Supplementary Information

Nitrogen-Enriched Polydopamine Analogue-Derived Defect-Rich Porous Carbon as Bifunctional Metal-Free Electrocatalysts for Highly Efficient Overall Water Splitting

Zheye Zhang,[a] Zhengran Yi,[a] Juan Wang,[a] Xin Tian,[a] Pei Xu,[a] Gaoquan Shi,[b] and Shuai Wang[a]*

[a]Key laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, 430074, China

[b]Department of Chemistry, Tsinghua University, Beijing, 100084, China

Corresponding author: *E-mail: chmsamuel@mail.hust.edu.cn (S. Wang).

1. Supplementary Figures

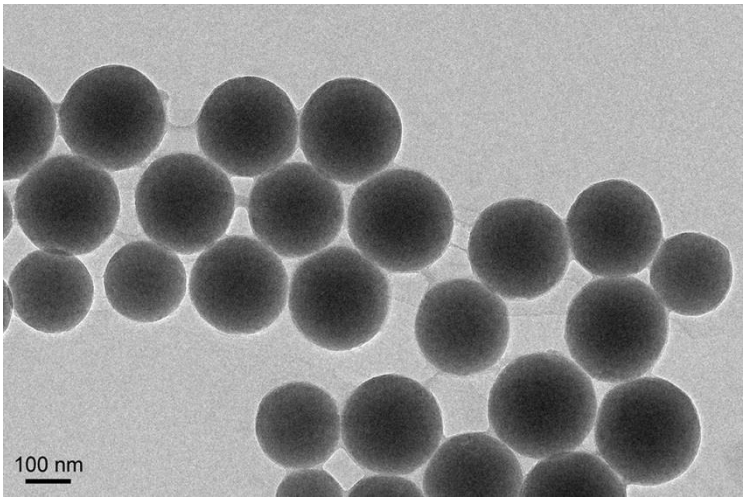

Figure S1. TEM image of spherical SiO_2 sample.

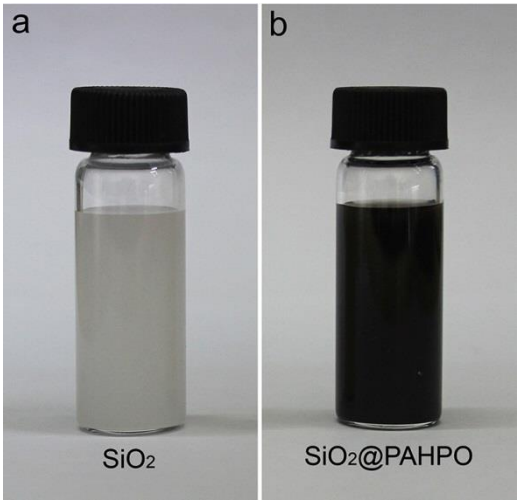

Figure S2. Photographs of (a) SiO_2 dispersion and (b) Polymerized dispersion.

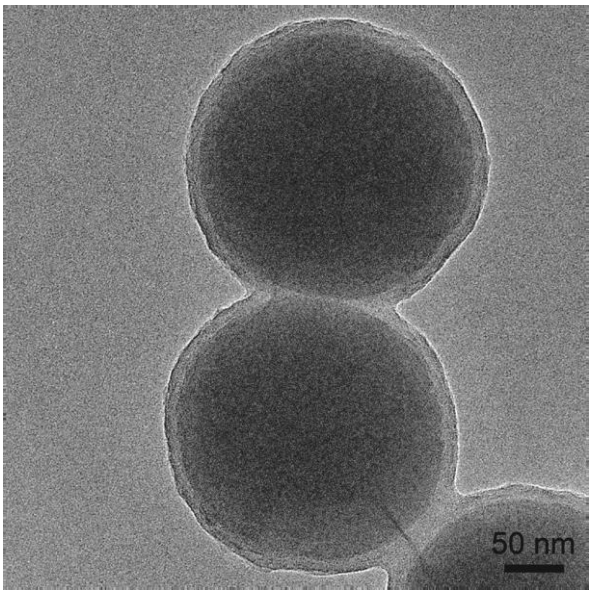

Figure S3. TEM image of SiO_2@PAHPO.

