Supporting Information

Trifunctional Ni-N/P-O-codoped graphene electrocatalyst enables dual-model rechargeable Zn-CO_2/Zn-O_2 batteries

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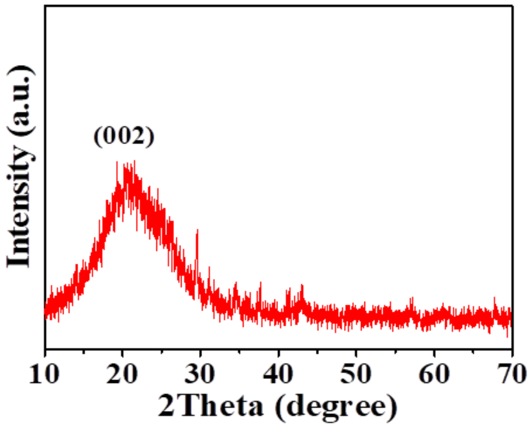

Figure S1. XRD patterns of NiPG.

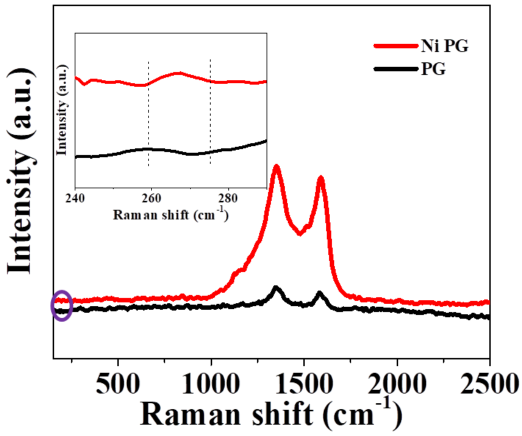

Figure S2. Raman spectra of NiPG and PG. The inset profile is the purple circle area.

There was obvious peak could be observed around 265 cm^{-1} by Raman which was marked in inset profile, suggesting the absence of Ni-N bond[1].

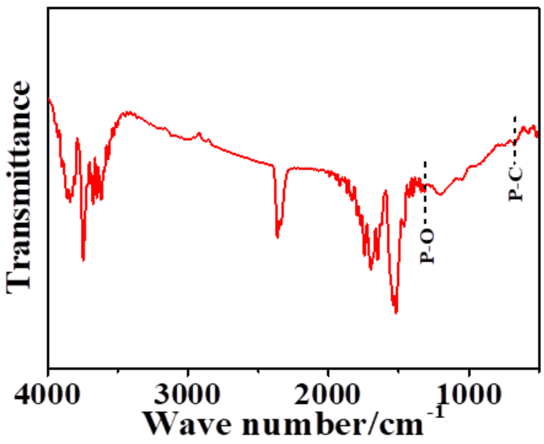

Figure S3. IR spectrum of NiPG.

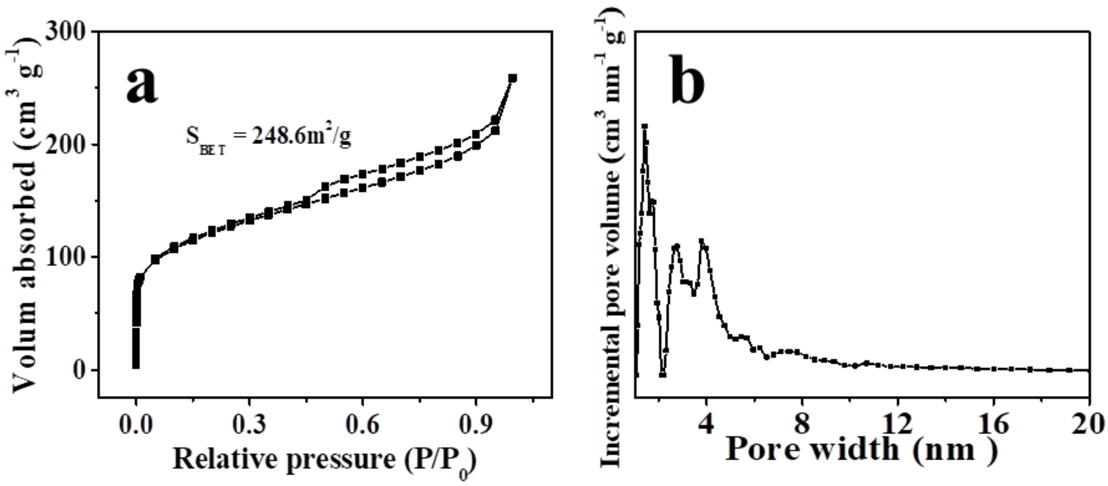

Figure S4. BET characterization of NiPG. (a) Nitrogen adsorption-desorption isotherm and (b) corresponding pore size distribution curve of NiPG.

