Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information for

One-pot synthesis of highly efficient graphene based three-dimensional hybrid as catalyst supporting material for electro-oxidation of liquid fuels

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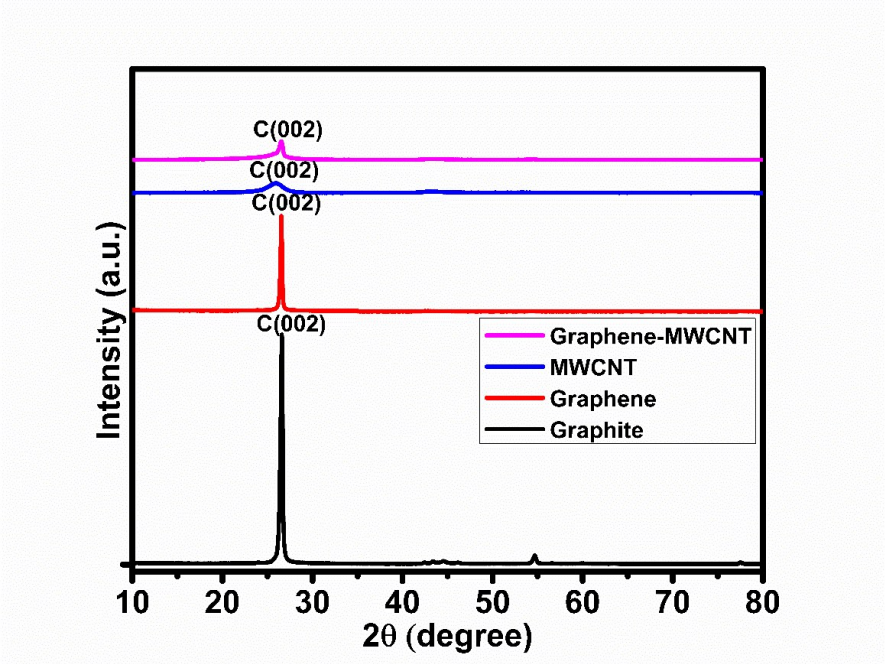

Fig. S1 XRD patterns of Graphite, Graphene, MWCNT, and Graphene-MWCNT.

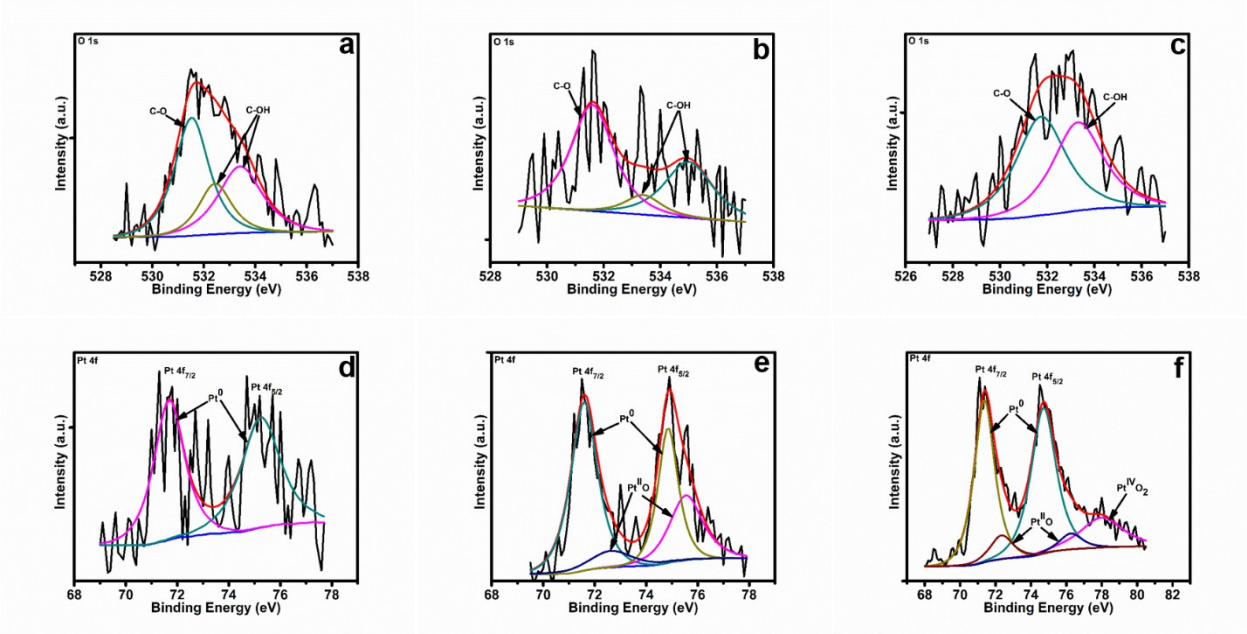

Fig. S2 XPS spectra of O1s (a, b, c), and Pt4f (d, e, f) on Graphene/Pt, MWCNT/Pt, and Graphene-MWCNT/Pt.

