Supporting Information

Synthesis.

Firstly, red phosphorus was pretreated by hydrothermally to remove impurity according to the previously reported.¹ In a typical experiment, 2 g commercial red phosphorus was added in 30 mL H₂O and put into 40 mL Teflon-lined stainless autoclave. The autoclave was treated at 200 °C for 12 h to clear surface oxidation. Similar methods according to previous literature reports, the G-P was prepared through ball-milling of graphite and P with a planetary (rotating) ball-mill apparatus (XQM-2).² In brief, 1 g of flake graphite (325 mesh, 99.99%), 1 g P and 100 g balls (6 mm in diameter) were put into an stainless steel milling vessel with an inner volume of about 100 mL. The crusher was then sealed and degassed in the argon-filled glove box. The ball-milling process was carried out under room temperature for 24 h with a constant milling rate of 500 rpm. G was syntheses by the same way without red phosphorus. All samples were wash by plenty of water and dry in vacuum at 60 °C with 24h. All samples were annealed at 650 °C in Ar atmosphere with a 50 sccm rate to remove the residual red P. Yield of G and G-P were 1.86g and 1.03g, respectively.

Characterizations.

X-ray photoelectron spectroscopic (XPS) measurements were performed on an ESCALAB 250Xi using a monochromic Al X-ray source (200 W, 20 eV). The Raman spectra were collected on a Raman spectrometer (Labram-010) using 633nm laser. The surface area was measured by nitrogen adsorption-desorption isotherms using the Brunauer Emmett Teller (BET) method on Micromeritics ASAP 2504N. The morphology of all samples was observed by scanning electron microscopy (SEM, Hitachi, S-4800) and scanning transmission electron microscopy (STEM, FEI, F20 S-TWIX). The crystal structures of the samples are characterized using powder X-ray diffraction (XRD, Rigaku D/MAX 2500 diffractometer, Cu K α radiation). The composition of the synthesized powders was analyzed by using inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectroblue, Spectro, Germany). Atomic force microscopy (AFM, Bioscope system, America) height image of G-P supported on mica substrates was obtained in tapping-mode (air, 25 °C).

Electrochemical Measurements.

The electrochemical tests were performed using a potentiostat (CHI 760 E, CH Instrument) in a typical three-electrode cell. Catalysts/glassy carbon (GC) electrodes, high purity graphite rod (99.99%), and saturated calomel electrode (SCE) were used as working, counter, and reference electrodes, respectively. All the experiments were conducted at ambient conditions. The working electrodes were prepared by applying respective catalyst inks onto the pre-polished glassy carbon (GC) disk electrodes. Briefly, 4 mg of catalysts was added into 1 ml ethanol to get a well dispersed suspension (4 mg mL⁻¹) under sonication. 50 µl of Nafion solution (5 wt %) was added into the catalyst suspension as a binder. A total of 9.8 µL of a well-dispersed catalyst ink was applied onto a pre-polished glassy carbon (GC) disk electrode (5 mm in diameter, catalyst loading was 0.2 mg cm⁻²). Linear sweep voltammetry curves for OER at a scan rate of 5 mV s⁻¹ in O₂-saturated 1 M KOH aqueous solution. SCE was calibrated with respect to reversible hydrogen

electrode (RHE) according to the previous work.^{3, 4} The result was illustrated in Figure S4. In brief, 1 M KOH electrolyte was saturated with high purity hydrogen and Pt wire was used as the working electrode. CVs were run at a scan rate of 1 mV s⁻¹ from -1.2 to -0.9 V. When the current was zero, the average value (1.05 V) of the two potentials was taken to be the thermodynamic potential for the hydrogen electrode reactions. So, it could be deduced with the equation: E (RHE) = E (SCE) + 1.05 V.



Figure S1. (a) EDX patterns of G-P. (b) XRD patterns of pristine graphite, G and G-P. (c) high-resolution XPS spectrum for Fe 2p.



Figure S2. TEM images of G-P at different locations.



Figure S3. AFM height image of G-P together with their thickness profiles (upper) and a height profile along the black broken line (lower).



Figure S4. Cyclic voltammograms with a scan rate of 1 mV s^{-1} in H₂-saturated 1 M KOH aqueous solution for RHE calibration.



Figure S5. Stability of G-P was tested by CV curves.



Figure S6. EDX patterns of G-P after stability test for OER.

Sample	Surface Area Pore Volume		Pore Size	
	(m^{2}/g)	(mL/g)	(Å)	
Pristine graphite	2.78	0.0016	22.70	
G	589.45	0.5789	19.64	
G-P	237.71	0.2718	45.74	

Table S1. BET surface areas of the pristine graphite, G and G-P.

Table S2. Surface elemental compositions (obtained from XPS) of pristine graphite, G and G-P.

Sample	С	0	Р
Pristine graphite	95.57	4.43	-
G	85.12	14.88	-
G-P	89.28	9.89	0.83

Table S3. EDX spectrum of G-P of before and after stability test for OER.

Sample	С	0	Р
before	88.04	11.12	0.84
after	89.31	9.92	0.77

Table S4. ICP-OES analysis results of G-P.

Element	Fe	Р
Content (W %)	0.014	1.01

Table S5. Comparison for OER catalysts.

Catalyst	Loading [mg cm ⁻²]	Electrolyte pH	Onset [V vs RHE]	<i>j</i> [mAcm ⁻²] @ η [V vs RHE]	Tafel slope [mV dec ⁻¹]
G-P(this work)	0.2	13	~1.48	10@1.564	62
C ₃ N ₄ -CNT-CF ⁵	0.5	14	1.52	10@1.60	45
P-doped C3N4/CFP ⁶	0.2	13	1.53	10@1.63	61.6
N-doped graphene/CNT ⁷	0.2548	13	1.5	10@1.63	83
N,P-GCNS ⁸	0.141	14	1.32	10@1.57	70
egg-CMS ⁹	2	13	1.51	-	59
echo- MWCNTs ¹⁰	1	13	~1.495	10@1.59	41

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