Supporting information

Carbon-thin-layer Protected WP with no Passivation Supported on Acid-treated Expanded Graphite as Efficient Pt Co-catalysts for Methanol Oxidation and Oxygen Reduction Reactions

Chunyue Zhang[a], Ying Dai[a,b], Hun Chen[a], Yuanyuan Ma[a], Baojian Jing[a], Zhuang Cai[a]*, Yaqiang Duan[a], Bo Tang[a], and Jinlong Zou[a,]*

[a]Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education of the People's Republic of China, School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China.

[b]School of Civil Engineering, Heilongjiang Institute of Technology, Harbin 150050, China.

Corresponding author (s):

*Zhuang Cai, Jinlong Zou.

[a]Xuefu Road 74#, Nangang District, Harbin, 150080, China.

Tel.: +86-451-86608549; Fax: +86-451-86608549.

E-mail: hlju_chem218c@163.com (Z. Cai); zoujinlong@aliyun.com (J. L. Zou).

Synthesis of AEG

4.0 g of 20-mesh natural flake graphite was mixed with 2.0 g of potassium permanganate ($KMnO_4$, A.R.) to obtain the suspension, which was then poured into a beaker containing 16 g of perchloric acid ($HClO_4$) in a water bath at 35 ^oC under continuous stirring for 40 min. The obtained samples were thoroughly washed with deionized water several times and then dried at 80 °C for 12 h to obtain the expandable graphite, which was then treated under microwave irradiation (760 W) for 20 s to obtain the EG. The EG was refluxed in boiling HNO_3 solution (65 %) for 90 min to obtain the AEG.

Table S1 ECSA and EIS data of Pt/C and Pt-WP-CL/AEG-x (x= 0, 1, 2, 3, 4 and 5).

Sample	ECSA (m^2 g^{-1}_{Pt})	R_{CT} (Ω)
Pt-WP-CL/AEG-0	94.66	21.61
Pt-WP-CL/AEG-1	29.29	72.29
Pt-WP-CL/AEG-2	74.84	31.44
Pt-WP-CL/AEG-3	123.05	17.41
Pt-WP-CL/AEG-4	42.13	40.75
Pt-WP-CL/AEG-5	23.94	80.42
Pt/C	64.16	73.54

Table S2 Mass activity and specific activity expressed as the positive scan peak current for all of catalysts in 1.0 M CH_3OH + 0.5 M H_2SO_4 (V vs. SCE).

Sample	Peak Potential	Mass activity (mA mg^{-1}_{Pt})		Specific activity (mA cm^{-2})	
		Peak	0.77 V	Peak	0.77 V
Pt-WP-CL/AEG-0	0.71	1233.6	1034.4	72.68	59.93
Pt-WP-CL/AEG-1	0.72	504	468	72.24	27.29
Pt-WP-CL/AEG-2	0.72	830.4	787.2	48.99	46.1
Pt-WP-CL/AEG-3	0.78	2234.4	2217.6	131.82	130.98
Pt-WP-CL/AEG-4	0.77	775.2	775.2	45.71	45.69
Pt-WP-CL/AEG-5	0.71	424.8	393.6	25.06	22.96
Pt/C	0.77	499.2	499.2	58.87	58.87

Table S3 Summarizea mass activity for Pt-WP-CL/AEG, Pt-MoP/C, Pt-NiP/C and Pt-CoP/C catalysts

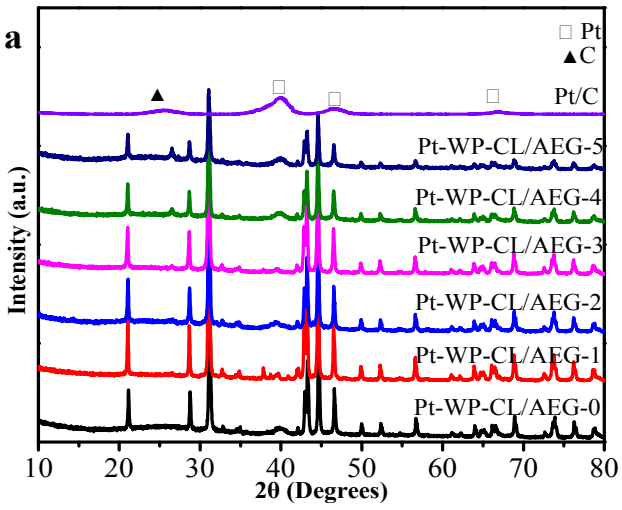
Catalysts	Pt (wt.%)	Mass activity (mA mg^{-1}_{Pt})	Scanning rate (mV/s)	Conditions	References
Pt-WP-CL/AEG	5	2234	50	0.5M H_2SO_4 + 1M CH_3OH	This work
Pt-MoP/C	5	681	50	1M H_2SO_4 + 1M CH_3OH	18
Pt-NiP/C	20	1475	50	0.5M H_2SO_4 + 1M CH_3OH	20
Pt-CoP/C	5	1706	50	0.5M H_2SO_4 + 1M CH_3OH	25

Table S4 The onset potentials and peak potentials (V vs SCE) for CO oxidation

Samples	Onset Potentials	Peak Potentials
Pt-WP-CL/AEG-0	0.49	0.62
Pt-WP-CL/AEG-1	0.51	0.64
Pt-WP-CL/AEG-2	0.46	0.61
Pt-WP-CL/AEG-3	0.41	0.58
Pt-WP-CL/AEG-4	0.44	0.64
Pt-WP-CL/AEG-5	0.43	0.58
Pt/C	0.57	0.69

Table S5 The onset potentials, half-wave potentials (V vs SCE) and limiting current density (mA cm^{-2}) of Pt-WP-CL/AEG-3 and Pt/C for ORR

Catalysts	Onset Potentials	Half-wave Potentials	limiting Current Density
Pt-WP-CL/AEG-3	0.72	0.61	7.01
Pt/C	0.69	0.58	6.88