<u>Post XPS analysis of Graphene-MWCNT/Pt modified catalyst:</u>

Figure S3 (a, b, c and d) shown the deconvolution of the C1s, O1s, Pt4f and S2p peaks of Pt decorated Graphene-MWCNT hybrid after recorded the cyclic voltammetry in 0.5 M H_2SO_4 + 1 M CH_3OH at a scan rate of 50 mV s^{-1} for 5 cycles. The main peak at 284.8 eV corresponding to the graphitic structure. The peaks observed at 285.2 eV and 286.2 eV, corresponding to epoxide (C-O-C) groups. This is confirmed by the peak, which located at 531.2 eV in O1s spectrum. Another two peaks located approximately at 531.9 eV and 533.0 eV can be assigned to C-O-C and C-O-H groups. The deconvoluted Pt4f spectra represents two main peaks at 70.72 eV and 74.12 eV, corresponding to Pt $4f_{7/2}$ and $4f_{5/2,}$ respectively. As shown in the spectrum, two different Pt entities could be identified as metallic

Pt(0) with binding energies (BE) of 70.69 and 74.07 eV, PtO with BE of 71.50 and 75.01 eV, respectively. However, the PtO_2 peak is not observed may be reduced by the reverse scan in cyclic voltammogram. Interestingly, the S2p spectra centered three peaks with BE of 167.9 eV, 168.6 eV and 169.53 eV, assigned to be sulfite, sulfate and metallic sulfates, respectively. From this, some of the Pt present on catalyst is reacted with sulfuric acid and causes the decrease in catalytic activity for fuels electro-oxidation.

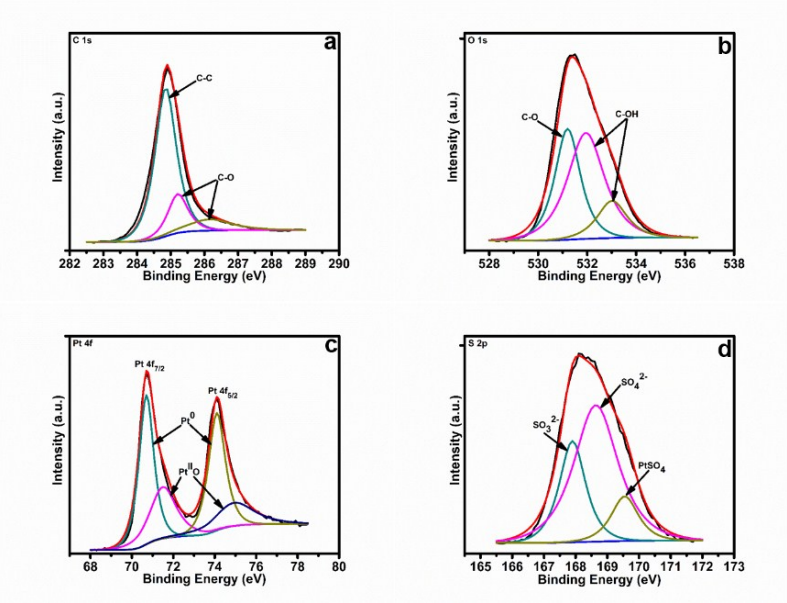

Fig. S3 XPS spectrum of (a) C1s, (b) O1s, (c) Pt4f, and (d) S2p of Graphene-MWCNT/Pt after recording cyclic voltammogram.

