Supporting information

Manipulation of Heteroatom Substitution on Nitrogen and Phosphorus Co-doped Graphene as High Active Catalyst for Hydrogen Evolution Reaction

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***Preparation of samples for Raman spectroscopy measurement*:**

In order to obtain the Raman signal purely from the doped-graphene without any interference from the CC or the graphene/CC assembly and avoid graphitization due to restaking of graphene we separately fabricated the sample on SiO_2. In a typical procedure, first the GO sample was dip-coated on to the SiO_2 surface, used N_2 gun to remove the extra graphene sample followed by heating the sample for 15 min at 90 ^{o}C (GO/SiO_2).

For rGO synthesis(i.e. rGO/SiO_2), the thermal reduction was carried out in a tubular furnace under a mixture gas of Ar/H_2 (80:20) at 900 ^{o}C for 15 min by maintain rate of heating to be 30 ^{o}C/min.

For obtaining NG, PG, NPG and PNG, first the GO/SiO_2 sample was introduced in the tubular furnace and respective exact procedures of heterogeneous doping with phosphorous and nitrogen as that of GO/CC (see experimental section in the main manuscript) was employed. Notably, the iron powder as used for the P-doping of GO/CC was also introduced in this case and inside the tubular furnace just adjacent to the GO/SiO_2 sample.
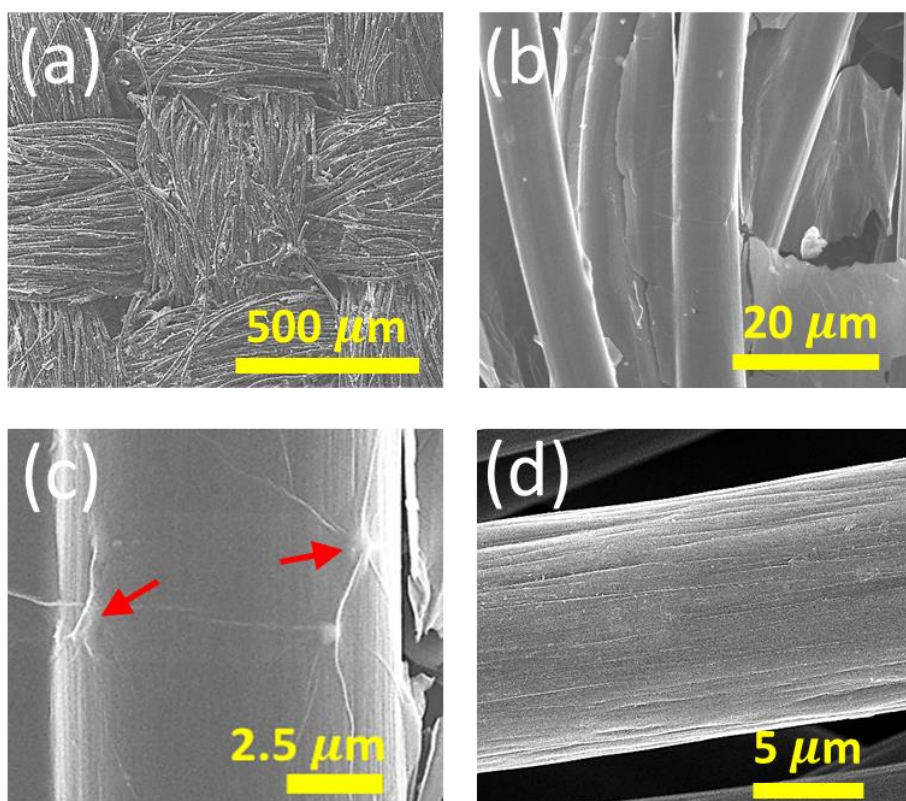
Fig. S1. Low magnification (a) and high magnification (b and c) SEM images of GO/CC assembly. (d) SEM image of bare carbon cloth. The high resolution image (c) clearly shows wrinkles (red arrow) originally present in bare CC (d) that are uniformly covered by graphene sheet.

