Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2017

Supporting Information

Cation Modulation Beneficial Electrocatalyst Derived from Bimetallic Metal-organic Frameworks for Overall Water Splitting

Yang Wang,[1,2] Wenting Wu,[1] Yuan Rao, [1] Zhongtao Li,[1] Noritatsu Tsubaki,*[,2] Mingbo Wu*[,1]

[1]State Key Laboratory of Heavy Oil Processing, College of Chemical Engineering, China University of Petroleum, Qingdao 266580, China

[2]Department of Applied Chemistry, Graduate School of Engineering, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan

*E-mail: tsubaki@eng.u-toyama.ac.jp (N. Tsubaki). Tel/Fax: (+81)-76-445-6846.

*E-mail:wumb@upc.edu.cn (M.B. Wu). Tel: (+86) 532-86983452. Fax: (+86) 532-86981787.

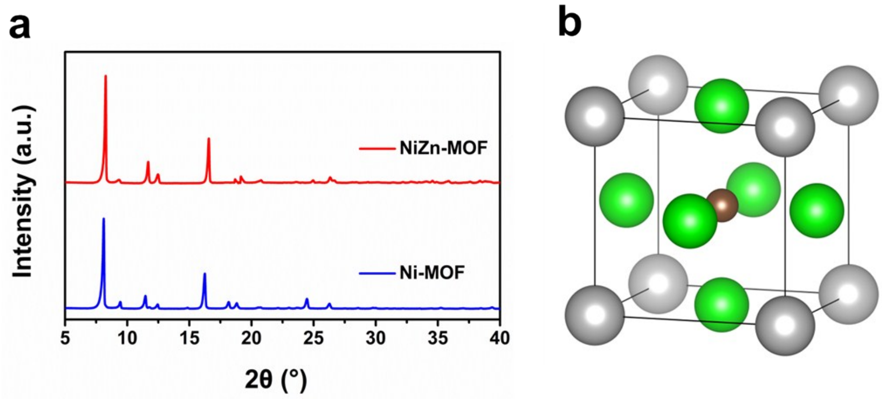

Fig. S1 (a)XRD patterns of Ni-MOF and bimetallic NiZn-MOF. (b) Cubic crystalline structure of $Ni_3ZnC_{0.7}$.

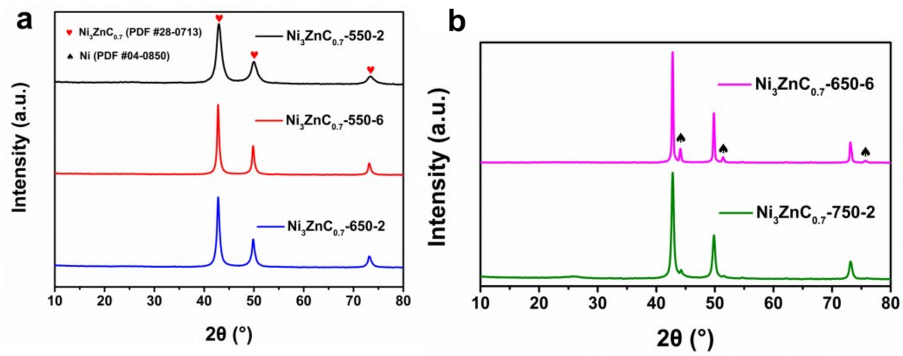

Fig. S2 (a) and (b) XRD patterns of catalysts prepared at different temperature (2 h and 6 h).