Figure S4. A photograph of DRPC powder.

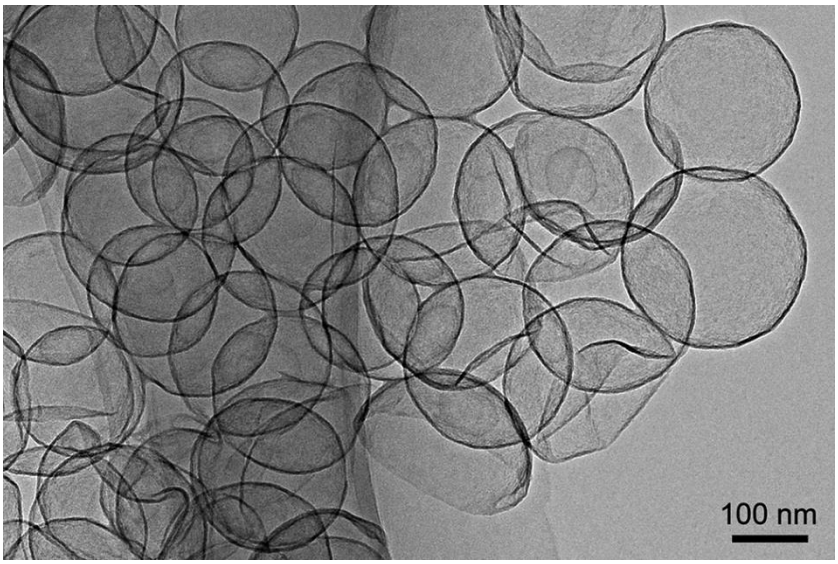

Figure S5. TEM image of PC.

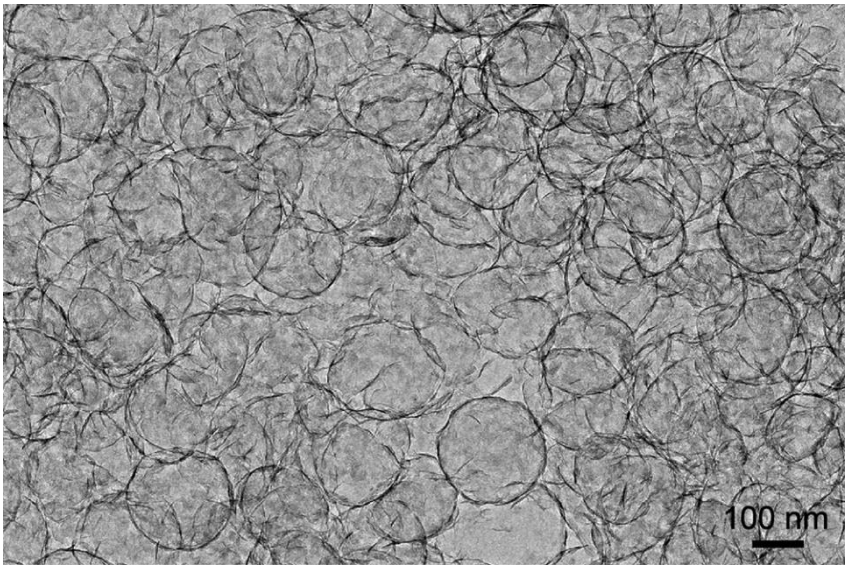

Figure S6. TEM image of DRPC.

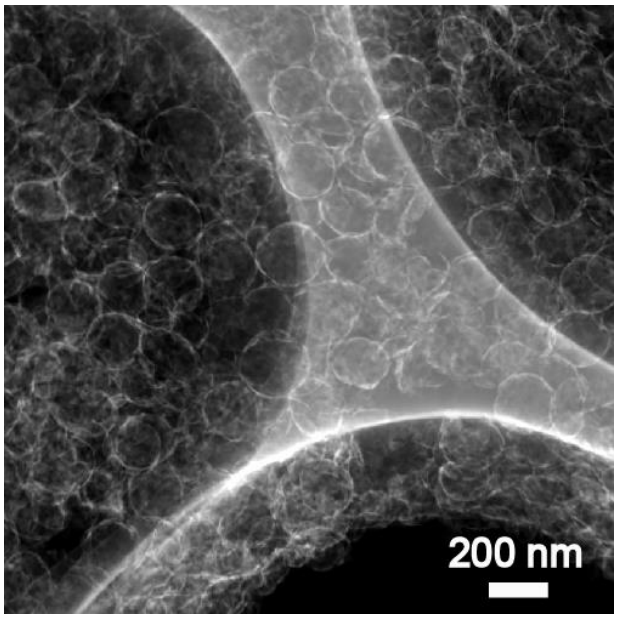

Figure S7. STEM image of DRPC.