Preparation of samples for sheet resistance measurement:

The rGO suspension (4 mg/ml) was dropped on the SiO_2 substrate followed by the spin coating of 1500 rpm (30 seconds). Then the samples was baked on the hot-plate at 120 ^oC for15 min followed by the doping process. The average sheet resistance was acquired from three different point on the sample (Fig. S2).
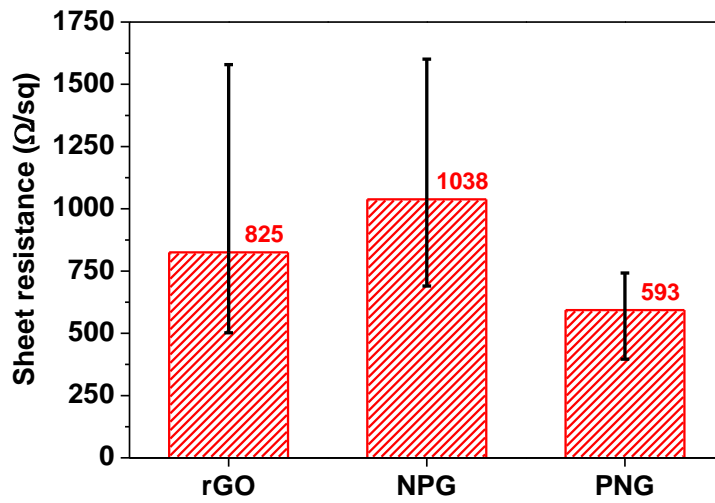
Fig. S2. The sheet resistance of the rGO, NPG, PNG (on SiO_2).

Lattice constant measurement:

The second ring of the diffraction pattern (DP) was assigned to the in-plane (110).

The radius (r_{110}) in the DP can be transformed to the lattice spacing (d_{110}) in the real

space by eq. (1). Fig. S4 shows the lattice between 2D crystal graphene, where the

lattice constant (**a**) can be estimated by eq(2). Note that the a is 0.246 nm for an ideal

graphene lattice. Based on this calculation, the correlation of lattice constant and lattice

spacing with various doping conditions was shown in Fig. S5). The result indicate that

the heteroatom substitution of P atoms in graphene lead to lattice expansion.

$$d_{110}=1/r_{110} \text{ (nm)}………..\text{eq. (1)}$$

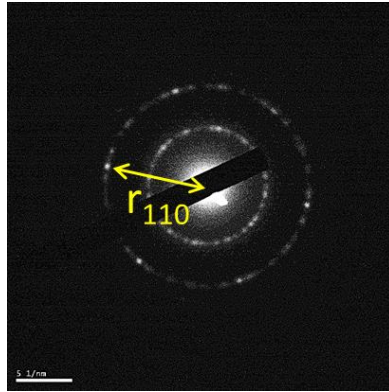$$a=2*d_{110}……..……..……\text{eq. (2)}$$

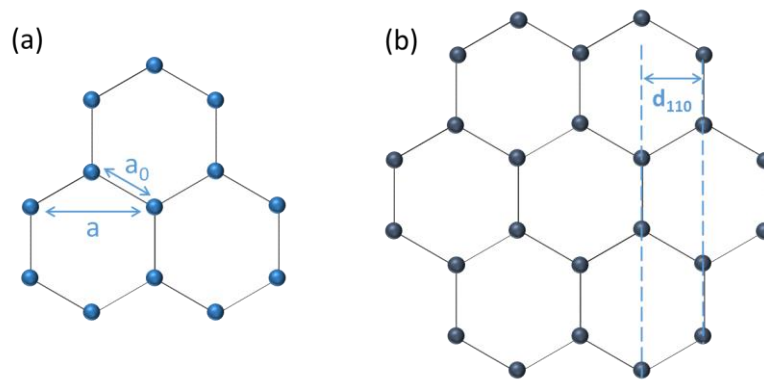Fig. S3. The diffraction pattern of PNG shows the radius of r_{110}.