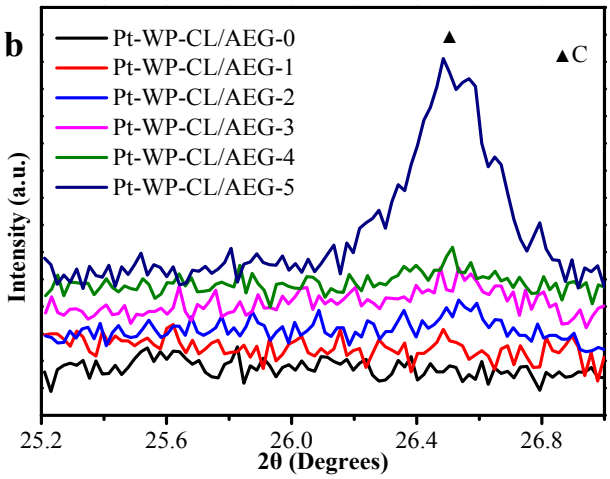
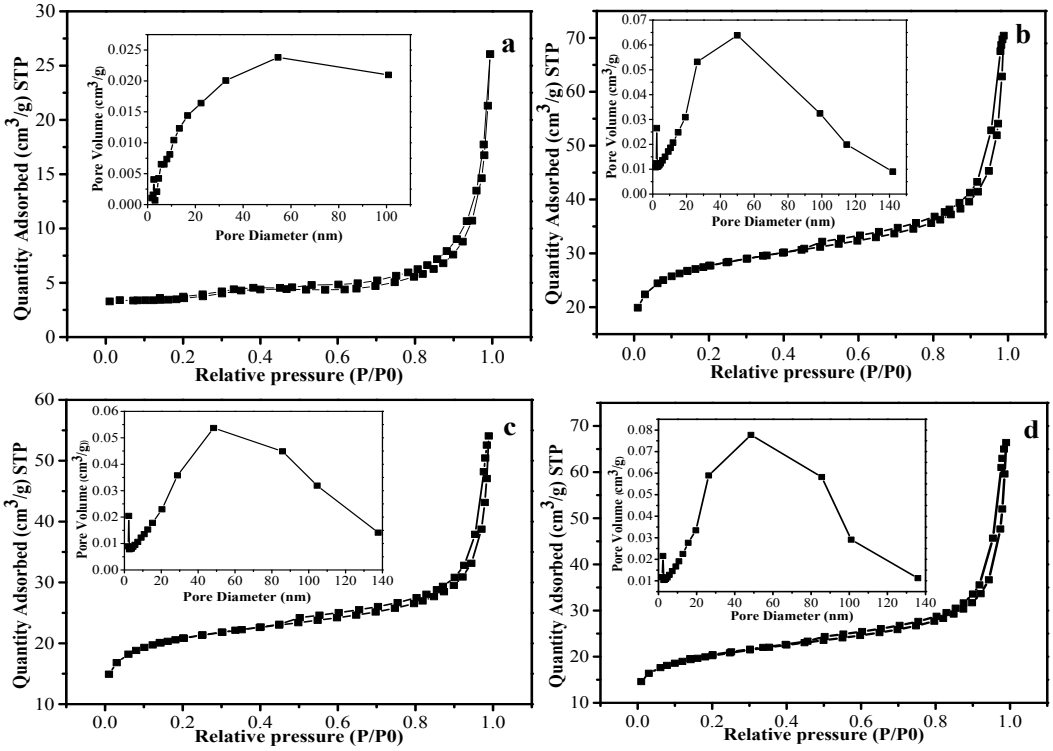


Fig. S1 (a) XRD patterns of Pt/C and Pt-WP-CL/AEG-x(x=0, 1, 2, 3, 4 and 5). (b) The (300) crystal plane of C in WP-CL/AEG-x(x=0, 1, 2, 3, 4 and 5).



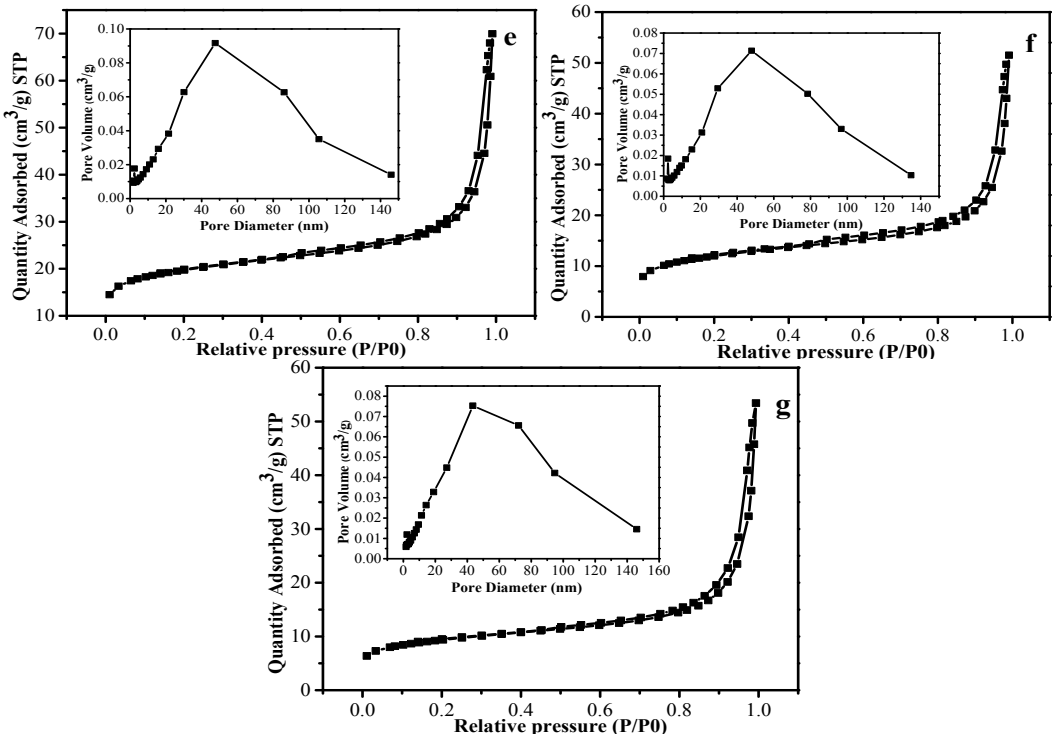
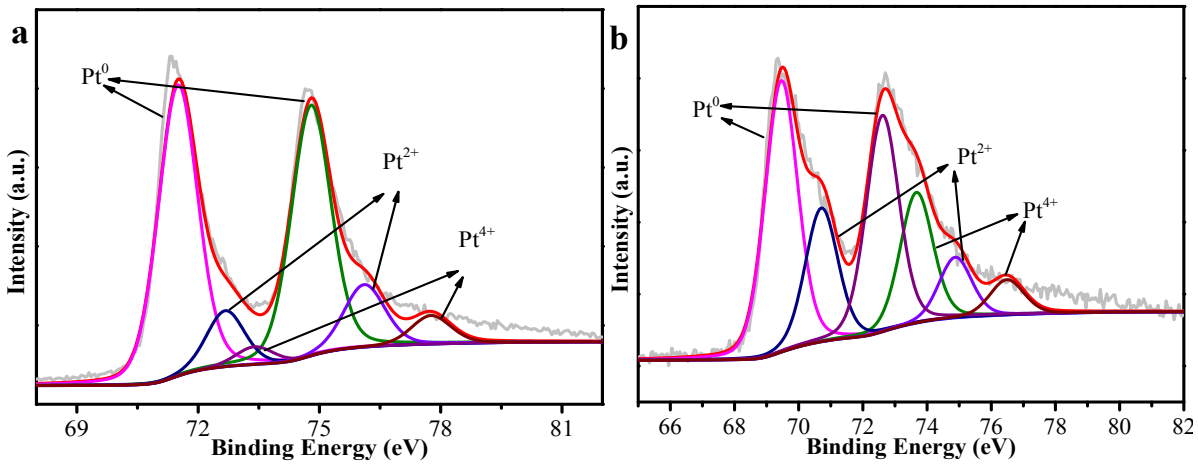