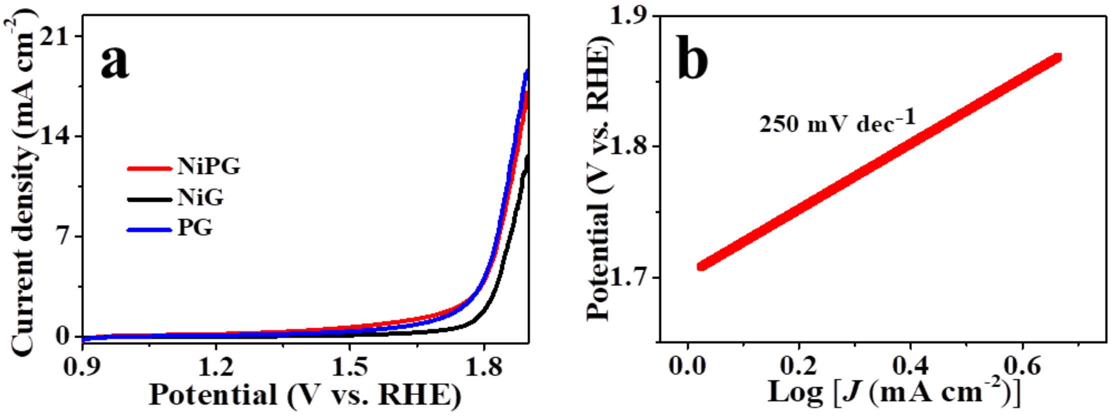

Figure S5. Neutral OER performance on NiPG, NiG and PG. (a) Neutral OER LSV curve and (b) Tafel slope of NiPG. Electrolyte: 3 M $KHCO_3$ solution including 1.5 M KCl.

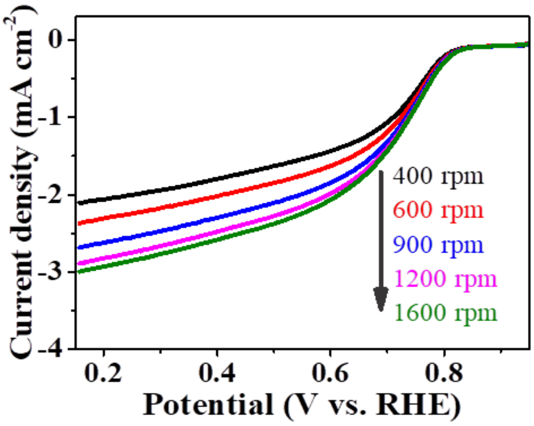

Figure S6. ORR LSV curves on NiPG at a series of rotating speeds. Electrolyte: 0.1 M KOH solution.

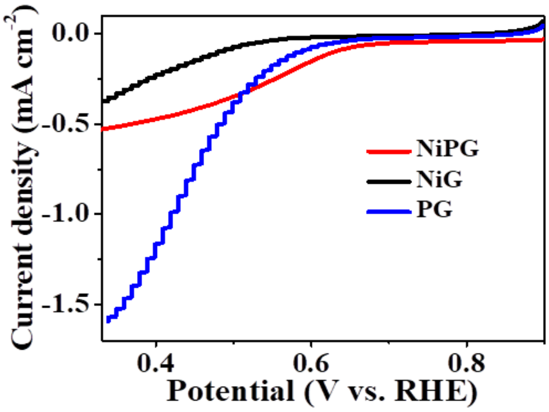

Figure S7. Neutral ORR performance on NiPG, NiG and PG. Electrolyte: 3 M $KHCO_3$ solution including 1.5 M KCl.

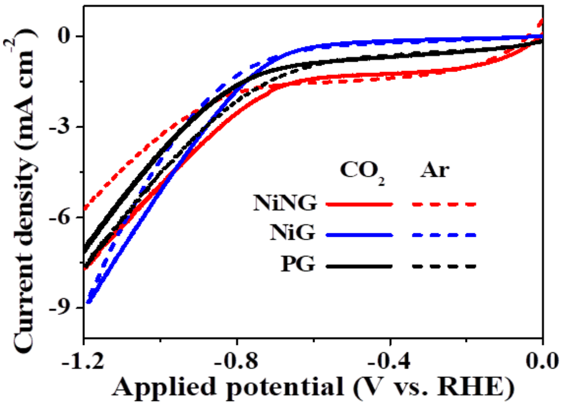

Figure S8. LSV scan of CDRR on NiPG, NiG and PG. Electrolyte: CO_2 saturated 0.1 M $KHCO_3$ solution.

