## **Supporting Information**

## Trifunctional Fishbone-like PtCo/Ir Enables High-performance Zinc-air Batteries to Drive the Water-splitting Catalysis

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**Figure S1.** (a, b) Representative TEM images of the products with the same reaction conditions as that of PtCo/Ir FBNWs except the use of 0 mg CTAC, (c, d) 0 mg glucose and (e, f) 0 mg Co(acac)<sub>3</sub>.



Figure S2. (a) Low- and (b) high-magnification TEM images of PtCo/Ir FBNWs.



Figure S3. XPS spectra of PtCo/Ir FBNWs. (a) Full survey, (b) Pt 4f, (c) Ir 4f and (d) Co 2p.



**Figure S4.** (a) The atomic resolution HAADF-STEM image of PtCo/Ir FBNW. (b) HAADF-STEM image of a single PtCo/Ir FBNW. The inset is FFT pattern of PtCo/Ir FBNW.



**Figure S5.** TEM-EDS images of PtCo/Ir FBNWs intermediates collected from (a) 15 min, (b) 60 min, (c) 180 min, (d) 240 min, (e) 300 min and (f) 480 min.



**Figure S6.** TEM (a, c, e, g) and TEM-EDS (b, d, f, h) images of products with the same reaction conditions as that of PtCo/Ir FBNWs except the use of (a, b) 0 mg, (c, d) 4 mg, (e, f) 8 mg and (g, h) 16 mg Ir(acac)<sub>3</sub>.



**Figure S7.** TEM (a) and TEM-EDS images (b) of products with the same reaction condition as that of PtCo/Ir FBNWs except the use of 20 mg Ir(acac)<sub>3</sub>.



Figure S8. PXRD patterns of rough  $Pt_{79}Co_{21}$  NWs,  $Pt_{65}Co_{27}/Ir_8$  FBNWs,  $Pt_{62}Co_{23}/Ir_{15}$  FBNWs and  $Pt_{50}Co_{24}/Ir_{26}$  FBNWs.



**Figure S9.** (a) PXRD patterns and (b,c) STEM images of  $Pt_{62}Co_{23}/Ir_{15}$  FBNWs/C before and after thermal treatment.



Figure S10. XPS spectra of  $Pt_{62}Co_{23}/Ir_{15}$  FBNWs/C. (a) Pt 4f, (b) Ir 4f and (c) Co 2p.



Figure S11. CVs of different catalysts recorded at room temperature in 0.1 M  $HClO_4$  solution at a sweep rate of 50 mV/s.



**Figure S12.** The HER overpotentials of various catalysts at current densities of 10 mA cm<sup>-2</sup> in 0.1 M  $HClO_4$  solution.



**Figure S13.** (a) ECSA- and (b) mass- normalized HER polarization curves of different catalysts in 0.1 M HClO<sub>4</sub> solution.



**Figure S14.** (a) ECSA- and (b) mass- normalized OER polarization curves of different catalysts in 0.1 M HClO<sub>4</sub> solution.



**Figure S15.** The OER overpotentials of various catalysts at current density of 10 mA cm<sup>-2</sup> in 0.1 M  $HClO_4$  solution.



Figure S16. XRD patterns of  $Pt_{62}Co_{23}/Ir_{15}$  FBNWs before and after HER and OER tests.



Figure S17. XPS spectra of  $Pt_{62}Co_{23}/Ir_{15}$  FBNWs/C. (a) Pt 4f and (b) Ir 4f.



**Figure S18.** (a) HER and (c) OER polarization curves of  $Pt_{62}Co_{23}/Ir_{15}$  FBNWs before and after 5,000 cycles in 0.1 M HClO<sub>4</sub> solution. CA tests of Pt/C and  $Pt_{62}Co_{23}/Ir_{15}$  FBNWs/C for (b) HER and (d) OER in 0.1 M HClO<sub>4</sub> solution.



Figure S19. TEM images of  $Pt_{62}Co_{23}/Ir_{15}$  FBNWs/C after (a, b) HER and (c, d) OER durability tests.



**Figure S20.** (a) CV activation process of  $Pt_{62}Co_{23}/Ir_{15}$  FBNWs/C for OER. TEM-EDS images of  $Pt_{62}Co_{23}/Ir_{15}$  FBNWs/C after (b) activation process and (c) durability tests, respectively.