Fig. S2 N_2 adsorption/desorption isotherms and pore size distributions (inset) curves of AEG (a) and WP-CL/AEG-x(x=0, 1, 2, 3, 4 and 5) (b, c, d, e, f and g)



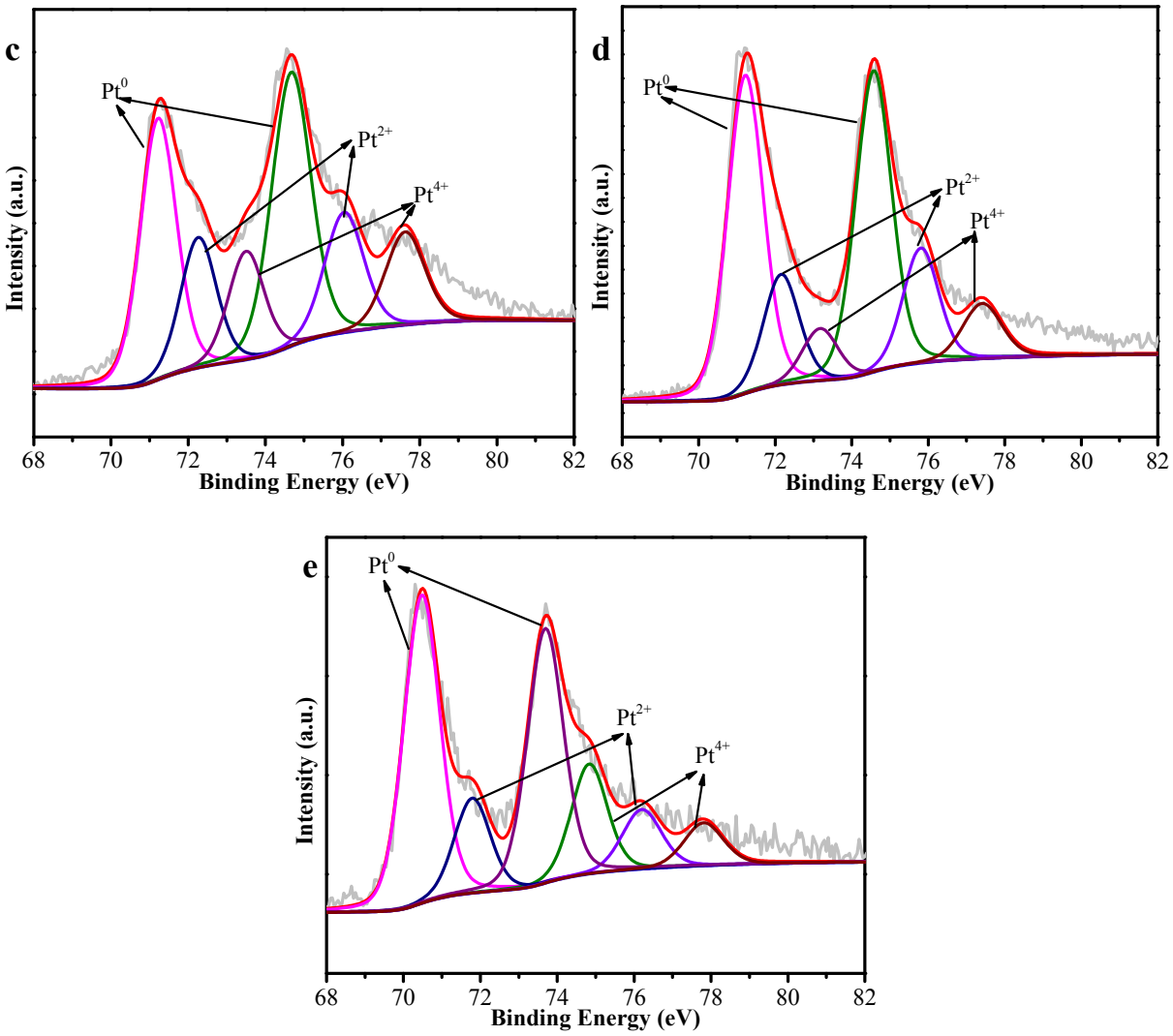
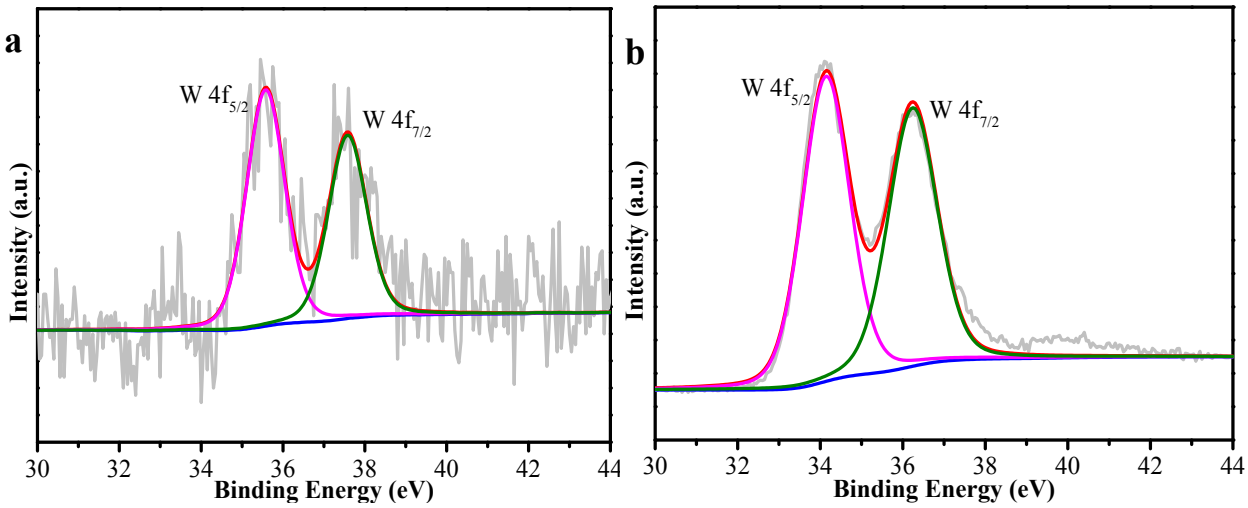