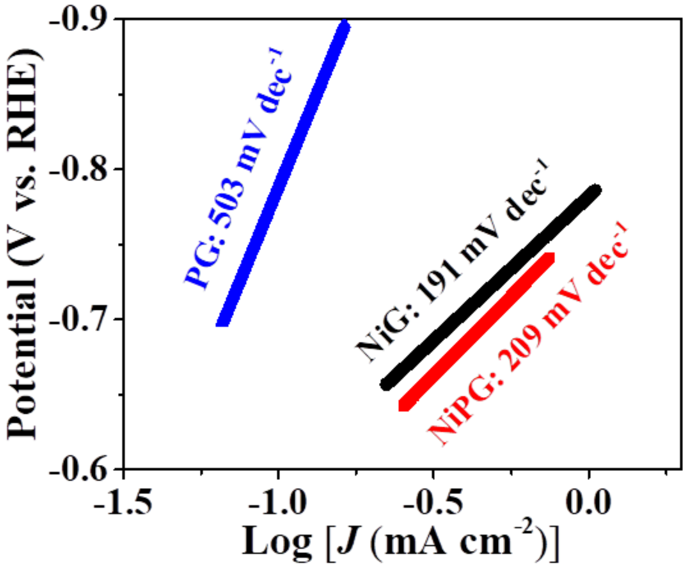

Figure S9. Tafel slope of CDRR on NiPG, NiG and PG. Electrolyte: 0.1 M $KHCO_3$ solution saturated with CO_2.

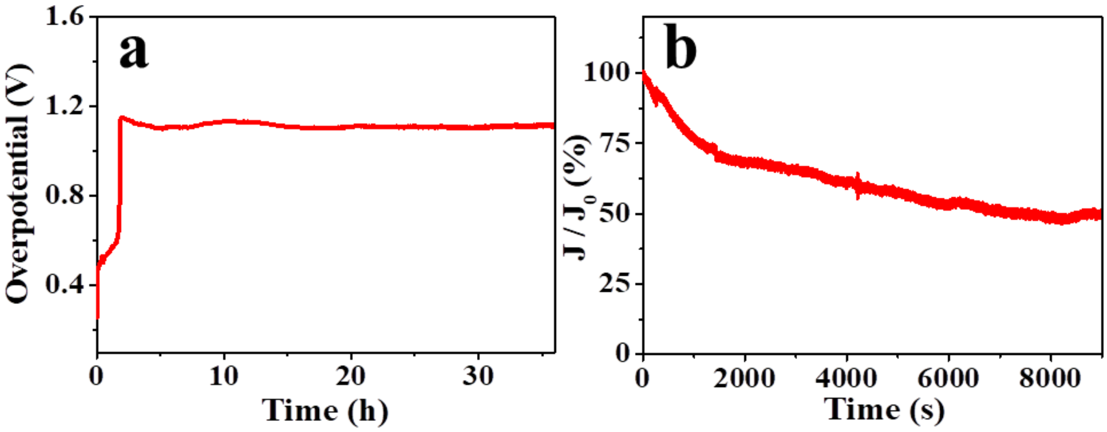

Figure S10. Electrocatalytic durability on NiPG in alkaline solution. (a) OER in 1 M KOH and (b) ORR in 0.1 M KOH solution.

The OER test was conducted at a constant current density of 5 mA cm^{-2} and the ORR test was conducted at a potential of 0.714 V vs. RHE.

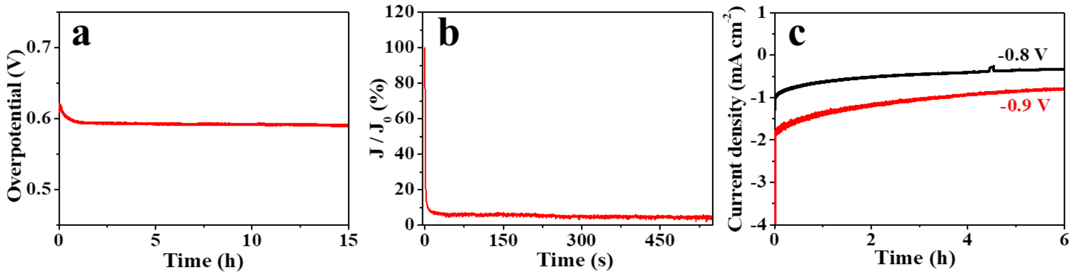

Figure S11. Electrocatalytic durability on NiPG in neutral solution. (a) OER and (b) ORR in 3 M $KHCO_3$ including 1.5 M KCl solution, and (c) CDRR in 0.1 M $KHCO_3$ solution, respectively.

