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

Supporting Information

Active and stable PtP_2-based electrocatalyst solves the phosphate poisoning issue of high temperature fuel cells

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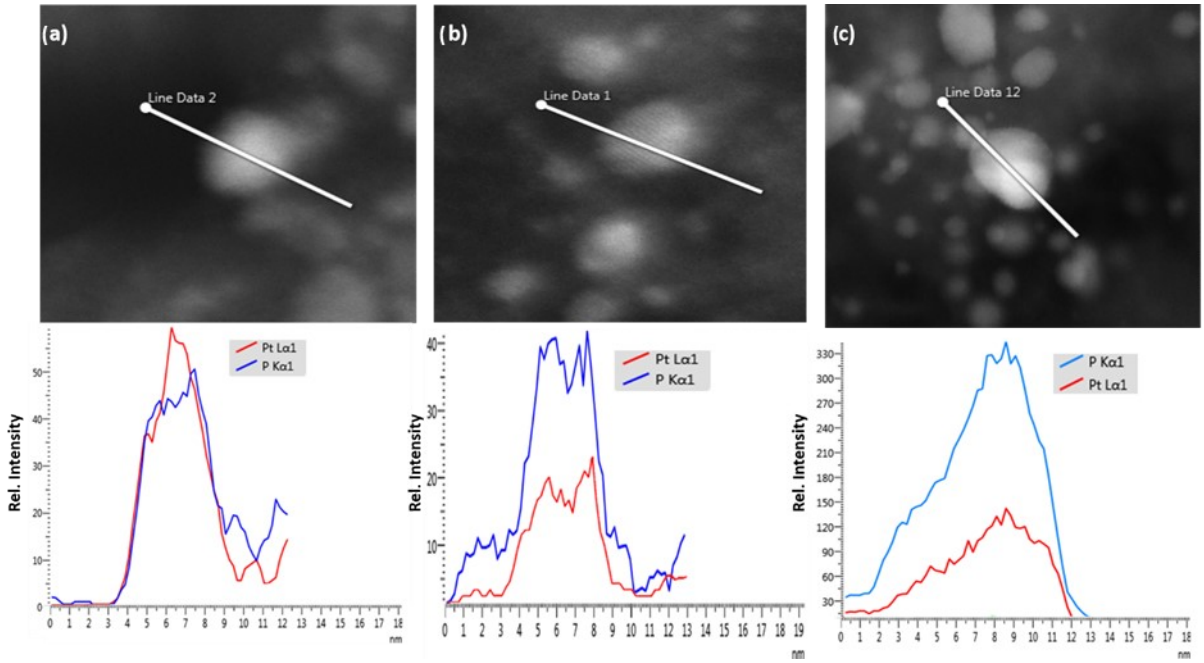

Fig. S1 STEM-EDX line profiles across as-prepared PtP_2 nanoparticle: STEM reference images and compositional (Pt and P) profiles of (a) (1:2) PtP_2/C-ASP, (b) (1:4) PtP_2/C-ASP and (c) (1:6) PtP_2/C-ASP.

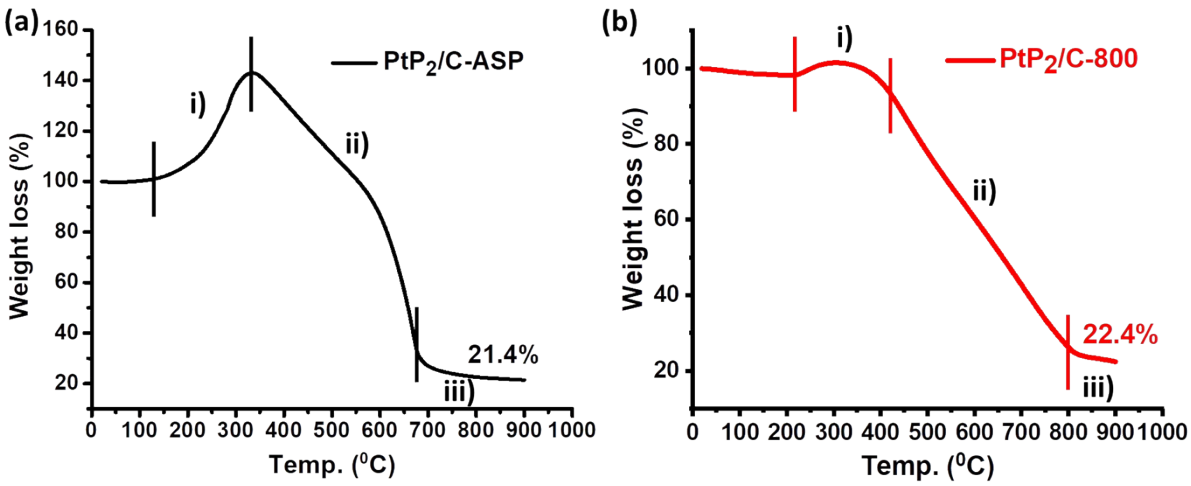

Fig. S2 Thermo-gravimetric-analysis (TGA) of (a) PtP_2/C-ASP and (b) PtP_2/C-800 in O_2 atmosphere.