Fig. S3 High resolution XPS of Pt 4f. Pt-WP-CL/AEG-0 (a), Pt-WP-CL/AEG-1 (b), Pt-WP-CL/AEG-2 (c), Pt-WP-CL/AEG-4 (d) and Pt-WP-CL/AEG-5 (e).



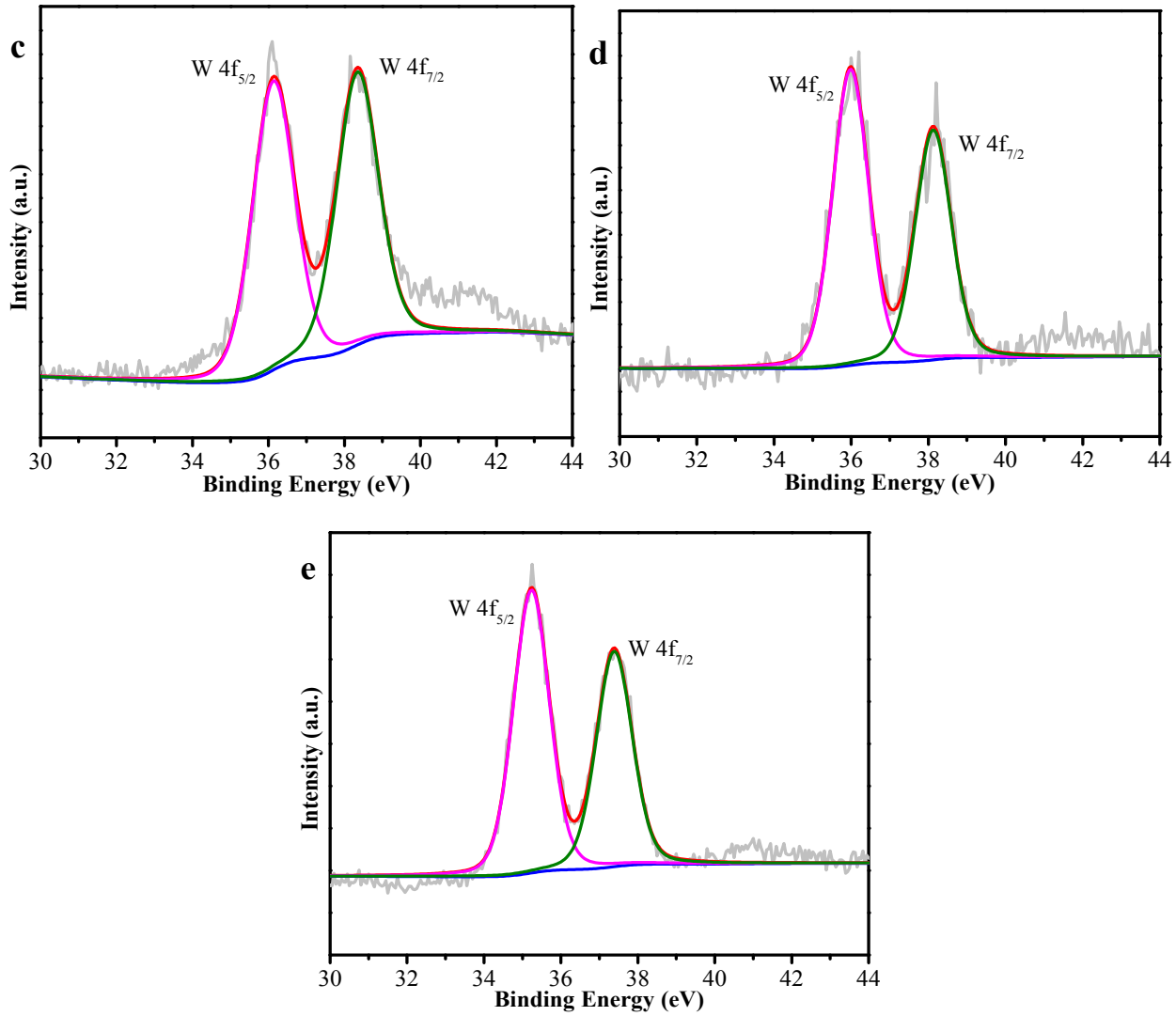
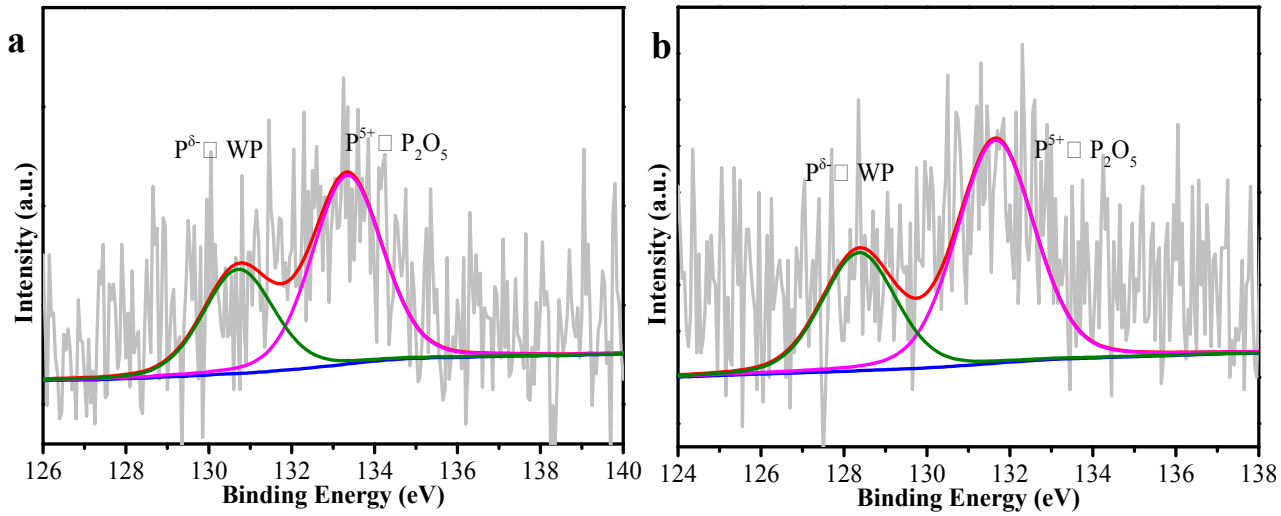