The OER test was conducted at a constant current density of 5 mA cm^{-2}. The ORR test was conducted at a potential of 0.45 V vs. RHE. The CDRR was tested at a potential of -0.8 V and -0.9 V vs. RHE.

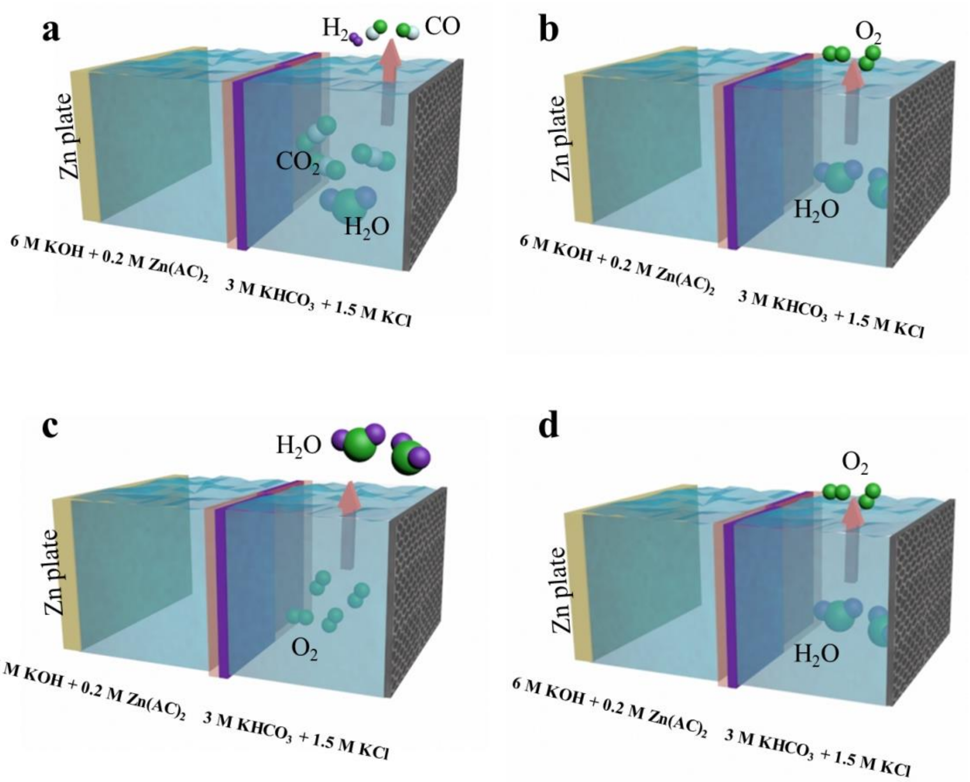

Figure S12. The scheme of aqueous rechargeable dual-model battery device. Zn CO_2 battery mode of (a) discharge and (b) charge process. Zn O_2 battery model of (c) discharge and (d) charge process.

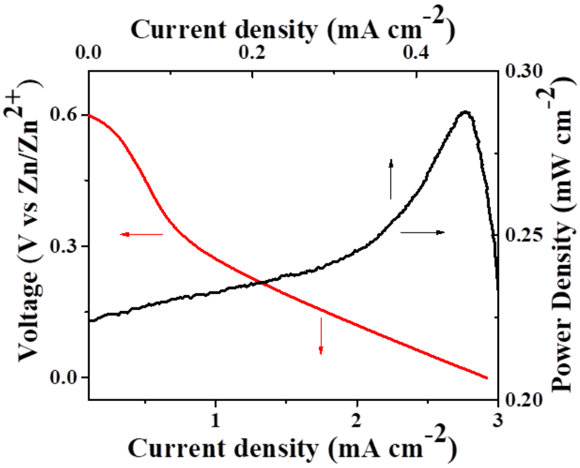

Figure S13. The Polarization and power density curves of rechargeable Zn-CO_2 batteries with NiPG as cathode.