The observed TGA peaks can be divided into 3 regions: i) oxidation of TOP polymer (~120 to 450 °C) in the PtP_2/C-ASP catalyst and conversion of lattice P into P_2O_5 (~250 to 450 °C) in the PtP_2/C-800 catalyst,[1,2] ii) oxidation of the ketjen-black-carbon support (450 to 680 °C), and iii) percentage of mass remained after the thermal treatment (<680 °C) in both catalysts. After the thermal oxidation in O_2 atmosphere, around 20% of the total mass remained for both samples in consideration of the stability of the PtP at high temperature. The remained mass can be attributed to the $PtPO_4$. Therefore, it can be concluded that the prepared catalysts contain mostly PtP_2 catalyst.

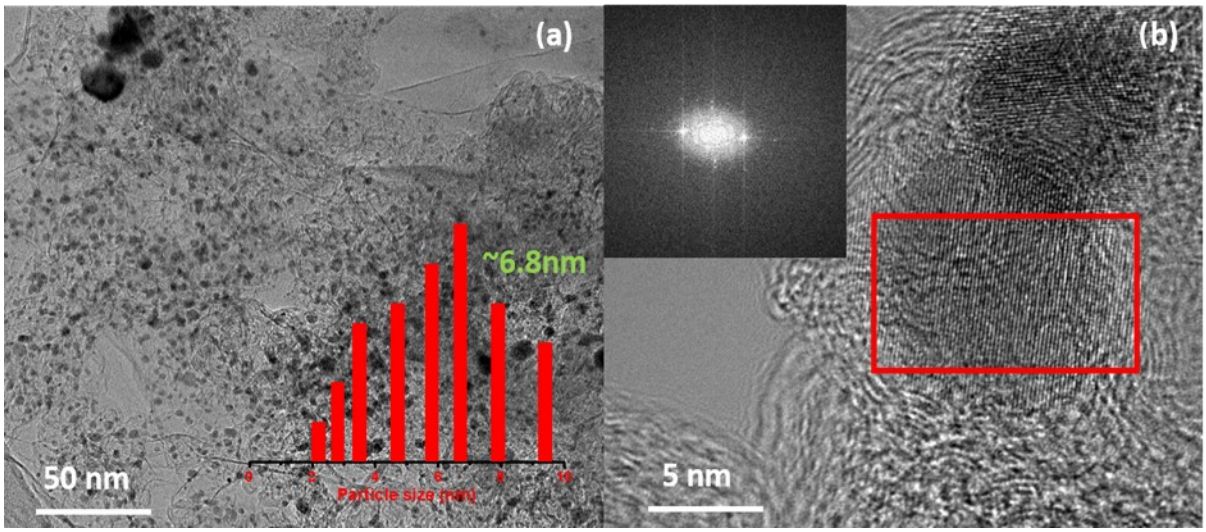

Fig. S3 (a) The TEM image of PtP_2/C-900 electrocatalyst along with inserted bar graph showing the PtP_2 particle size distribution and average PtP_2 particle size (~6.8 nm) and (b) HR-TEM image of PtP_2/C-900 electrocatalyst and inset showing the FFT image of the red squared area.