Fig. S4. The illustration relates to the lattice between 2D crystal graphene. (a) a_0 is the distance between the nearest atoms, a is the lattice constant for graphene. (b) The in-plan spacing is d_{110}.
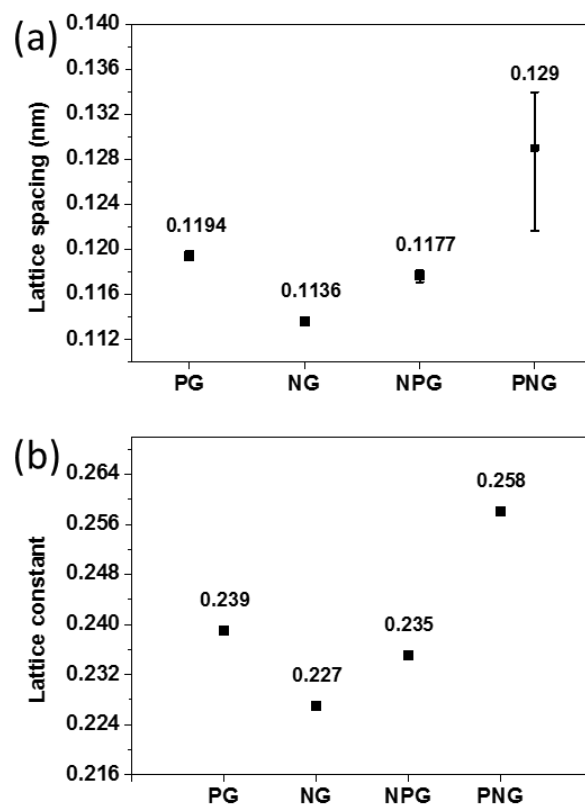
Fig. S5. (a) The lattice spacing and (b) constants for PG, NG, NPG, PNG of d_{110}.
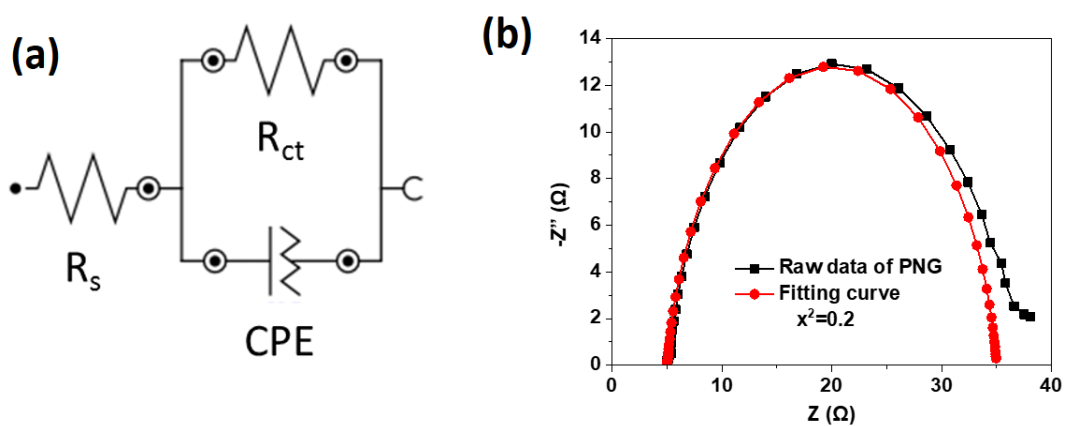

Fig. S6. (a) The corresponding equivalent circuit (R_{ct}: charge-transfer resistance; R_s: internal resistance of solution and electrode). (b) The equivalent circuit to simulate the EIS curve of PNG sample.