Fig. S4 High resolution XPS of W 4f. Pt-WP-CL/AEG-0 (a), Pt-WP-CL/AEG-1 (b), Pt-WP-CL/AEG-2 (c), Pt-WP-CL/AEG-4 (d) and Pt-WP-CL/AEG-5 (e).



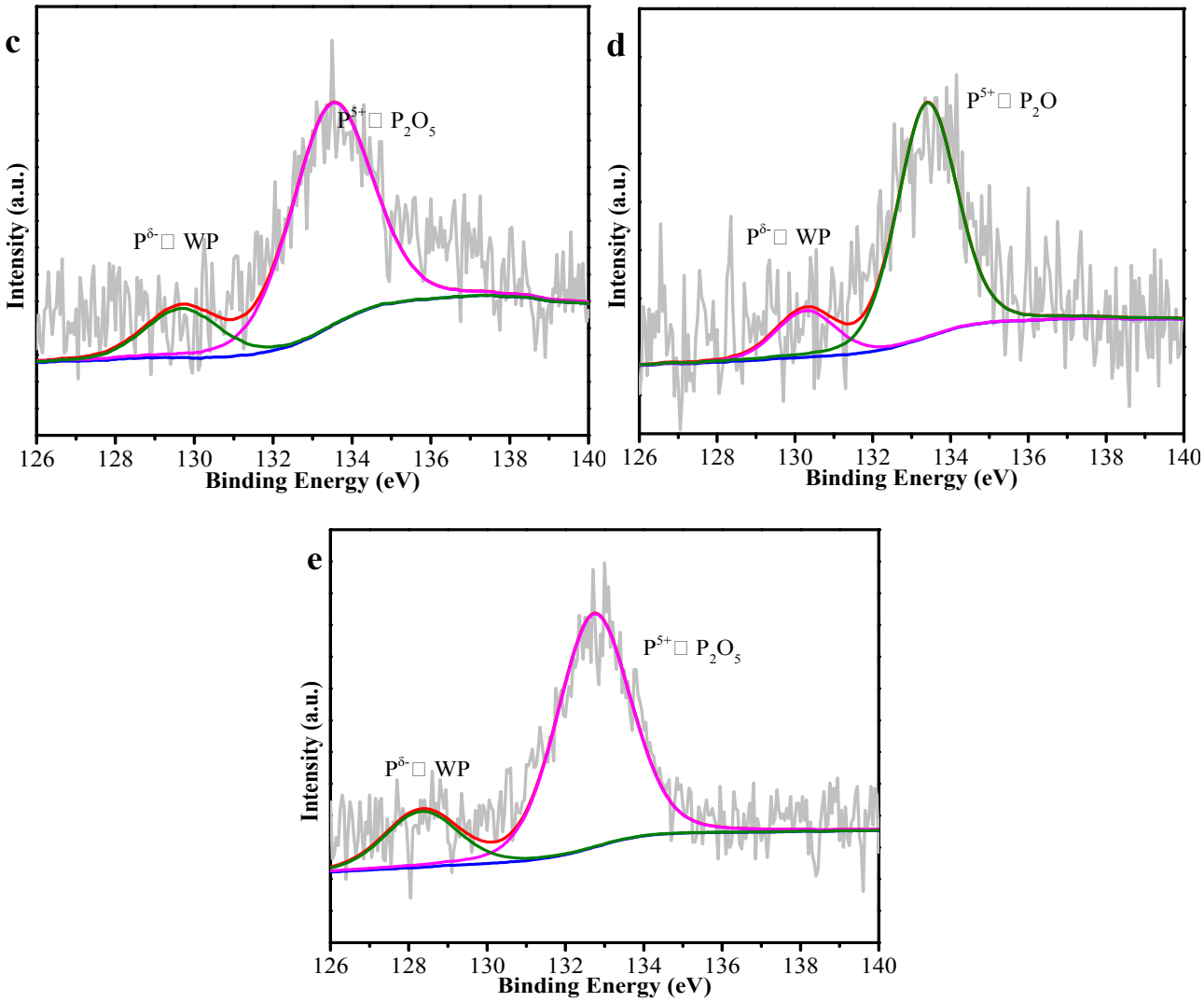
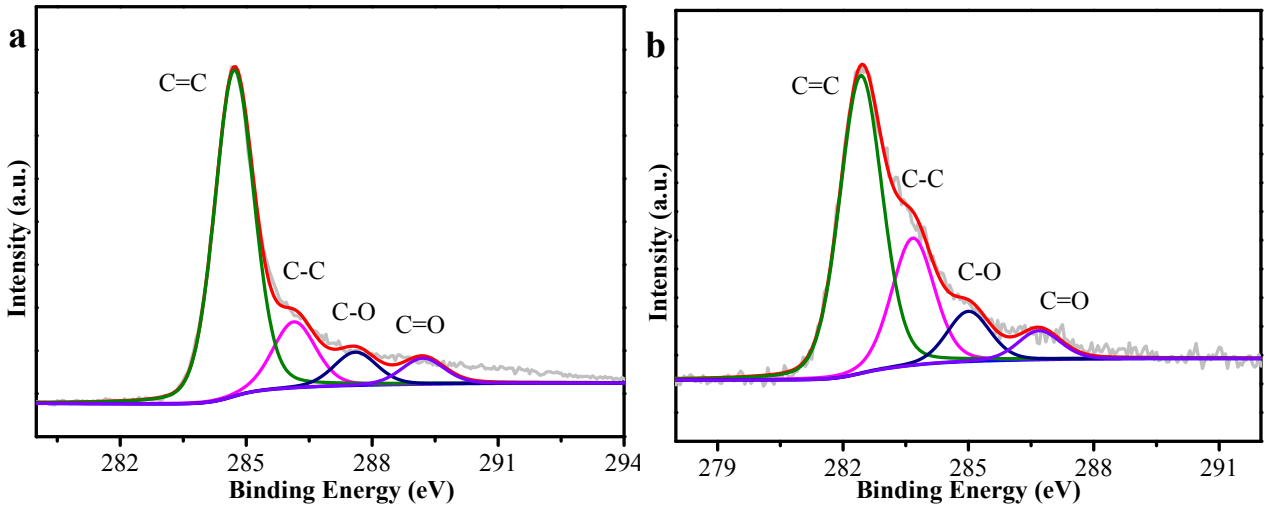