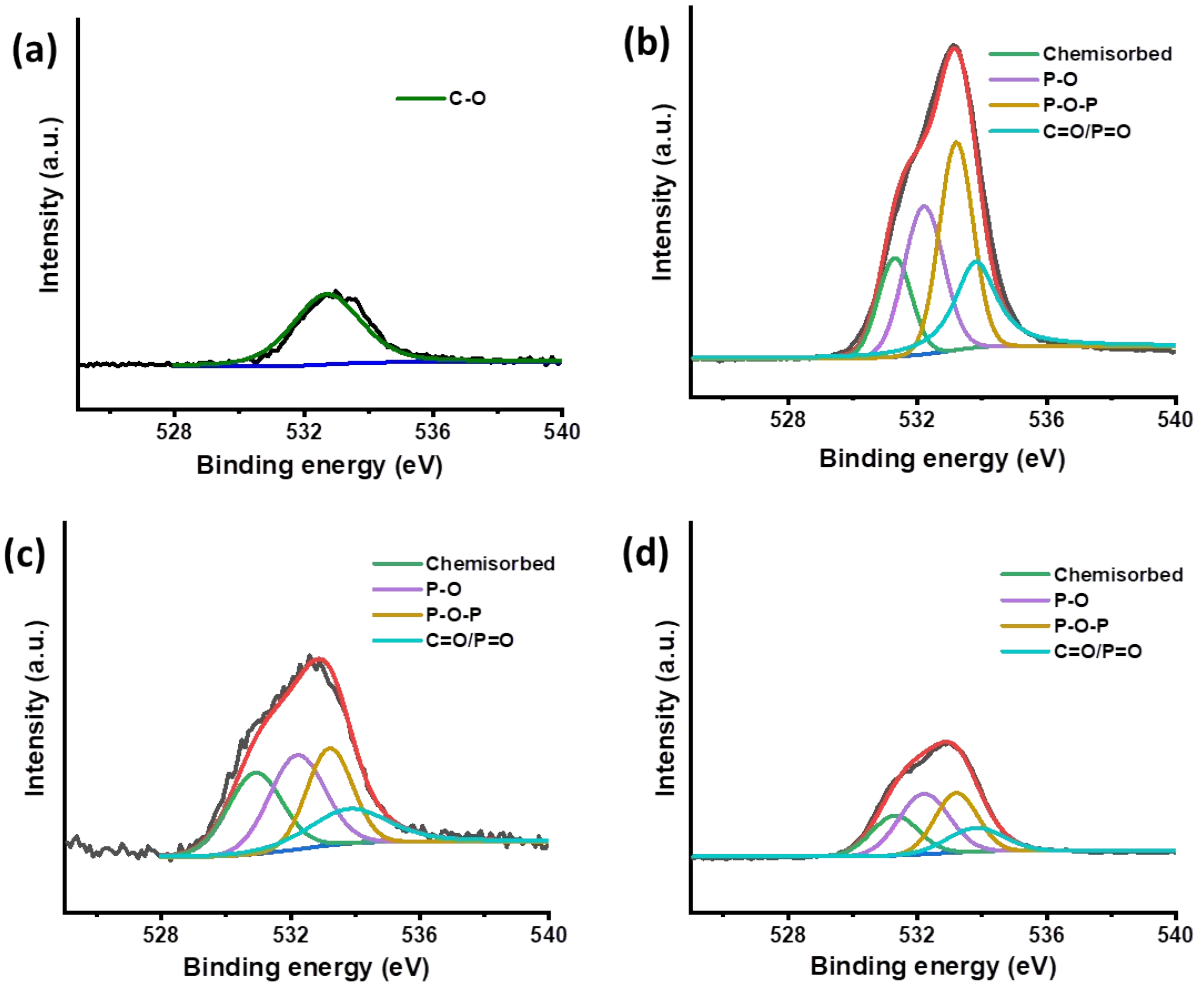

Fig. S4 XPS profiles of O 1s for (a) Ketjen black, (b) PtP_2/C-ASP, (c) PtP_2/C-800 and (d) PtP_2/C-900.