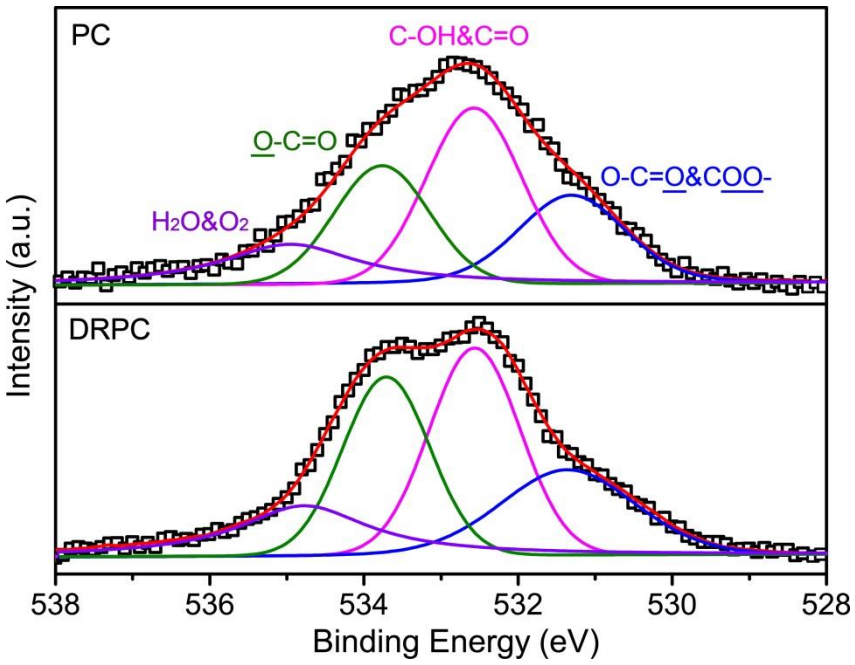

Figure S8. High-resolution XPS spectra of the O 1s core level for PC and DRPC.

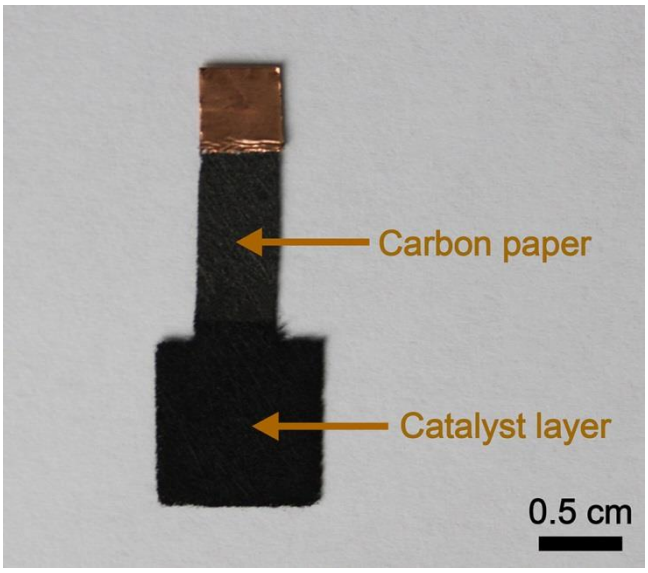

Figure S9. A photograph of DRPC catalyst on carbon fiber paper.