Fig. S5 High resolution XPS of P 2p. Pt-WP-CL/AEG-0 (a), Pt-WP-CL/AEG-1 (b), Pt-WP-CL/AEG-2 (c), Pt-WP-CL/AEG-4 (d) and Pt-WP-CL/AEG-5 (e).



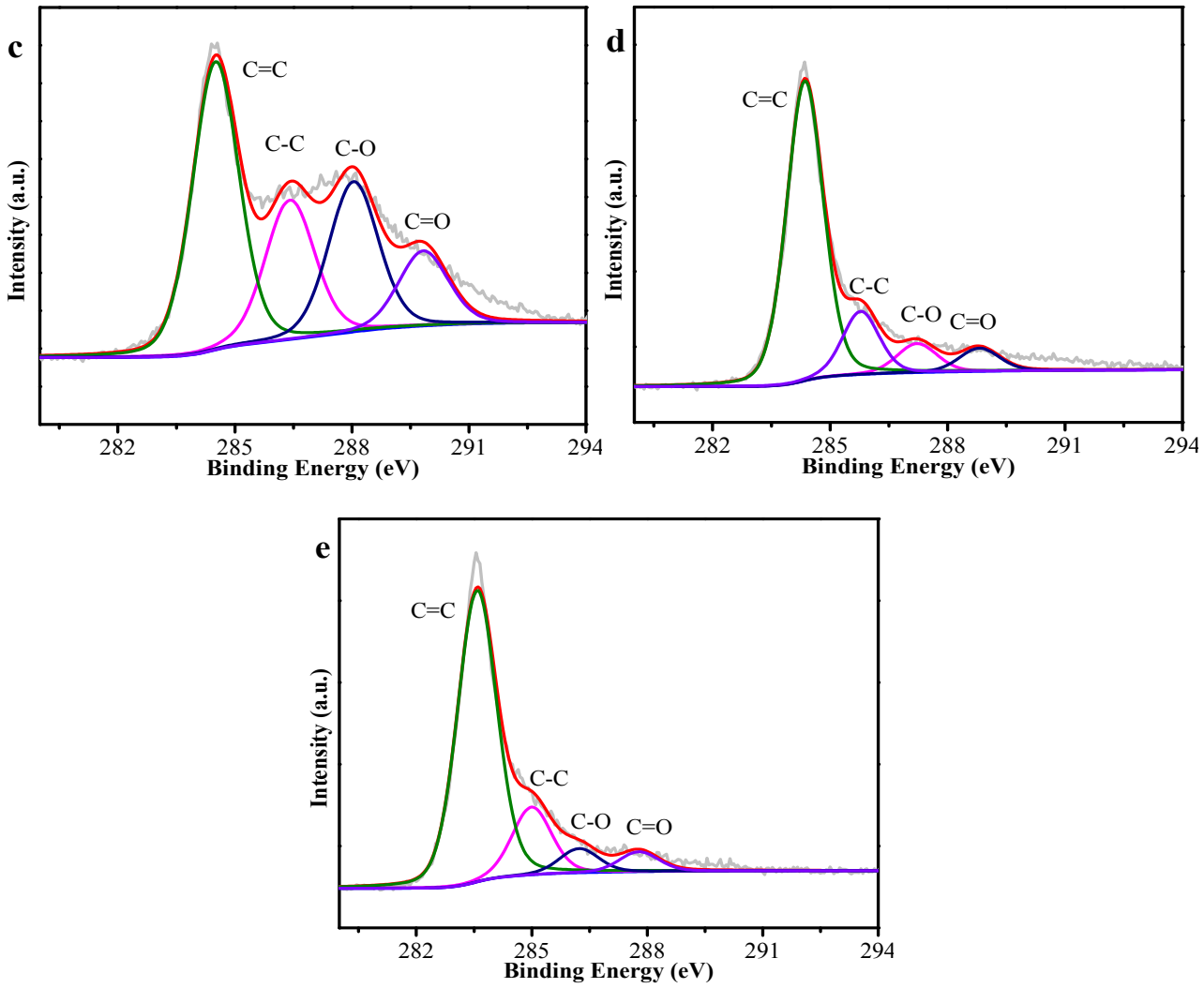
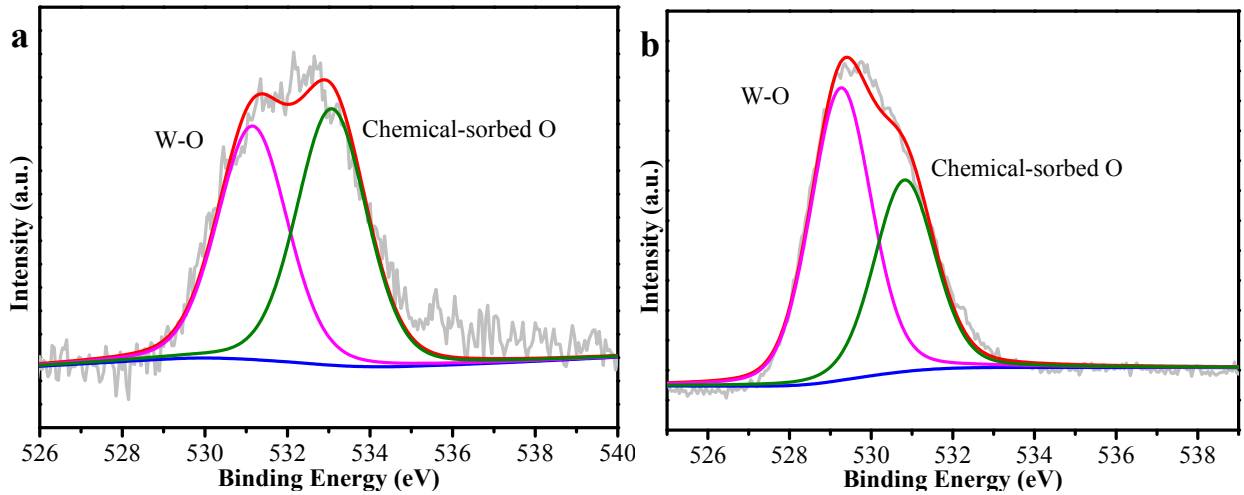