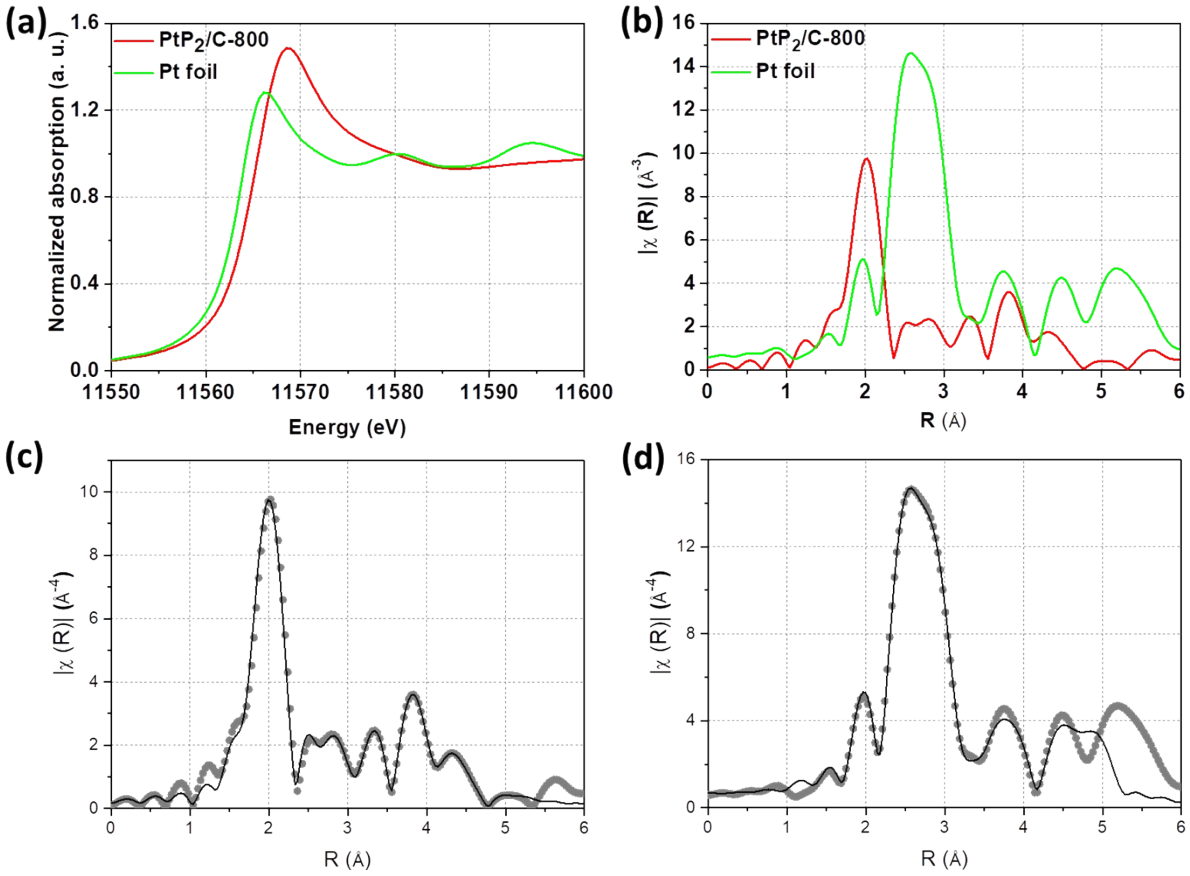

Fig. S5 (a) XANES and (b) EXAFS profiles of PtP_2/C-800 and Pt foil. Fourier-transforms of k^3-weighted EXAFS spectra (circle) and their best fits (solid line) for (c) PtP_2/C-800 and (d) Pt foil.

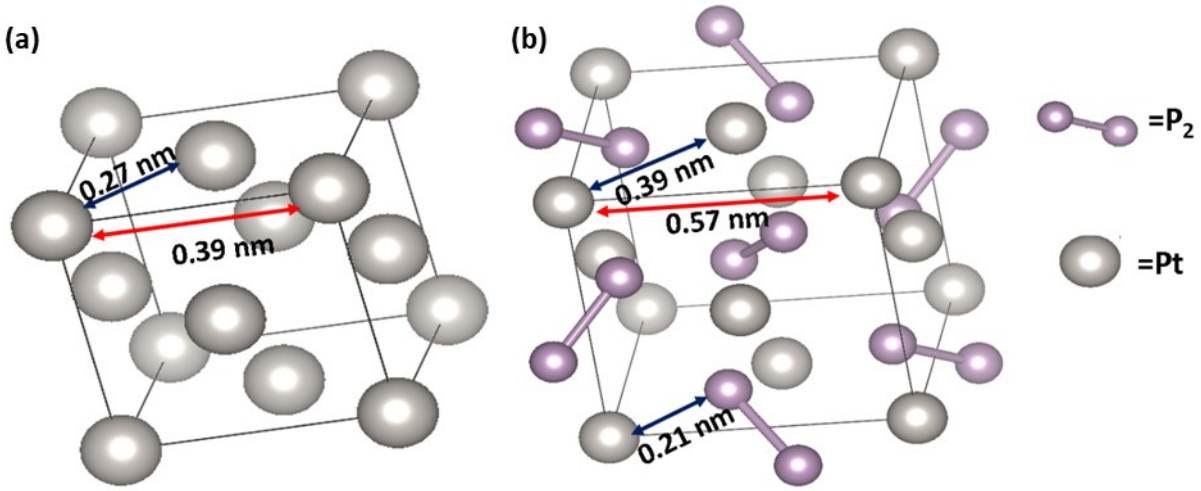

Fig. S6 The unit cell structures of (a) Pt and (b) PtP_2, demonstrating the orientation of Pt and P atom in the unit cell and the effective distance between each atom. The effective distance between each atom is calculated from the lattice parameters of the unit cells of Pt and PtP_2 as illustrated in Fig. 1d through the Rietveld refinement.

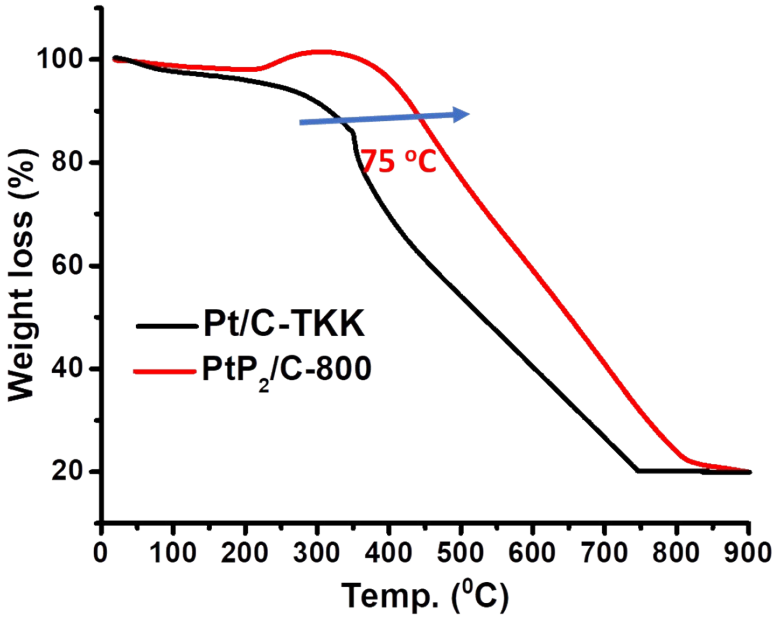

Fig. S7 TGA analysis of PtP_2/C-800 and commercial 20 wt.% Pt/C in O_2 atmosphere. Around 20% of mass remained after the completion of the TGA analysis.