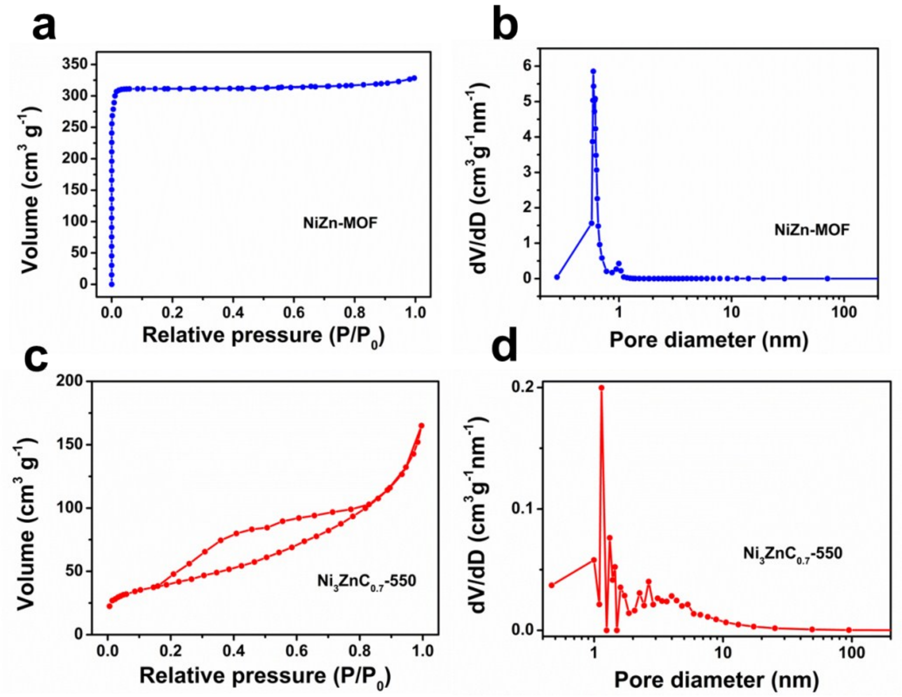

Fig. S3 N_2 adsorption and desorption isotherms of NiZn-MOF (a) and $Ni_3ZnC_{0.7}$-550 (c), pore size distribution of NiZn-MOF (b) and $Ni_3ZnC_{0.7}$-550 (d).

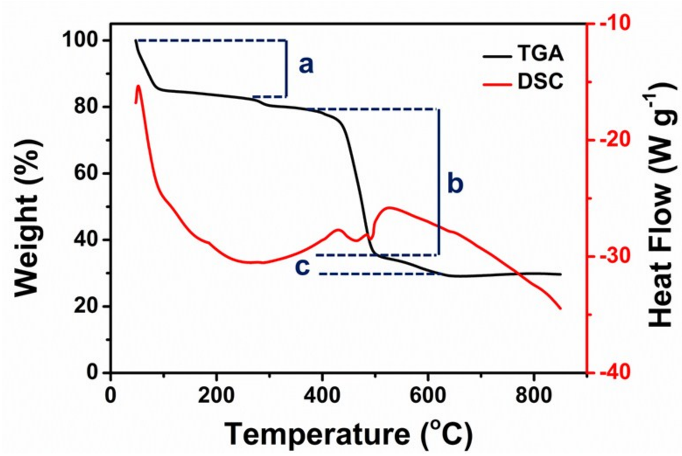

Fig. S4 TGA-DSC curves of NiZn-MOF measured in N_2 atmosphere.