Fig. S6 High resolution XPS of C 1s. Pt-WP-CL/AEG-0 (a), Pt-WP-CL/AEG-1 (b), Pt-WP-CL/AEG-2 (c), Pt-WP-CL/AEG-4 (d) and Pt-WP-CL/AEG-5 (e).



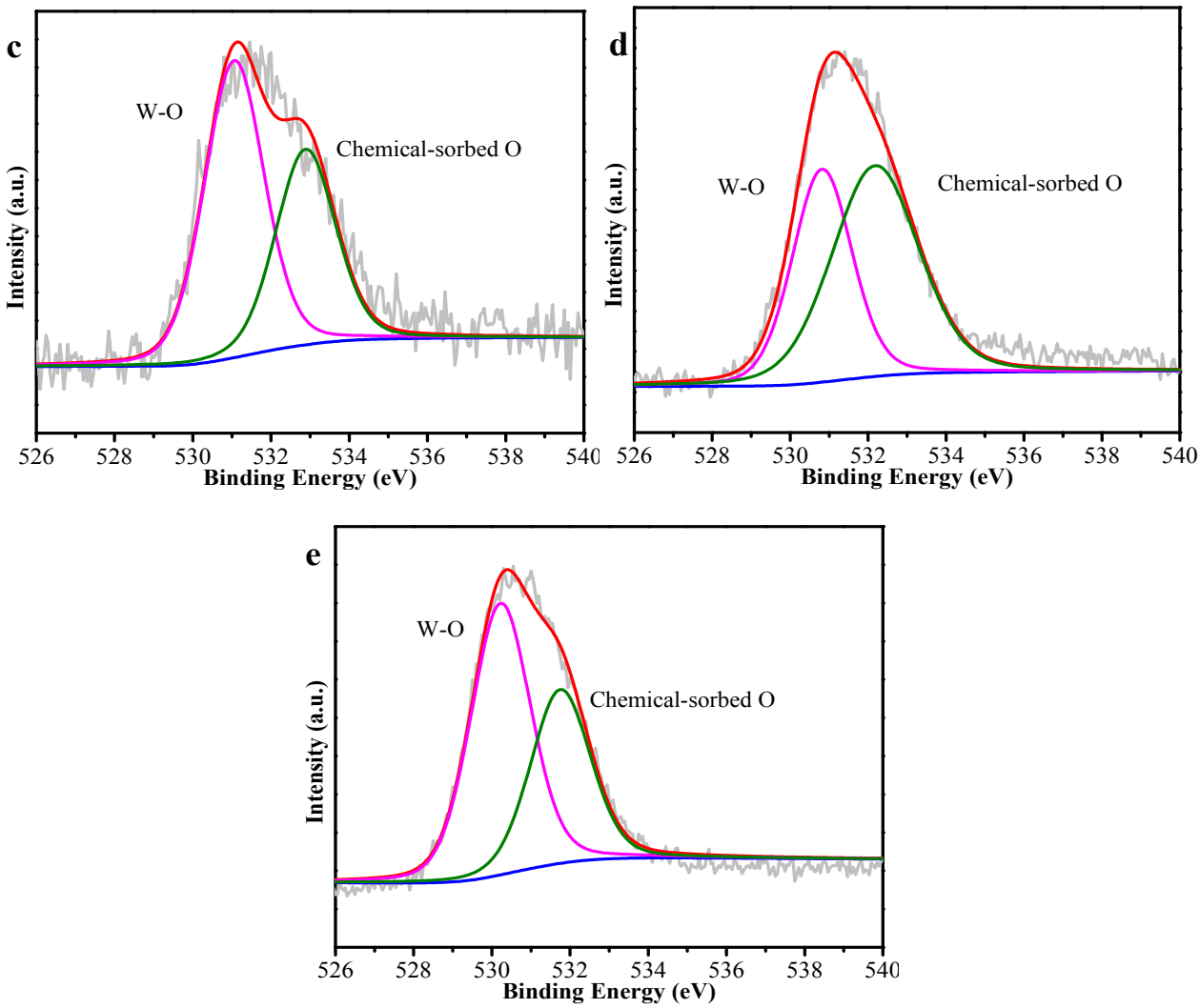


Fig. S7 High resolution XPS of O 1s. Pt-WP-CL/AEG-0 (a), Pt-WP-CL/AEG-1 (b), Pt-WP-CL/AEG-2 (c), Pt-WP-CL/AEG-4 (d) and Pt-WP-CL/AEG-5 (e).

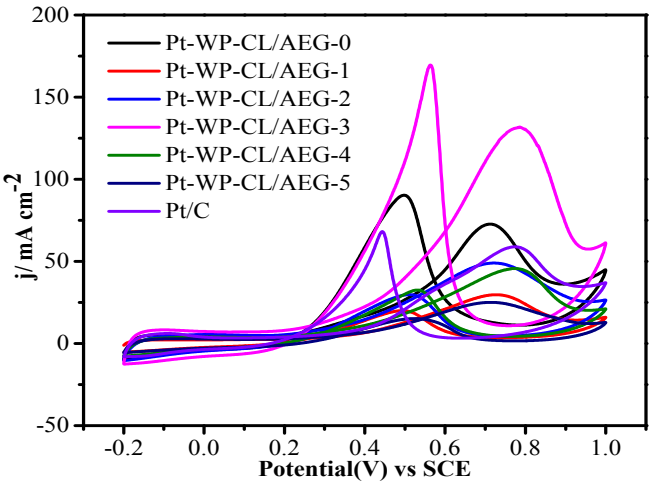


Fig. S8 The specific activity of Pt/C and Pt-WP-CL/AEG-x (x= 0, 1, 2, 3, 4 and 5).