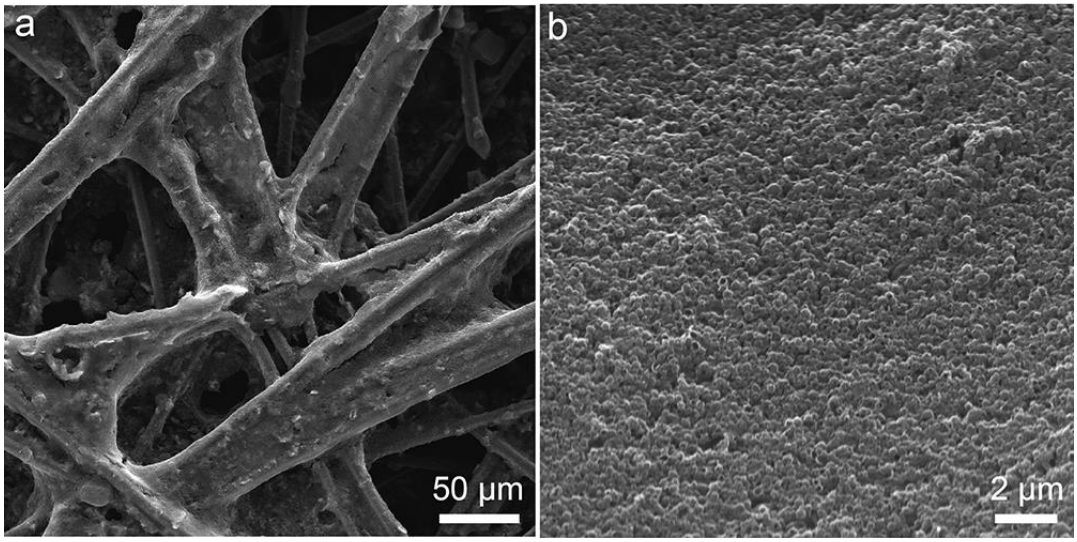

Figure S10. SEM images of the DRPC catalyst on carbon fiber paper.

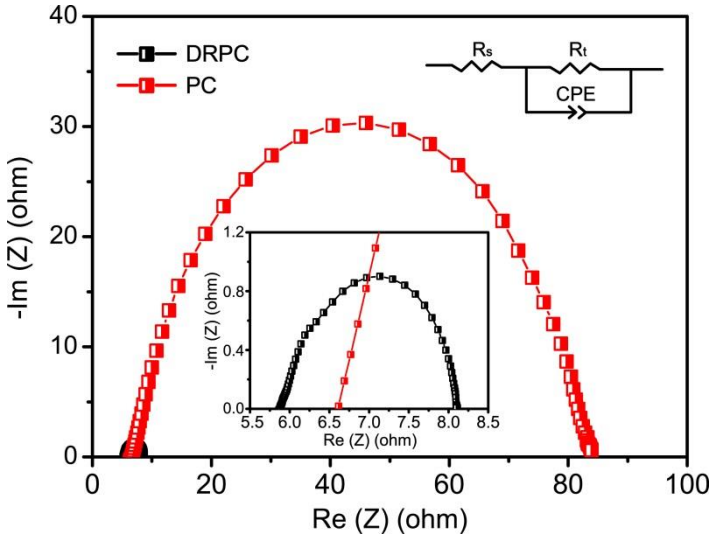

Figure S11. EIS plots of the catalysts. The inset is the enlarged version of the DRPC and PC catalysts.