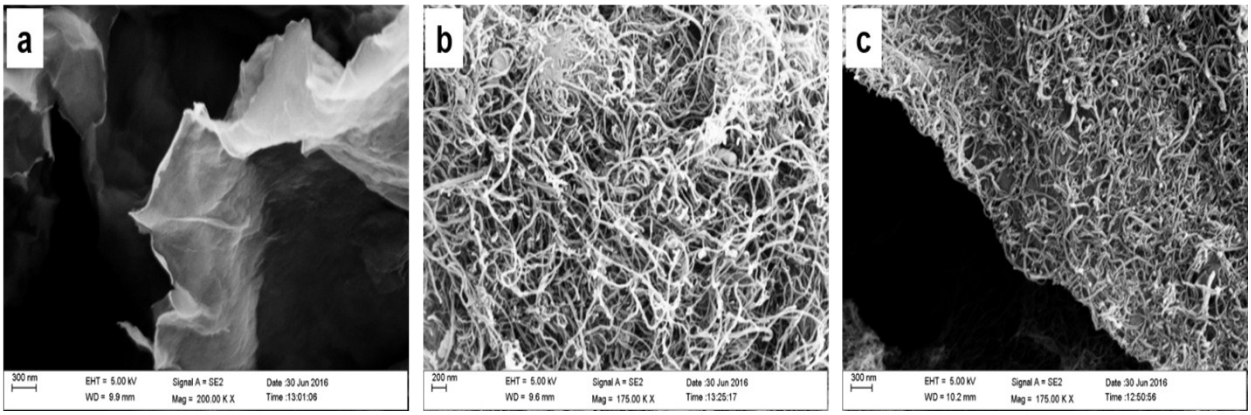

Fig. S4 FESEM images of (a) Graphene, (b) MWCNT, and (c) Graphene-MWCNT hybrid.

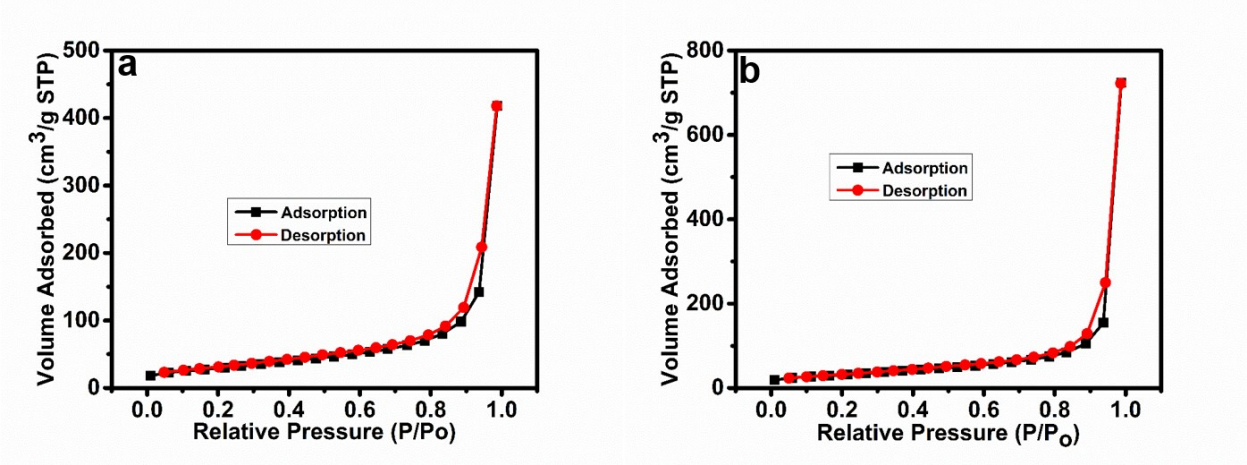

Fig. S5 Nitrogen adsorption - desorption isotherm curves of the (a) Graphene-MWCNT, and (b) Graphene-MWCNT/Pt material.

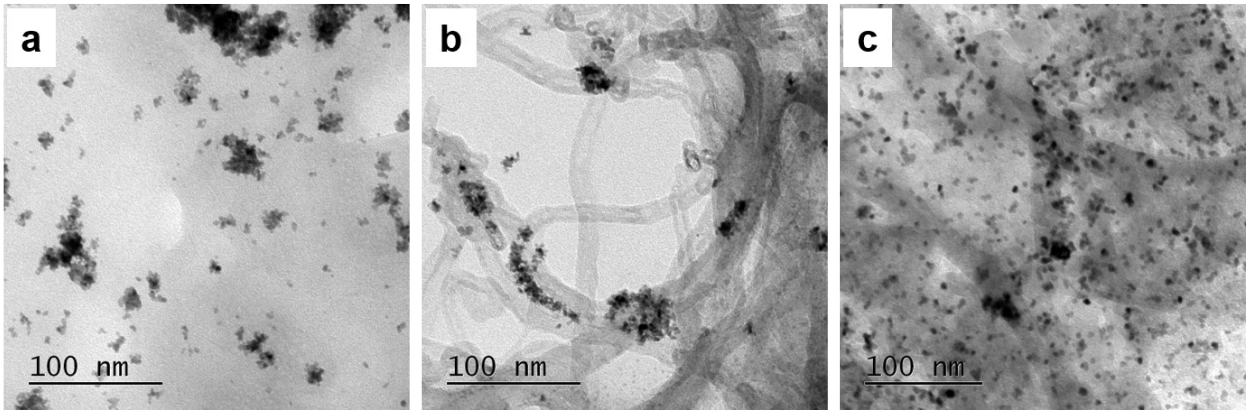

Fig. S6 HRTEM images of (a) Graphene/Pt, (b) MWCNT/Pt, and (c) Graphene-MWCNT/Pt.