**Figure S21.** (a) HER polarization curves and (b) TOF values of PtCo/Ir FBNWs/C, PtCo NWs/C and commercial Pt/C in 0.1 M KOH solution. (c) OER polarization curves and (d) TOF values of PtCo/Ir FBNWs/C, PtCo NWs/C and commercial Pt/C in 0.1 M KOH solution.



**Figure S22.** Polarization curves of  $Pt_{62}Co_{23}/Ir_{15}$  FBNWs/CFP and Pt/C-Ir/C for overall water-splitting catalysis in (a) 0.1 M KOH solution and (b) 0.1 M PBS solution at a scan rate of 5 mV s<sup>-1</sup>.



**Figure S23.** (a) ORR polarization curves and (b) histogram of mass and specific activities of Pt/C and  $Pt_{62}Co_{23}/Ir_{15}$  FBNWs/C. (c) Cycling performance of the rechargeable zinc–air batteries based on the  $Pt_{62}Co_{23}/Ir_{15}$  FBNWs/C and commercial Pt/C+IrO<sub>2</sub> at 2 mA cm<sup>-2</sup> with 10 min discharge and 10 min charge.



**Figure S24.** The (a) 1<sup>th</sup>, (b) 10<sup>th</sup> and (c) 20<sup>th</sup> discharge/charge profiles. (d) Cycling performance of the aprotic lithium-O<sub>2</sub> batteries with  $Pt_{62}Co_{23}Ir_{15}$  FBNWs/C and carbon as cathodes with a limited capacity of 1000 mAh g<sup>-1</sup> at the current density of 200 mA g<sup>-1</sup>.

Electrocatalysts	Pt loading (µg/cm <sup>2</sup> )	Ir loading (µg/cm²)
Commercial Pt/C	8.7	
Commercial Ir/C		8.2
Pt <sub>79</sub> Co <sub>21</sub> NWs/C	8.3	
Pt <sub>65</sub> Co <sub>27</sub> /Ir <sub>8</sub> FBNWs/C	8.8	1.0
Pt <sub>62</sub> Co <sub>23</sub> /Ir <sub>15</sub> FBNWs/C	8.4	1.98
$Pt_{50}Co_{24}/Ir_{26}FBNWs/C$	9.2	4.7

**Table S1.** The Pt or Ir loading of different catalysts on the glass carbon electrode (calculated by ICP-AES).

	Pt	PtO <sub>x</sub>	Ir	IrO <sub>x</sub>
Before annealing	59.2	40.8	56.1	43.9
After annealing	59.1	40.9	55.9	44.1

**Table S2.** Proportions of metallic and oxidation states for Pt and Ir before and after 220 °C thermal annealing.

Catalysts	ECSA (m <sup>2</sup> /g)
Commercial Pt/C	59.9
Commercial Ir/C	43.7
Pt <sub>79</sub> Co <sub>21</sub> NWs/C	49.8
Pt <sub>65</sub> Co <sub>27</sub> /Ir <sub>8</sub> FBNWs/C	62.6
Pt <sub>62</sub> Co <sub>23</sub> /Ir <sub>15</sub> FBNWs/C	66.4
Pt <sub>50</sub> Co <sub>24</sub> /Ir <sub>26</sub> FBNWs/C	61.7

 Table S3. ECSA values of various catalysts.

