}$	70.72	73.2	2.59	Pt^0
		$4f_{5/2}$	74.10		2.12	
		$4f_{7/2}$	73.72	26.8	2.88	Pt-O*x*
		$4f_{5/2}$	77.15		2.97	

Table-S3. Quantitative measurement of elemental and chemical composition for catalysts used before and after Electro-Chemical Experiment (ECE) by using XPS.

References:

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