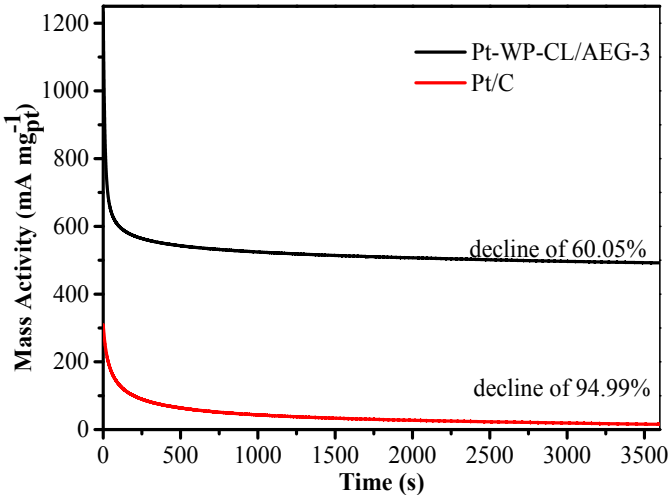


Fig. S9 CA curves of Pt-WP-CL/AEG-3 and Pt/C under 0.6V measured in 0.5 M H_2SO_4 + 1 M CH_3OH

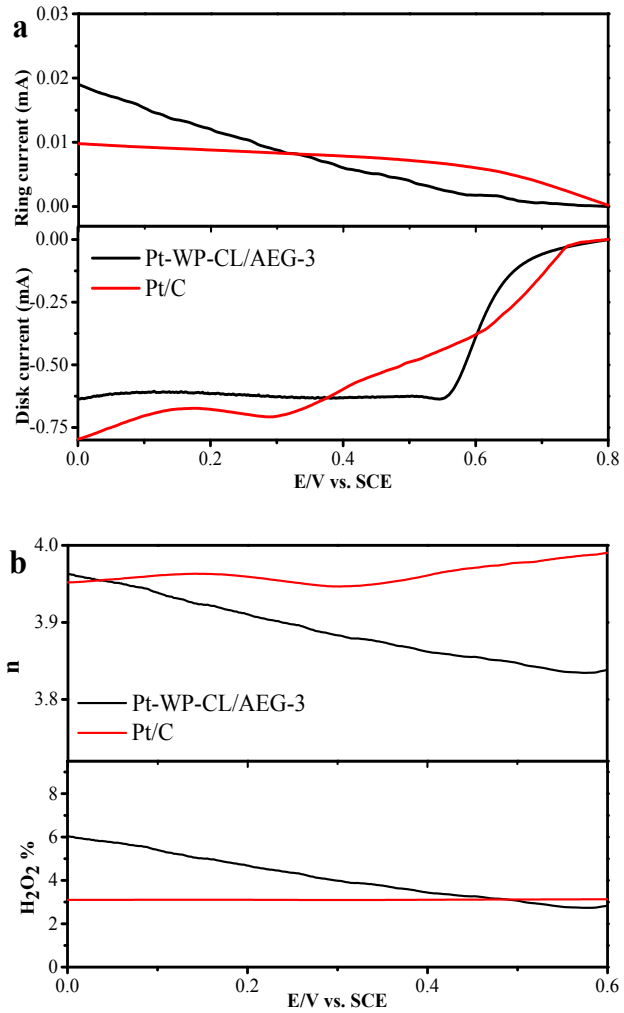


Fig. S10. (a) RRDE voltammograms of Pt-WP-CL/AEG-3 and Pt/C in O_2-saturated 0.5 M H_2SO_4 solution at 1600 rpm. The disk is scanned at 10 mV s^{-1} and the ring potential is kept constant at 1.2 V (vs. SCE). (b) H_2O_2 yields and the corresponding electron transfer number (n) of Pt-WP-CL/AEG-3 and Pt/C