The onset of carbon degradation is observed at ~350 ^{0}C for Pt/C catalyst and ~425 ^{0}C for PtP_2/C-800 catalyst. A hump before carbon degradation in PtP_2/C catalyst can be assigned to the oxidation of P. Due to the oxidation of P, the oxidation of carbon has been shifted to the right , indicating the presence of P improves the oxidative stability of carbon.

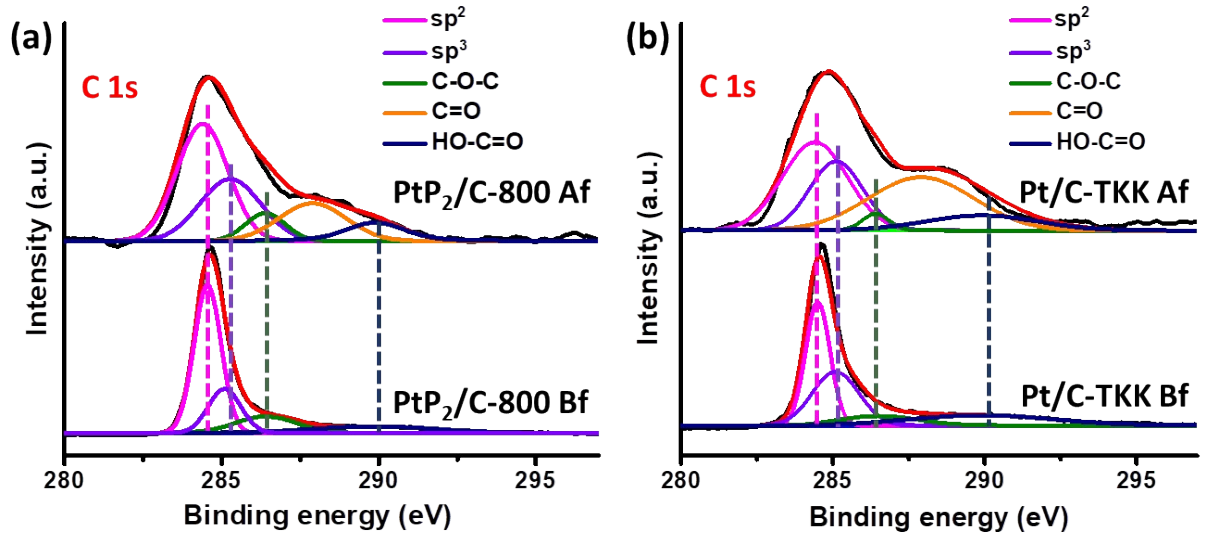

Fig. S8 XPS deconvolution of C 1s spectra of (a) PtP_2/C-800 cathode catalyst and (b) commercial 46.3 wt.% Pt/C-TKK catalyst before and after long-term test of 10K cycles which is carried out in an O_2-saturated 0.1 M $HClO_4$ electrolyte as shown in Fig. 5.