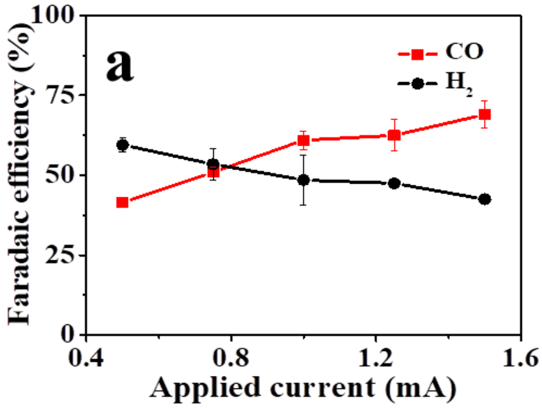

Figure S14. CO and H_2 FEs of Zn-CO_2 batteries with error bar at a series of discharge currents.

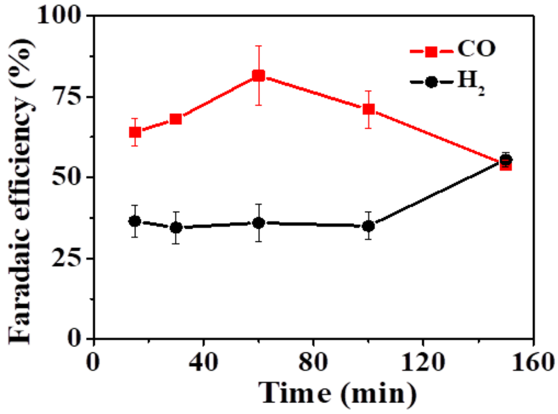

Figure S15. CO and H_2 FEs of Zn-CO_2 batteries at discharge current of 0.5 mA.

Table S1. Comparison in OER and ORR performance of some multifunctional catalysts reported recently in literatures.

Catalysis	E (V) @j_{10} (1 M KOH)	$E_{1/2}$ (V) (0.1 M KOH)	Ref.
	OER	ORR	
NiPG	1.65	0.736	This work
N,P and F tri-doped Graphene	1.80	0.72	Angew. Chem. Int. Ed., 2016, 55, 13296-13300
Co/N-C-800	1.60	0.74	Nanoscale, 2014, 6, 15080-15089
Fe@N-C-700	1.71	0.83	Nano Energy, 2015, 13, 387-396
$Fe-N_4$ SAs/NPC	1.66	0.885	Angew. Chem. Int. Ed., 2018, 57, 8614-8618
N/Co-doped PCP//NRGO	1.66	0.86	Adv. Funct. Mater., 2015, 25, 872-882
N-graphene/CNT	1.65	0.69	Angew. Chem. Int. Ed., 2014, 53, 6496-6500
Defect Graphene	[a]N.A.	0.76	Adv. Mater. 2016, 28, 9532–9538
Fe-N/C-800	N.A.	0.899	J. Am. Chem. Soc. 2016, 138, 3570-3578
Fe-N/C-800	N.A.	0.81	J. Am. Chem. Soc. 2015, 137, 5555-5562

Note: [a]N.A. stands for not given. All the potentials are calibrated and converted to reversible hydrogen electrode.

Table S2. Summary of overpotentials for CO_2 reduction to CO on reported catalysts

Catalysis	Electrolyte	Initial CO FE (overpotential)	Max CO FE (overpotential)	Ref.
NiPG	0.1 M $KHCO_3$	56% (530 mV)	>90% (690mV)	This work
Ni-N-Gr	0.1 M $KHCO_3$	20% (390 mV)	~90% (590 mV)	Small 2016, 12, 6083-6089
Ni-N4	0.5 M $KHCO_3$	67% (290 mV)	99% (700mV)	J. Am. Chem. Soc. 2017, 139, 14889-14892
NCNTs	0.5 M $NaHCO_3$	<10% (290 mV)	90% (790 mV)	ChemSusChem 2016, 9, 1085-1089
FC	0.1 M $KHCO_3$	~58% (370 mV)	89% (510 mV)	Angew. Chem. Int. Ed. 2018, 57, 9640 – 9644
3D NG	0.1 M $KHCO_3$	25% (190 mV)	85% (470 mV)	Nano Lett. 2016, 16, 466 – 470

Note: All the potentials are calibrated and converted to reversible hydrogen electrode.

Reference:

[1] R. Wysokinski, B. Morzyk-Ociepa, T. Glowiak, D. Michalska, *J. Mol. Struct.* **2002**, *606*, 241-251.