Table S1. Percentage of various elements and N- and P- functional groups in the singly and co-doped graphene from XPS

At. %	C	O	P	N	P-C	P-O	Pyridinic-N	Pyrrolic-N	Graphitic-N
PG	78.8	15.2	6.0	--	3.17	2.83	--	--	--
NG	88.2	6.8	--	5.0	--	--	3.05	1.20	0.75
NPG	83.1	9.2	4.2	3.5	2.43	1.77	1.68	0.56	1.26
PNG	81.3	8.4	4.0	6.3	2.58	1.42	4.16	1.26	0.88

Table S2. Comparison of overpotential (@10 mA/cm^2), Tafel slopes and exchange current density of present work with the literature reports on metal-free or non-precious metal carbon/graphene materials.

Catalysts	Precursor	Doping method	Temperature and doping efficiency	η@10 mA/cm^2 (mV, RHE)	Tafel slope (mV/dec)	Exchange current density (mA/cm^2)	Ref.
PG	Red phosphorous	Pyrolysis	700 ^{o}C; P: 6.0%	--	347.6	76.3	This work
NG	NH$_3$ gas	CVD	900 ^{o}C; N: 5.0%	--	405.0	86.0	This work
NPG	Red phosphorous & NH$_3$ gas	Pyrolysis & CVD	900 ^{o}C; P: 4.2% N: 3.5%	--	565.1	265.0	This work
PNG	Red phosphorous & NH$_3$ gas	Pyrolysis & CVD	900 ^{o}C; P: 4.0% N: 6.3%	379.7	125.5	21.0	This work
N-doped graphene	melamine	Pyrolysis	950 ^{o}C; N: 4.6%	490.0	116.0	7.0×10^{-5}	2
P-doped graphene	triphenylphosphine	Pyrolysis	950 ^{o}C; P: 1.6%	553.0	133.0	9.0×10^{-6}	2
N, P-doped graphene	melamine & triphenylphosphine	Pyrolysis	950 ^{o}C; P: 1.6% N: 4.6%	422.0	91.0	2.44×10^{-4}	2
N-doped graphene	pyridine	CVD	800 ^{o}C; N: 1.9%	559.0	232.0	3.7×10^{-3}	3
N, P-doped graphene	dicyandiamide & triphenylphosphine	Pyrolysis	900 ^{o}C; P: 2.1% N: 42.1%	340.0	90.0	3.33×10^{-3}	4
N,P-doped carbon networks	melamine & phytic acid	Pyrolysis	1000 ^{o}C; P: ~2% N: ~3%	163.0	89.0	1.6×10^{-1}	5
N, P-doped carbon nanotube	1,4-butylenebisphosphonic acid & N$_2$ gas	Pyrolysis	800 ^{o}C; P: 5.4% N: 3.2%	550.0	139.3	--	6
C$_3$N$_4$@NG hybrid	melamine	Pyrolysis	600 ^{o}C; N: 55.2%	240.0	51.5	3.5×10^{-4}	7

N,P-codoped carbon networks	phytic acid	Pyrolysis	1000 ºC; P: ~2.00% N: ~3.00%	290.0	89.0	0.16	8
N, P co-doped porous carbon	phytic acid & PANI-PA	Pyrolysis	900 ºC; P: 1.77% N: 3.27%	151.0	69.0	--	9
MoS_x/3D-graphene	$(NH_4)_2MoS_4$	Pyrolysis	100 ºC Mo:S=0.39	163.0	41.0	1.1×10^{-3}	10
N, P doped hollow carbon/ MoS_2	aniline & pyrrole & NaH2PO4	Annealing	900 ºC; P: 1.18% N: 3.00%	178.0	58.0	--	11
Cu_3P/ N, P doped Carbon	HEDP & pyrazine & NaH_2PO_2	Annealing	650 ºC; P: N:	89.0	76.0	--	12

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