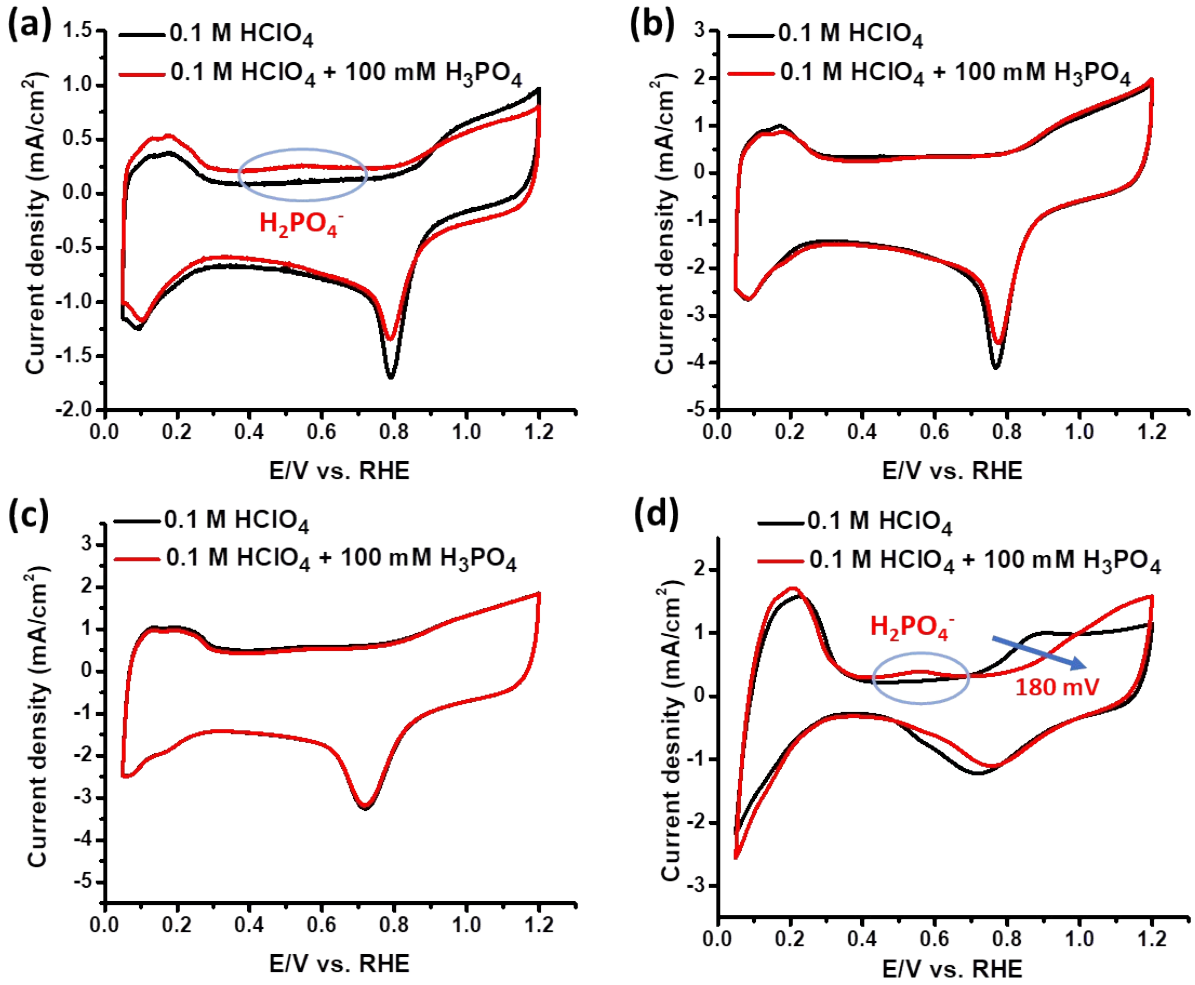

Fig. S9 CV curves recorded for (a) PtP_2/C-ASP, (b) PtP_2/C-800, (c) PtP_2/C-900, and (d) commercial 46.3 wt.% Pt/C-TKK in O_2-saturated 0.1M $HClO_4$ and 0.1 M $HClO_4$ + 0.1 M H_3PO_4 electrolytes, respectively.

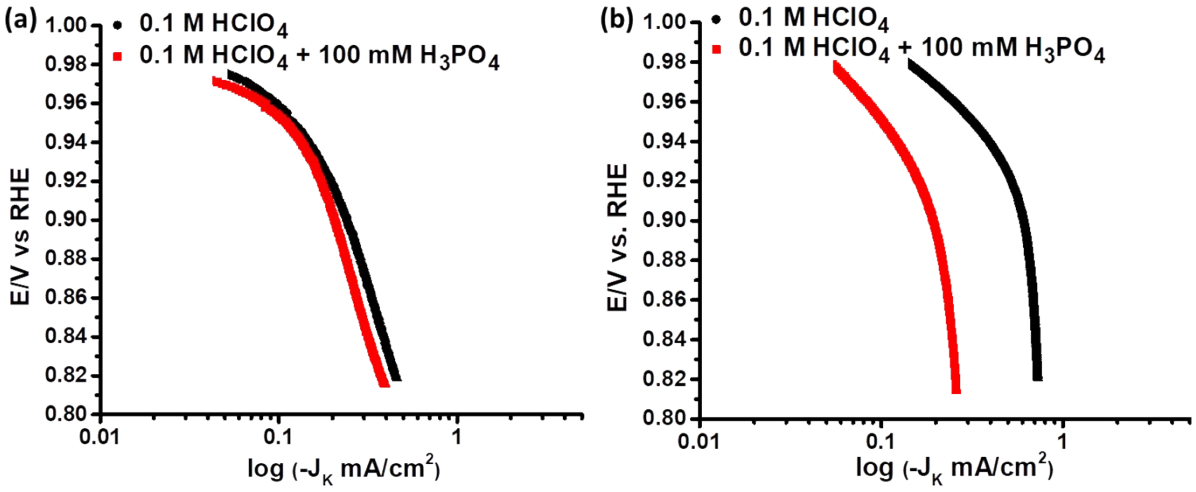

Fig. S10 Mass transport-corrected Tafel plots obtained from LSV curves for (a) PtP_2/C-800, and (b) Pt/C-TKK in O_2-saturated 0.1 M $HClO_4$ (black line) and 0.1 M $HClO_4$ + 0.1 M H_3PO_4 (red line) electrolytes, respectively.