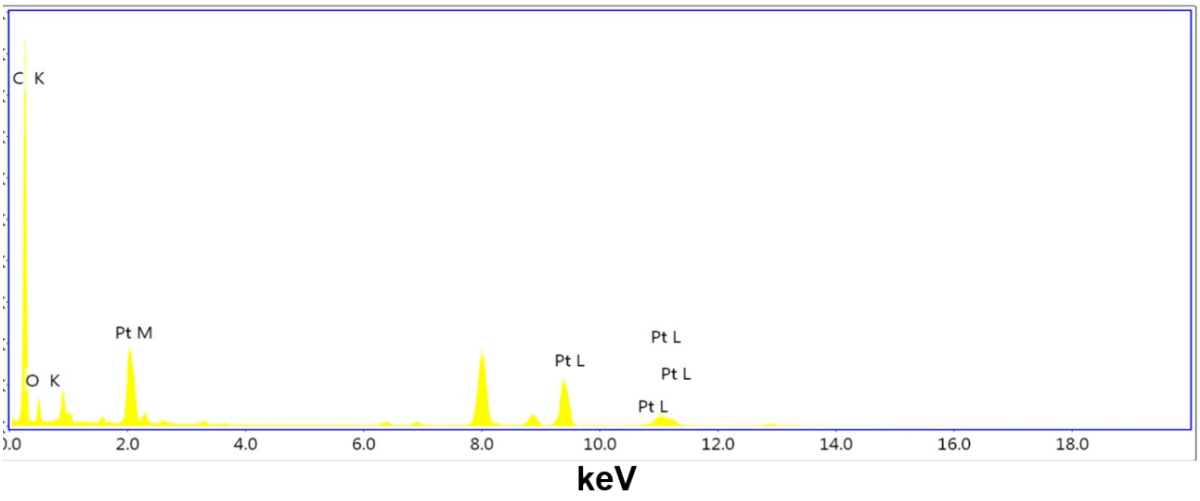

Fig. S7 EDX analysis of the Graphene-MWCNT/Pt catalyst.

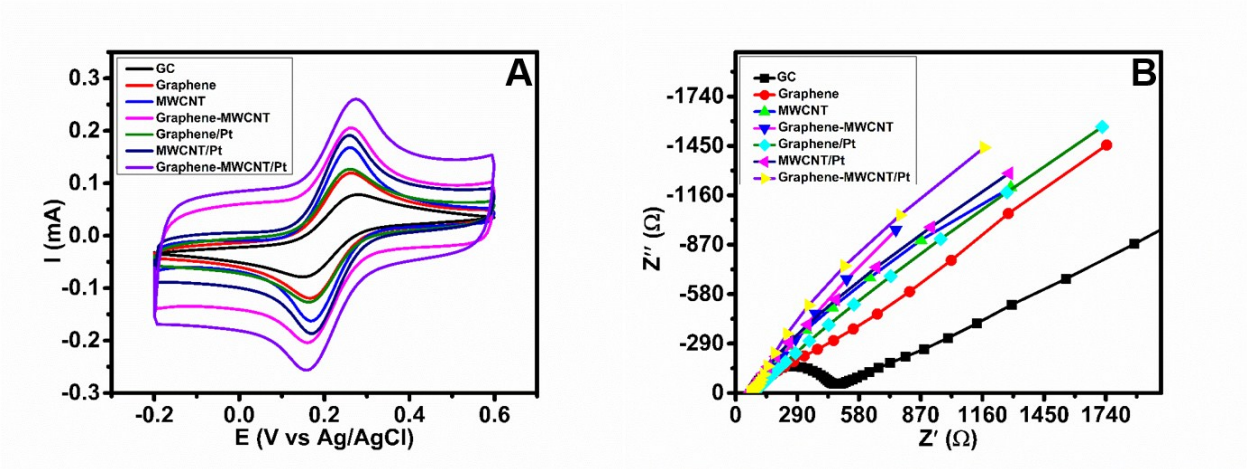

Fig. S8 (A) CVs and (B) EIS of 5.0 mM $[Fe(CN)_6]^{3-/4-}$ (1:1) with 0.1 M KCl on bare GC, Graphene, MWCNT, Graphene-MWCNT, Graphene/Pt, MWCNT/Pt and Graphene-MWCNT/Pt electrodes.