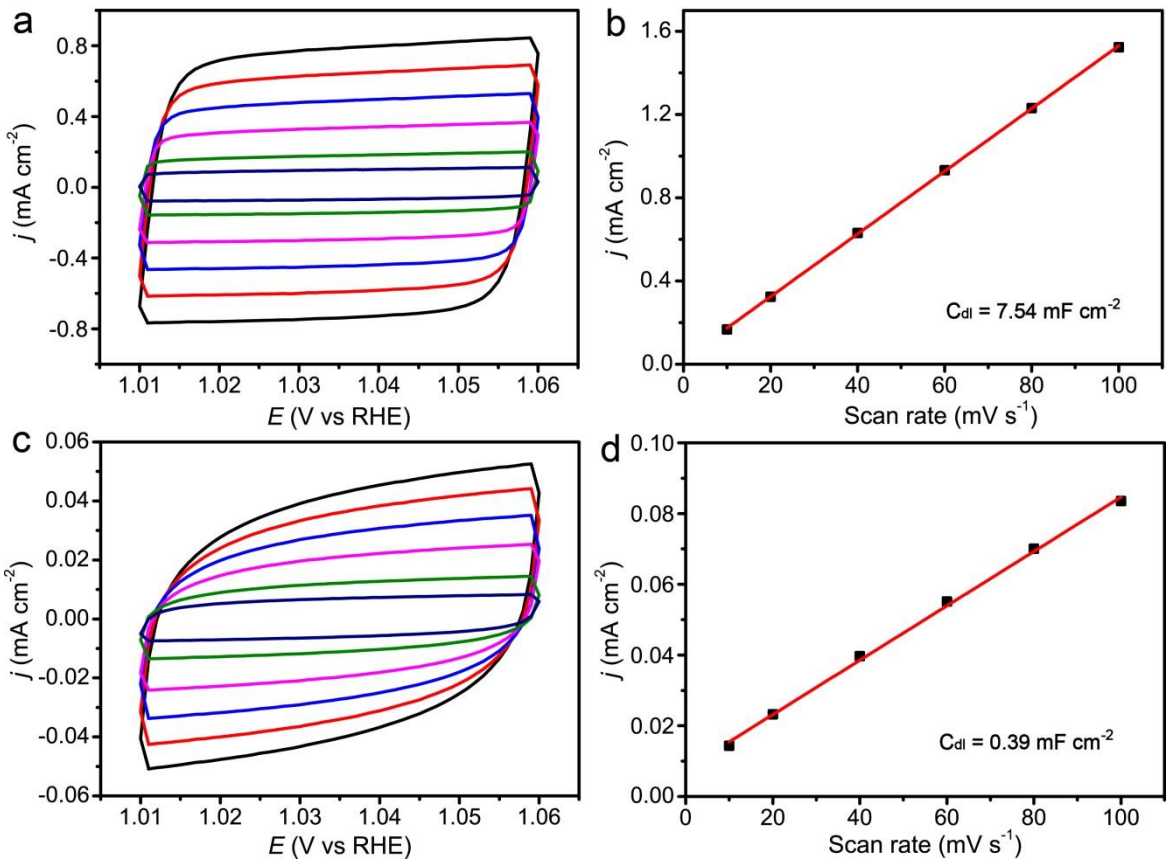

Figure S12. CV curves of (a) DRPC and (c) PC with various scan rates (10, 20, 40, 60, 80 and 100 mV s^{-1}). The charging current density differences plotted against scan rates for (b) DRPC and (d) PC. The calculated C_{dl} values are shown in insets.

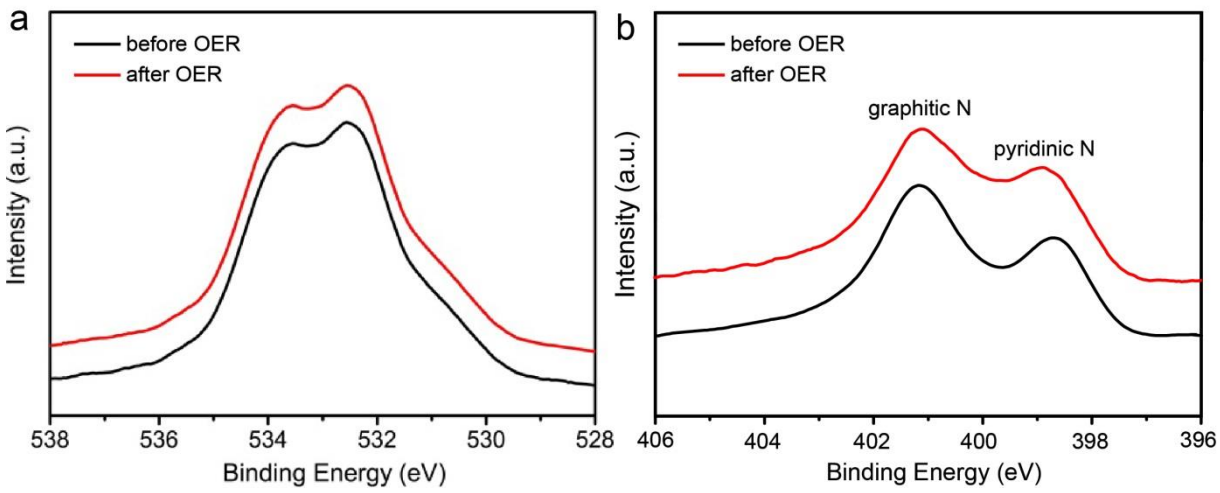

Figure S13. (a) The O 1s and (b) N 1s spectra of DRPC catalysts before and after OER tests.

