## **Supporting Information**

## Active P species in P-doped graphite carrier improving the catalytic performance of supported Pt towards the hydrogen evolution reaction

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Figure S1. The detailed Raman spectrum of Pt@PDG1 (a), Pt@PDG2 (b), Pt@PDG3 (c),

Pt@PDG4 (d) and Pt@PDG5 (e).

The D band located at ~1350 cm<sup>-2</sup> and the G band located at ~1580 cm<sup>-2</sup> reflect the degree of lattice defects and the  $E_{2g}$  vibration of carbon atoms, respectively. The other two peaks at ~1220 cm<sup>-2</sup> and ~1500 cm<sup>-2</sup> can be classified as I band and D" band, respectively. The I band corresponds to the disorder in the graphitic lattice, sp<sup>2</sup>-sp<sup>3</sup> bonds, or the presence of polyenes, and the D" band is generally considered to be related to the presence of amorphous carbon.



**Figure S2.** The CVs of Pt@PDG1, Pt@PDG2, Pt@PDG3, Pt@PDG4 and Pt@PDG5 and 20% Pt/C in N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> (a) and 0.1 M KOH (b) solutions.

Electrochemically active surface area (ECSA) values can be calculated from the coulombic charge for the hydrogen adsorption and desorption ( $Q_H$ ) in the negative-going potential scan according to the following formula <sup>1</sup>: ECSA= $Q_H$  / [Pt] (0.21), where [Pt] represents the platinum loading (g cm<sup>-2</sup>) in the electrode,  $Q_H$  is the charge for hydrogen desorption (mC cm<sup>-2</sup>), and 0.21 represents the charge required to oxidize a monolayer of H<sub>2</sub> on bright Pt (mC cm<sup>-2</sup>).



**Figure S3.** The relevancy between the TOF of Pt@PDG1 (**■**), Pt@PDG2 (**■**), Pt@PDG3 (**■**) and Pt@PDG4 (**■**) at -0.2 V overpotential and the P species contents in them under acidic media.



**Figure S4.** The relevancy between the TOF of Pt@PDG1 (■), Pt@PDG2 (■), Pt@PDG3 (■) and Pt@PDG4 (■) at -0.335 V and the P species contents in them under alkaline media.



Figure S5. Dependences of area and mass specific activities of Pt@PDG1 (■), Pt@PDG2 (■), Pt@PDG3 (■) and Pt@PDG4 (■) on total P, C<sub>3</sub>-P=O, C-P-O and C-O-P contents under acid media (a and c) and alkaline media (b and d).



Figure S6. The relevancy between the area specific activities of Pt@PDG1 (■), Pt@PDG2 (■), Pt@PDG3 (■) and Pt@PDG4 (■) at -0.2 V and the P species contents in them in acid medium.



Figure S7. The relevancy between the area specific activities of Pt@PDG1 (■), Pt@PDG2 (■),

Pt@PDG3 (**•**) and Pt@PDG4 (**•**) at -0.215 V and the P species contents in them in alkaline medium.



Figure S8. The relevancy between the mass specific activities of Pt@PDG1 (•), Pt@PDG2 (•),

Pt@PDG3 (**•**) and Pt@PDG4 (**•**) at -0.2 V and the P species contents in them in acid medium.



**Figure S9.** The relevancy between the mass specific activities of Pt@PDG1 (**■**), Pt@PDG2 (**■**), Pt@PDG3 (**■**) and Pt@PDG4 (**■**) at -0.215 V and the P species contents in them in alkaline medium.

	ECSA(m <sup>2</sup> g <sup>-1</sup> )		Area specific activities (mA cm <sup>-2</sup> <sub>Pt</sub> )		Mass specific activities (A g <sup>-1</sup> <sub>Pt</sub> )	
	acidic	alkaline	acidic	alkaline	acidic	alkaline
Pt@PDG1	130.050	148.917	4.395	1.636	5715.92	2436.28
Pt@PDG2	136.547	149.061	4.403	1.663	6012.16	2478.88
Pt@PDG3	139.093	153.068	4.415	1.680	6140.96	2571.54
Pt@PDG4	144.155	159.169	5.668	1.691	8170.71	2691.55
Pt@PDG5	112.576	137.759	4.248	1.630	4782.23	2245.47
20 %Pt/C	247.797	270.833	1.262	0.375	3126.62	1015.62

**Table S1.** The ECSAs of Pt@PDG1, Pt@PDG2, Pt@PDG3, Pt@PDG4 and Pt@PDG5 and 20% Pt/C together with area and mass specific activities at -0.2 and -0.215 V in acidic and basic media.

## Reference

[1] H.J. Huang, Y. Fan, X. Wang, Electrochim. Acta., 2012, 80, 118-125.