Catalysts	Ir loading µg/cm²	Electrolyte	Current density	η/mV	References
Pt <sub>62</sub> Co <sub>23</sub> /Ir <sub>15</sub> FBNWs	1.98	0.1 M HClO <sub>4</sub>	10 mA/cm <sup>2</sup>	308	This work
IrCoNi PHNC	10	0.1 M HClO <sub>4</sub>	10 mA/cm <sup>2</sup>	303	Adv. Mater., 2017, 29, 1703798
IrNi oxide	~20	0.1 M HClO <sub>4</sub>	10 mA/cm <sup>2</sup>	310	J. Am. Chem. Soc., 2015, 137,13031
Ir <sub>0.7</sub> Ru <sub>0.3</sub> Ox	60	0.5 M H <sub>2</sub> SO <sub>4</sub>	100 A/g	270	Nano Energy <b>2017</b> , <i>34</i> , 385
IrW	10.2	0.1 M HClO <sub>4</sub>	8.1 mA/cm <sup>2</sup>	300	ACS Cent. Sci., 2018, 4, 1244
Ir WNWs	~31	0.5 M HClO <sub>4</sub>	10 mA/cm <sup>2</sup>	270	Nanoscale, <b>2018</b> , 10, 1892
Ir <sub>6</sub> Ag <sub>9</sub> NTs	13.3	0.05M H <sub>2</sub> SO <sub>4</sub>	10 mA/cm <sup>2</sup>	296	Nano Energy <b>2019</b> , <i>56</i> , 330
Ir <sub>3</sub> Cu	~25	0.1 M HClO <sub>4</sub>	10 mA/cm <sup>2</sup>	298	ACS Energy Lett. 2018, 3, 2038
IrNi	10.2	0.1 M HClO <sub>4</sub>	10 mA/cm <sup>2</sup>	293	Small Methods 2019, 1900129
Ir/GF	820	0.5 M H <sub>2</sub> SO <sub>4</sub>	10 mA/cm <sup>2</sup>	290	Nano Energy <b>2017</b> , 40, 27
Co-IrCu ONC	20	0.1 M HClO <sub>4</sub>	10 mA/cm <sup>2</sup>	293	Adv. Funct. Mater. 2017, 27, 1604688
IrNi <sub>0.56</sub> Fe <sub>0.82</sub>	~92	0.5 M HClO <sub>4</sub>	$10 \text{ mA/cm}^2$	284	J. Mater. Chem. A 2017, 5, 24836

**Table S4.** Comparisons of OER activities of  $Pt_{62}Co_{23}/Ir_{15}$  FBNWs with those of recently reported Irbased OER catalysis in acidic electrolyte.

	Pt	PtO <sub>x</sub>	Ir	IrO <sub>x</sub>
Before tests	59.1	40.9	55.9	44.1
After HER	58.9	41.1	55.7	44.3
After OER	61.8	38.2	51.9	48.1

**Table S5.** Proportions of metallic and oxidation states for Pt and Ir before and after HER and OER electrochemical test.

Catalysts	Ir loading µg/cm <sup>2</sup>	Electrolyte	Current density	η/mV	References
Pt <sub>62</sub> Co <sub>23</sub> /Ir <sub>15</sub> FBNWs	8	0.1 M HClO <sub>4</sub>	10 mA/cm <sup>2</sup>	300	This work
IrCoNi PHNC		0.5 M H <sub>2</sub> SO <sub>4</sub>	2 mA/cm <sup>2</sup>	330	Adv.Mater., 2017, 29, 1703798
IrNi	12.5	0.5 M H <sub>2</sub> SO <sub>4</sub>	10 mA/cm <sup>2</sup>	350	Adv. Funct. Mater.,2017,27,1700886
IrW	30	0.5 M H <sub>2</sub> SO <sub>4</sub>	10 mA/cm <sup>2</sup>	250	ACS Cent. Sci., 2018, 4, 1244
Ir/GF	820	0.5 M H <sub>2</sub> SO <sub>4</sub>	10 mA/cm <sup>2</sup>	320	Nano Energy <b>2017</b> , 40, 27
Ir WNWs	30.6	0.1 M HClO <sub>4</sub>	10 mA/cm <sup>2</sup>	390	Nanoscale, <b>2018</b> , 10, 1892
Ir <sub>6</sub> Ag <sub>9</sub> NTs		0.5 M H <sub>2</sub> SO <sub>4</sub>	10 mA/cm <sup>2</sup>	320	Nano Energy <b>2019</b> , <i>56</i> , 330
IrNi NFs	30	0.5 M H <sub>2</sub> SO <sub>4</sub>	10 mA/cm <sup>2</sup>	370	Small Methods 2019, 1900129
IrNi NCs	12.5	0.5 M H <sub>2</sub> SO <sub>4</sub>	10 mA/cm <sup>2</sup>	350	Adv. Funct. Mater. 2017, 27, 1700886
IrNi <sub>0.56</sub> Fe <sub>0.82</sub>	200	0.5 M HClO <sub>4</sub>	10 mA/cm <sup>2</sup>	410	J. Mater. Chem. A 2017, 5, 24836

**Table S6.** Comparisons of overall water splitting activities of  $Pt_{62}Co_{23}/Ir_{15}$  FBNWs with those of recently reported Ir-based overall water splitting catalysis in acidic electrolyte.