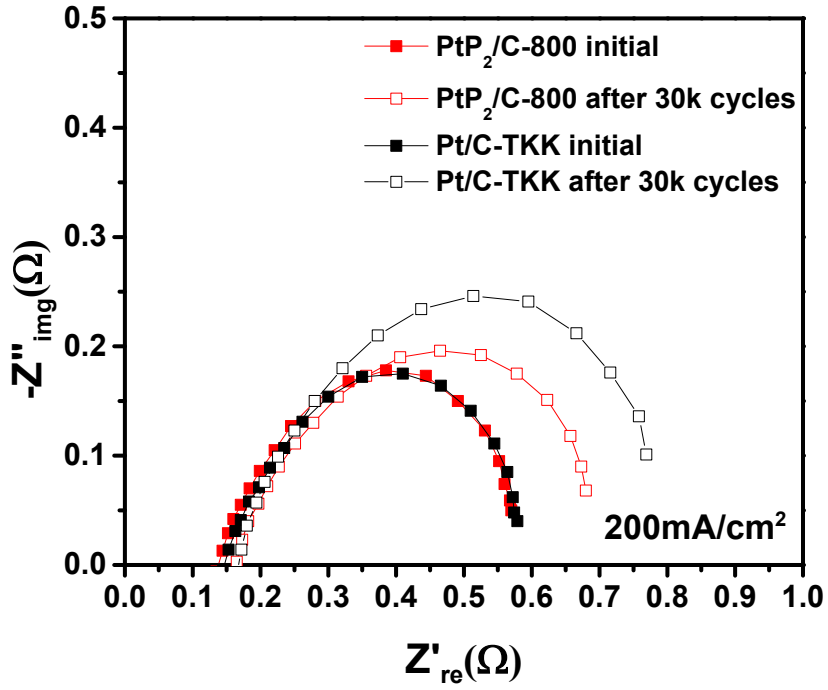

Fig. S11 EIS results for PtP_2/C-800 and Pt/C-TKK at a constant current density of 200 mA/cm^2 before and after the 30k ADT in HT-PEMFC as shown in Fig. 9. EIS were conducted at 1.5 bar O_2 backpressure and 180 °C cell temperature.