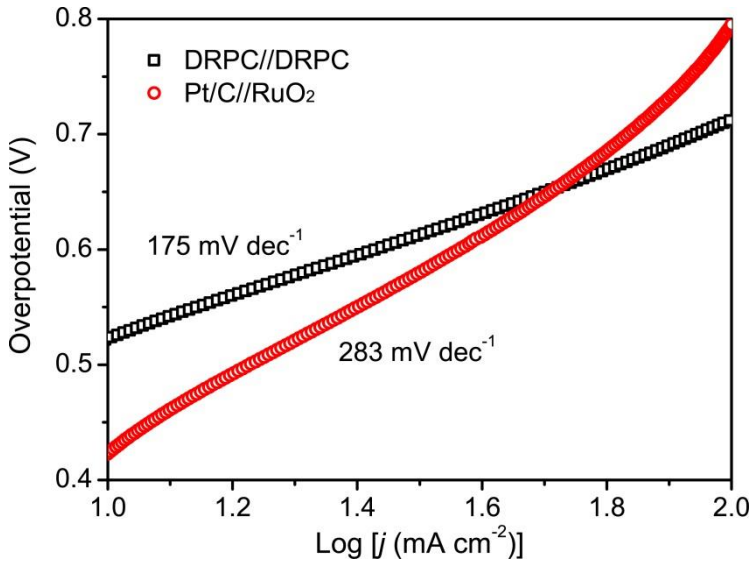

Figure S14. Tafel plots of the DRPC//DRPC and Pt/C//RuO_2 electrolysers. The calculated Tafel slope values are shown in insets.

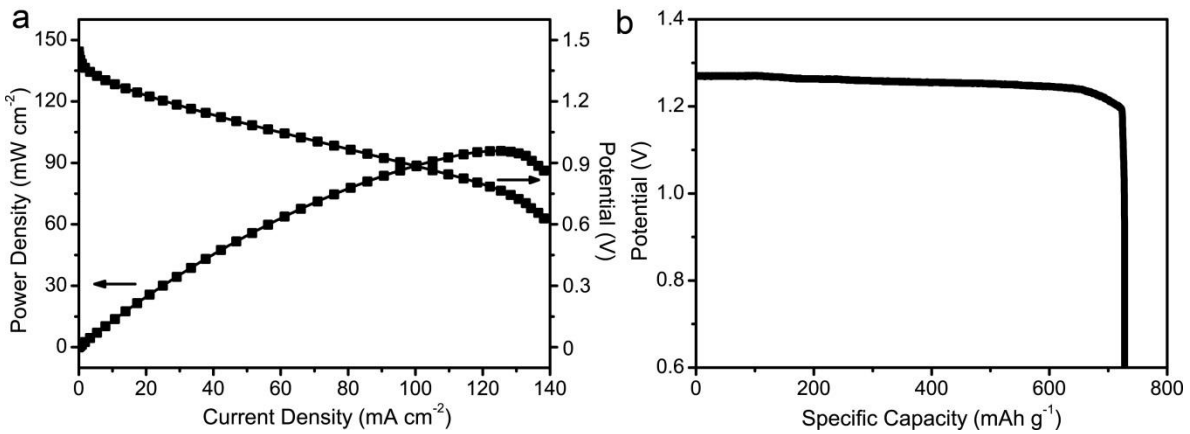

Figure S15. (a) Polarization and power density curves of primary Zn-air battery using DRPC as the ORR electrocatalyst. (b) Long-time galvanostatic discharge curves of primary Zn-air battery with DRPC as cathode catalyst until complete consumption of Zn anode.

2. Supplementary tables

Table S1. HER parameters of the typical comparable samples.