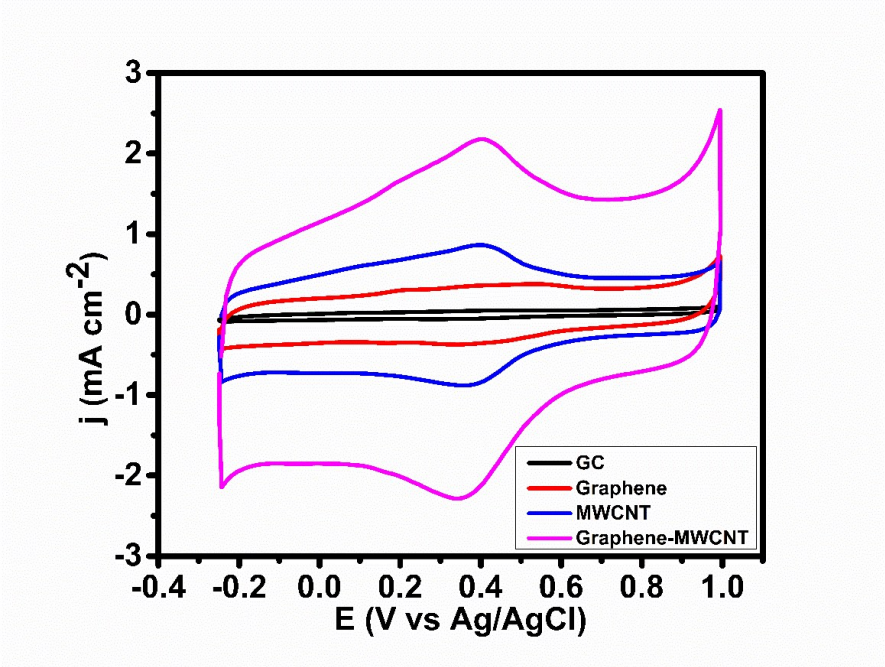

Fig. S9 CVs of the GC, Graphene, MWCNT and Graphene-MWCNT electrodes in 0.5 M H_2SO_4 solution at scan rate of 50 mV s^{-1}.