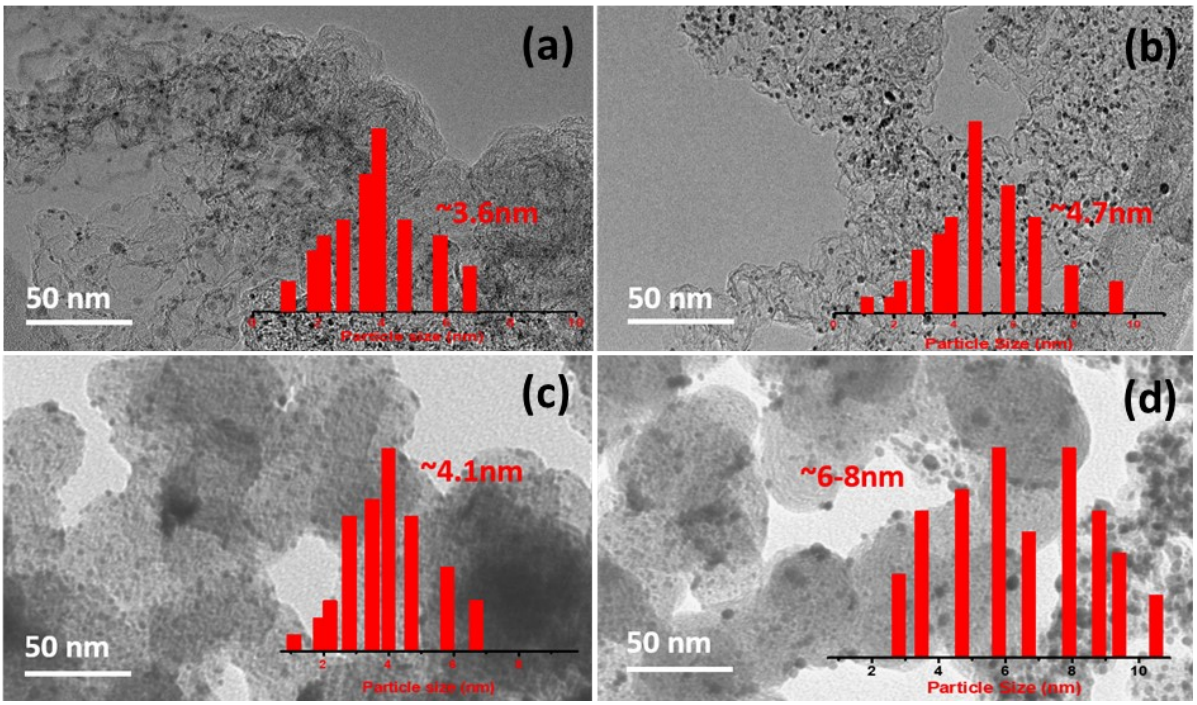

Fig. S12 HR-TEM analysis of (a) and (b) PtP_2/C-800 and (c) and (d) commercial 46.3 wt.% Pt/C-TKK before and after 30k ADT, respectively in HT-PEMFC as shown in Fig. 9. (Inset) shows the particle size distribution histogram for each catalyst before and after the durability test.

Table S1 Physical and electrochemical properties of the prepared PtP_2/C catalysts and commercial Pt/C-TKK catalyst.

Sr. No.	Sample Name	BET surface area (m^2/g)	Pt composition (ICP)	Pt composition (XPS)	Mass-normalized electrochemical Surface area ($m^2g_{Pt}^{-1}$)	Particle Size nm (TEM)	Crystallite Size nm (XRD)
1	Pt/C-TKK	368	46.3%	46%	53	4.1	4.5
2	PtP_2/C-ASP	650	19.7 %	20.7%	47	2.8	--
3	PtP_2/C-800	575	20.4%	20.1%	52	3.9	3.8
4	PtP_2/C-900	430	20.1%	19.4%	48	6.8	10.5

Table S2 Atomic percentage of C, P, and O determined by XPS survey scans of Ketjen black and PtP_2-based catalysts.

Sample	C 1s (at%)	P 2p (at%)	O 1s (at%)
Ketjen black	97.24	0.0	2.76
PtP_2/C-ASP	73.94	5.74	20.32
PtP_2/C-800	83.87	4.43	11.7
PtP_2/C-900	92.85	3.82	3.33

Table S3 Fourier transformed EXAFS fitting parameters for PtP_2/C-800 and Pt foil. (N = coordination number, R = interatomic distance, σ^2 = Debye-Waller factor (bond disorder), R-Factor = a measure of the quality of EXASFS fit)

Sample	Path	N	R (Å)	σ^2 (Å^2)	R-factor (%)
PtP_2/C-800	Pt-P	3.8 ± 0.7	2.374 ± 0.015	0.003 ± 0.001	
	Pt-P	3.3 ± 1.5	3.580 ± 0.029	0.005 ± 0.001	
	Pt-Pt	12.9 ± 2.8	4.055 ± 0.036	0.007 ± 0.003	
	Pt-P	1.8 ± 1.3	4.728 ± 0.048	0.011 ± 0.003	0.8
	Pt-Pt	2.3 ± 1.2	2.751 ± 0.025	0.005 ± 0.001	
	Pt-Pt	4.4 ± 1.2	3.821 ± 0.030	0.007 ± 0.003	
	Pt-Pt	1.4 ± 0.5	4.957 ± 0.039	0.010 ± 0.004	
Pt foil	Pt-Pt	11.0 ± 0.8	2.767 ± 0.003	0.004 ± 0.001	
	Pt-Pt	4.6 ± 2.3	3.902 ± 0.013	0.005 ± 0.003	1.1
	Pt-Pt	17.5 ± 6.6	4.821 ± 0.011	0.007 ± 0.002	

Table S4 Theoretical ORR overpotentials. The table shows the adsorption energies (before zero-point energy and free energy corrections) in eV for the key reaction intermediates of ORR as obtained from an HSE06/DFT calculations and the estimated theoretical, thermodynamic overpotentials for ORR to H_2O on (111) facets of Pt, Pt-terminated PtP_2 (^{t}Pt-PtP_2) and P-terminated PtP_2 and oxidized PtP_2, in both cases at a P-defect site.

	ΔE_{ads} (*OOH) (eV)	ΔE_{ads} (*O) (eV)	ΔE_{ads} (*OH) (eV)	η (H_2O) (V)
Pt	**3.79**	**1.26**	**0.69**	**0.79**
^{t}Pt-PtP_2	**3.49**	**1.07**	**0.37**	**1.52**
^{t}P,P_{def}-PtP_2	**4.70**	**2.64**	**0.88**	**0.60**
^{t}P,P_{def}-PtP_2O_5	**3.72**	**1.67**	**0.20**	**1.28**

Notes and references

(1) S. E. Habas, F. G. Baddour, D. A. Ruddy, C. P. Nash, J. Wang, M. Pan, J. E. Hensley and J. A. Schaidle, *Chem. Mater.*, 2015, **27**, 7580-7592.
(2) A.R.J. Kucernak, K.F. Fahy and V. N. N. Sundaram, *Catalysis Today*, 2016, **262,** 48-56.