Catalyst	Catalyst loading (mg cm^{-2})	η_{10} (mV)	Tafel slope (mV dec^{-1})	Electrolyte	Ref.
DRPC	**0.16**	**217**	**98**	**1.0 M KOH**	**This work**
C_3N_4@NG	0.10	~240	51	0.5 M H_2SO_4	Nat. Commun. 2014, 5, 3783
N,S-G	0.20	~274	/	1.0 M KOH	Adv. Mater. 2017, 29, 1604942
N,P-G	0.20	~422	91	0.5 M H_2SO_4	ACS Nano 2014, 8, 5290
N,O,P-G	0.10	~446	154	1.0 M KOH	Energy Environ. Sci. 2016, 9, 1210
N,S-CNT	0.20	~450	133	1.0 M KOH	Adv. Energy Mater. 2017, 7, 1602068
N-G	0.20	~488	/	0.5 M H_2SO_4	ACS Nano 2014, 8, 5290
S-G	0.20	~550	/	0.5 M H_2SO_4	ACS Nano 2014, 8, 5290
Amorphous Co_2B	0.21	~328	92	1.0 M KOH	Adv. Energy Mater. 2016, 6, 1502313
Co-NRCNT	0.28	~370	/	1.0 M KOH	Angew. Chem., Int. Ed. 2014, 53, 4372
Co-NG	0.28	~270	/	1.0 M NaOH	Nat. Commun. 2015, 6, 8668
CoO_x@CN	0.12	~232	/	1.0 M KOH	J. Am. Chem. Soc. 2015, 137, 2688

η_{10}: current density @ 10 mA cm^{-2}

Table S2. OER parameters of the typical comparable samples.

Catalyst	Catalyst loading (mg cm^{-2})	η_{10} (mV)	Tafel slope (mV dec^{-1})	Electrolyte	Ref.
DRPC	**0.16**	**360**	**57**	**1.0 M KOH**	**This work**
B-CNTs	0.04	~600	51	1.0 M KOH	Electrochim. Acta 2014, 143, 291
N,S-G	0.20	~450	/	1.0 M KOH	Adv. Mater. 2017, 29, 1604942.
N,O,P-G	0.10	~400	84	1.0 M KOH	Energy Environ. Sci. 2016, 9, 1210
N-PCC	8.00	~360	98	1.0 M KOH	Energy Environ. Sci. 2016, 9, 3411
N,S-GF	/	~355	78	1.0 M KOH	Adv. Energy Mater. 2016, 6, 1501492
N,S-CNT	0.20	~360	56	1.0 M KOH	Adv. Energy Mater. 2017, 7, 1602068
RuO_2	0.16	~385	98	1.0 M KOH	This work
Amorphous Co_2B	0.21	~380	45	1.0 M KOH	Adv. Energy Mater. 2016, 6, 1502313
Ni-NG	/	~370	190	1.0 M KOH	Energy Environ. Sci., 2013, 6, 3693
CoO-NG	0.70	~340	71	1.0 M KOH	Energy Environ. Sci. 2014, 7, 609

η_{10}: current density @ 10 mA cm^{-2}

Table S3. Atomic content of PC and DRPC calculated from the XPS survey spectra.

Sample	C	O	N
PC	90.29 %	6.69 %	3.02 %
DRPC	80.29 %	10.35 %	9.36 %

Table S4. The sp^2, sp^3 carbon, C-O&C-N, C=O relative content and sp^2/sp^3 in the samples of PC and DRPC.

C species	sp^2	sp^3	C-O&C-N	C=O	sp^2/sp^3
PC	57.6 %	21.7 %	13.5 %	7.2 %	2.65
DRPC	51.3 %	23.9 %	15.7 %	9.1 %	2.14

Table S5. The percent composition for C-O, C=O and oxygen or absorbed water in the samples of PC and DRPC.

O species	COO-&O-C=O	C-OH&C=O	O-C=O	O_2&H_2O
PC	1.48 %	2.62 %	1.72 %	0.87 %
DRPC	1.98 %	3.92 %	2.89 %	1.56 %

3. Supplementary vedio

Video S1. The evolution of H_2 and O_2 in the DRPC catalyst couple-based alkaline water electrolyzer (20 mA cm^{-2} overall water splitting current).