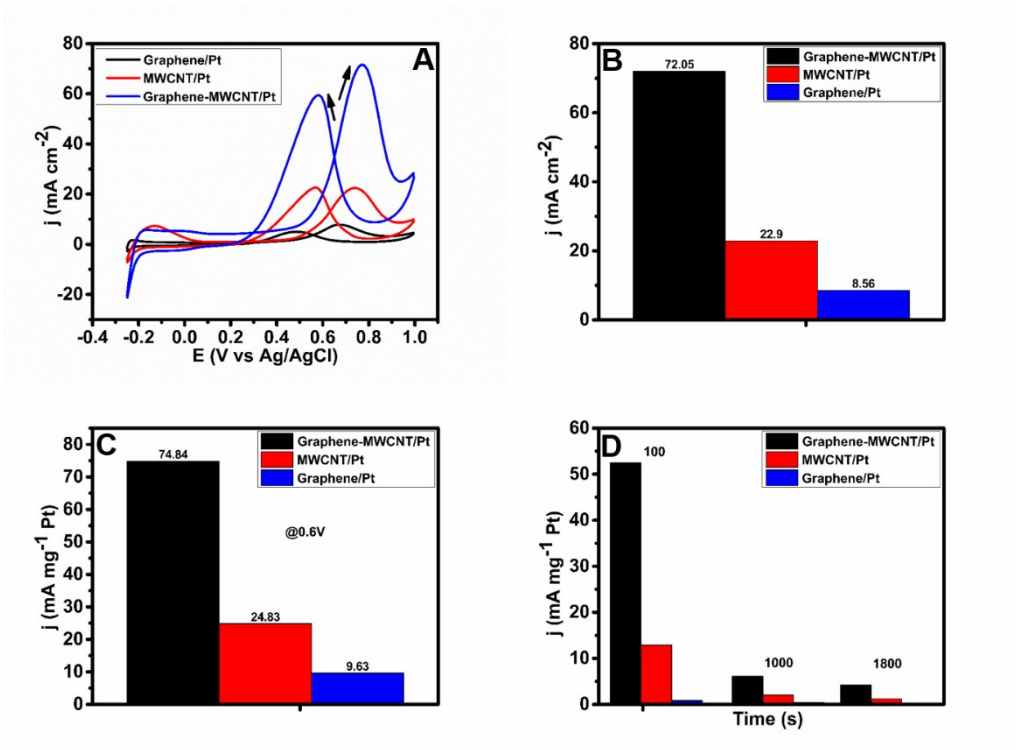

Fig. S10 (A) CVs of the Graphene/Pt, MWCNT/Pt and Graphene-MWCNT/Pt electrodes in mixture of 0.5 M H_2SO_4 + 1 M CH_3OH solution at a scan rate of 50 mV s^{-1}; (B) bar plots of forward peak current densities for these three catalysts; (C) bar plots of current densities for these three catalysts at 0.6 V (vs Ag/AgCl) in LSV; (D) bar plots of current densities for these three catalysts at 100 s, 1000 s and 1800 s time intervals in Chronoamperometry.

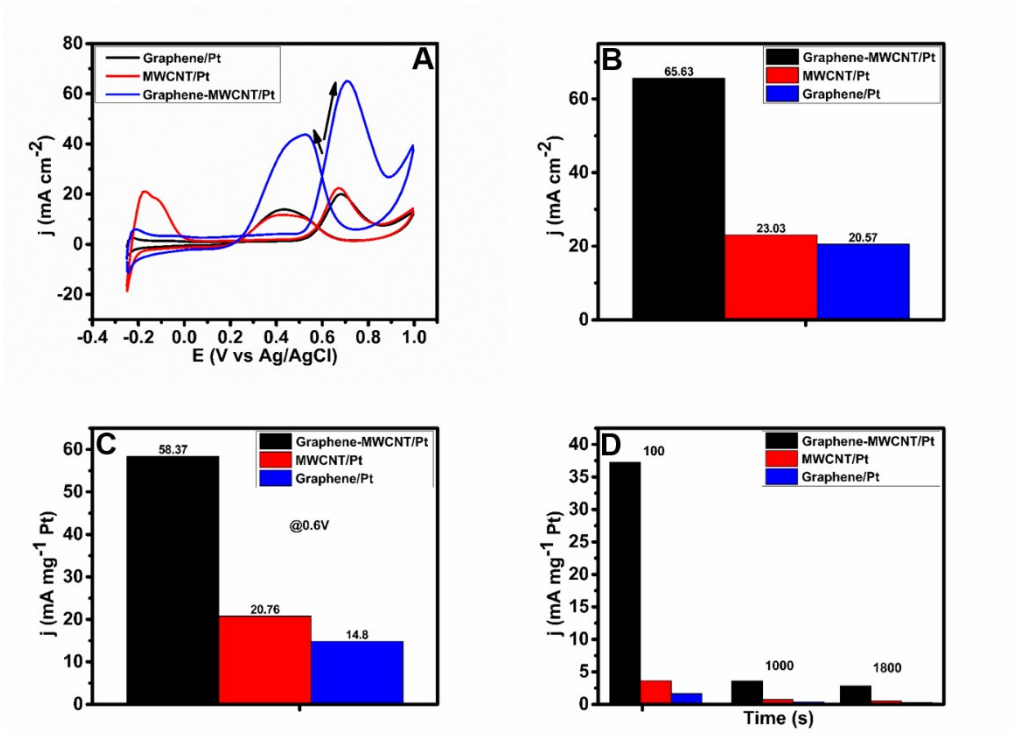

Fig. S11 (A) CVs of the Graphene/Pt, MWCNT/Pt and Graphene-MWCNT/Pt electrodes in mixture of 0.5 M H_2SO_4 + 1 M $HOCH_2CH_2OH$ solution at a scan rate of 50 mV s^{-1}; (B) bar plots of forward peak current densities for these three catalysts; (C) bar plots of current densities for these three catalysts at 0.6 V (vs Ag/AgCl) in LSV; (D) bar plots of current densities for these three catalysts at 100 s, 1000 s and 1800 s time intervals in Chronoamperometry.

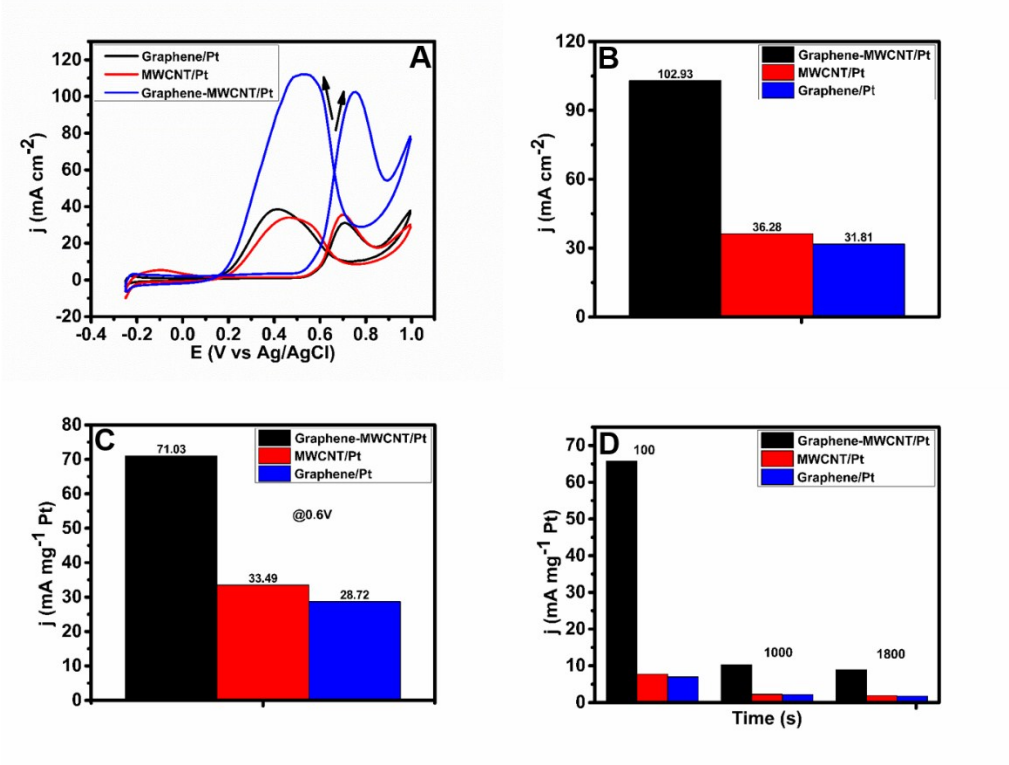

Fig. S12 (A) CVs of the Graphene/Pt, MWCNT/Pt and Graphene-MWCNT/Pt electrodes in mixture of 0.5 M H_2SO_4 + 1 M HCHO solution at a scan rate of 50 mV s^{-1}; (B) bar plots of forward peak current densities for these three catalysts; (C) bar plots of current densities for these three catalysts at 0.6 V (vs Ag/AgCl) in LSV; (D) bar plots of current densities for these three catalysts at 100 s, 1000 s and 1800 s time intervals in Chronoamperometry.

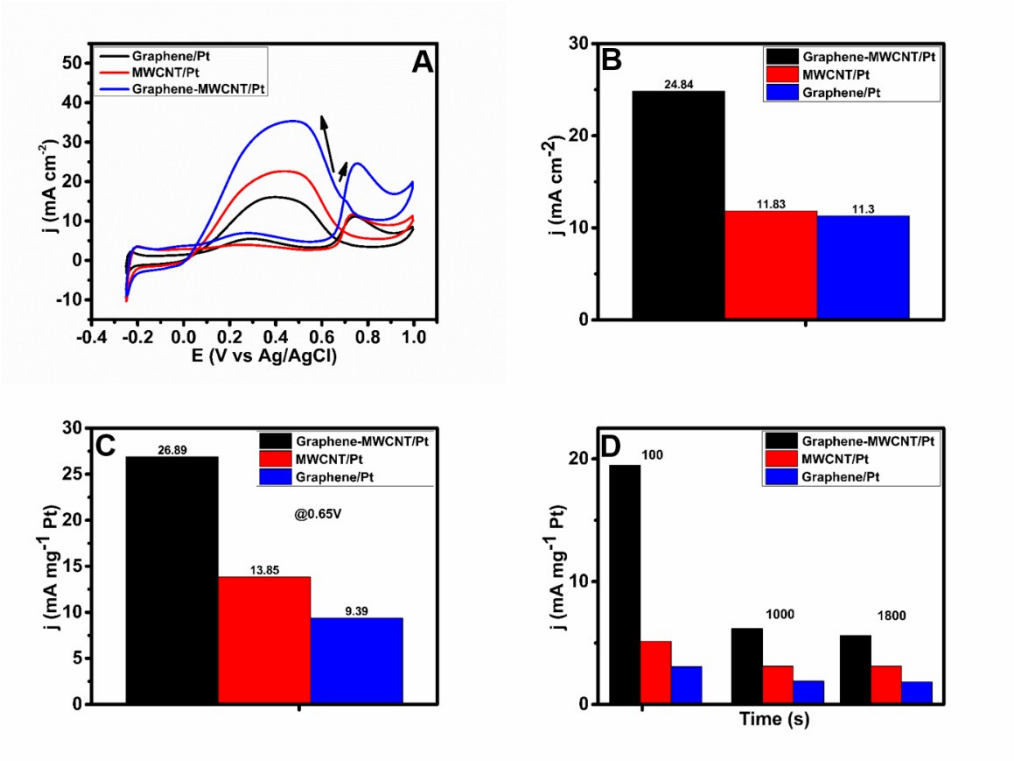

Fig. S13 (A) CVs of the Graphene/Pt, MWCNT/Pt and Graphene-MWCNT/Pt electrodes in mixture of 0.5 M H_2SO_4 + 1 M HCOOH solution at a scan rate of 50 mV s^{-1}; (B) bar plots of forward peak current densities for these three catalysts; (C) bar plots of current densities for these three catalysts at 0.65 V (vs Ag/AgCl) in LSV; (D) bar plots of current densities for these three catalysts at 100 s, 1000 s and 1800 s time intervals in Chronoamperometry.

TABLES

Table S1. Raman spectroscopy parameters of Graphite, Graphene, MWCNT, Graphene-MWCNT, Graphene/Pt, MWCNT/Pt and Graphene-MWCNT/Pt.

	D (cm^{-1})	G (cm^{-1})	2D (cm^{-1})	D + G (cm^{-1})	I_D/I_G	I_{2D}/I_{D+G}
Graphite	1350	1573	2701	-	0.17	-
Graphene	1351	1585	2712	2946	0.63	2.19
MWCNT	1353	1584	2690	2939	1.12	1.58
Graphene-MWCNT	1353	1588	2703	2949	1.05	2.91
Graphene/Pt	1358	1570	2701	2931	0.85	2.81
MWCNT/Pt	1353	1584	2701	2939	1.17	3.57
Graphene-MWCNT/Pt	1353	1599	2701	2946	1.15	3.81

Table S2. Pore structure parameters of Graphene-MWCNT and Graphene-MWCNT/Pt.

Sample	BET surface area ($m^2\,g^{-1}$)	Total pore volume ($cm^3\,g^{-1}$)
Graphene-MWCNT	106	0.64
Graphene-MWCNT/Pt	113	1.12

Table S3. Catalytic performance of the Graphene-MWCNT/Pt catalyst compared with literature.

S.No	Electrode	Scan rate (**mV s^{-1}**)	Electrolyte (**mol.dm^{-3}**) H_2SO_4: CH_3OH/ $(CH_2OH)_2$/HCHO/HCOOH	CH_3OH (**mA mg^{-1}**)	$(CH_2\text{-}OH)_2$ (**mA mg^{-1}**)	HCHO (**mA mg^{-1}**)	HCOOH (**mA mg^{-1}**)	Ref.
1	Ni_{50}/Pt/CNFs	50	0.5:1.0	10.9 mA cm^{-2}	-	-	-	1
2	Pt nanoflowers/ RGO/CC	50	1.0/0.5:0.5	133.43	-	-	54.14	2
3	PtPdPt/GN	100	1.0:0.5	25.63	-	-	-	3
4	graphene/Au@ $Pt_{0.64}Ag_{0.36}$ NRs	50	2.0:0.5	124.00	-	-	-	4
5	Pt/NG-800	20	1.0:1.0	135	-	-	-	5
6	Pt Ru/DWNTs	50	0.5:0.5	0.037 mA/ cm^2	-	-	-	6
7	PtRuIr/C-Beef	50	0.5:0.5	5.1 mA cm^{-2}	-	-	-	7
8	$Pt/G_3\text{-}(CN)_7$	20	1.0:2.0	15.7 mA cm^{-2}	-	-	-	8
9	$Pt_5Ru_4Sn_1/C$	50	0.5:2.0	-	87.5 mA cm^{-2}	-	-	9
10	Pt-Ru/CNT	50	0.5:0.5	-	12.62 mA.cm^{-2}	-	-	10

11	Pt Pd/PPy CNT	50	0.5:0.5	-	-	38.5 $mA.cm^{-2}$	32.6 $mA.cm^{-2}$	11
12	CC/Pt	50	0.1:0.75	-	-	65.57 mA/cm^2	49.43 mA/cm^2	12
This work	Graphene-MWCNT/Pt	50	0.5 : 1.0	168.41	153.13	241.14	58.29	

Notes and references

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