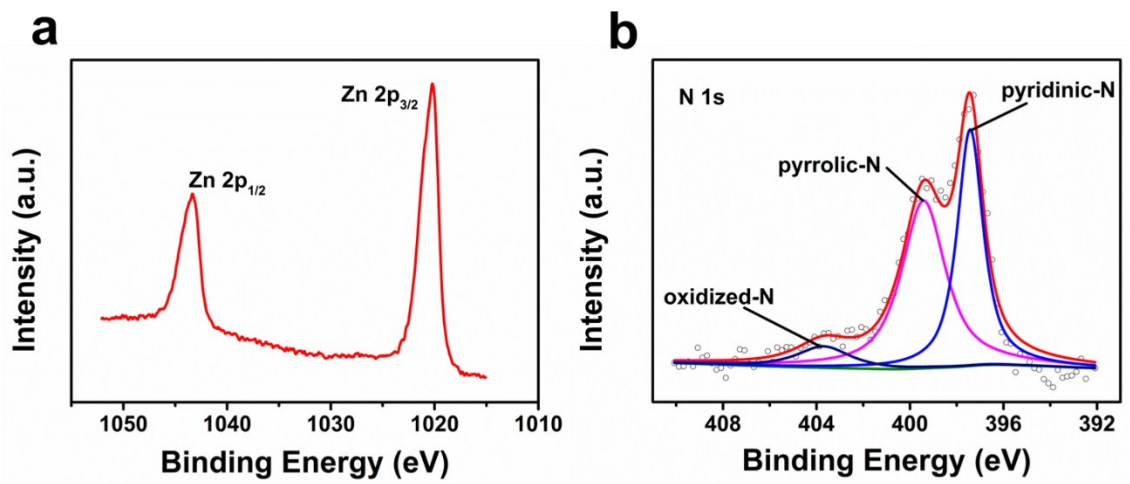

Fig. S5 High-resolution deconvoluted Zn 2p (a) and N 1s (b) spectra of $Ni_3ZnC_{0.7}$-550.

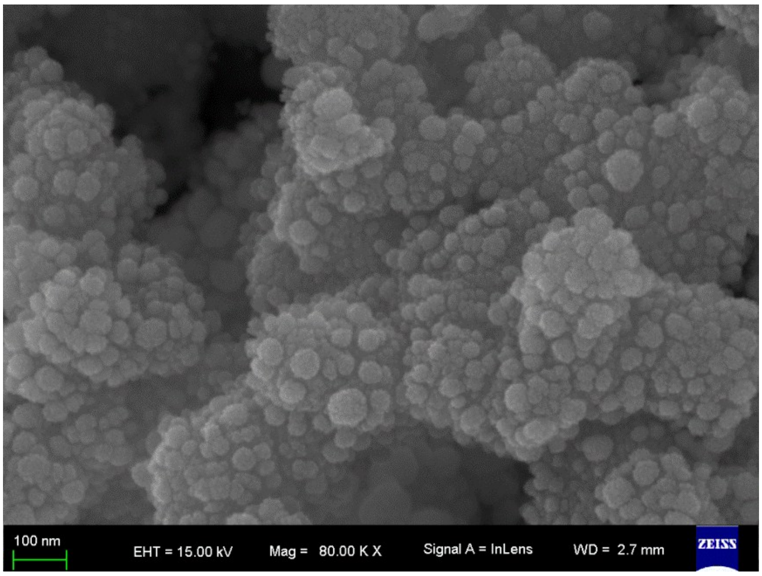

Fig. S6 SEM image of $Ni_3ZnC_{0.7}$-550.

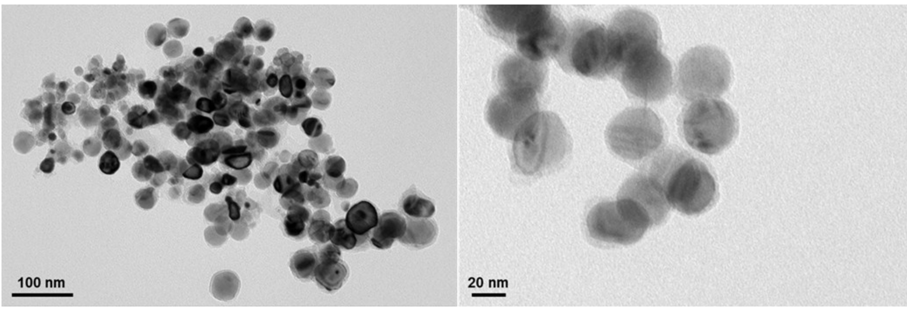

Fig. S7 TEM images of $Ni_3ZnC_{0.7}$-650.

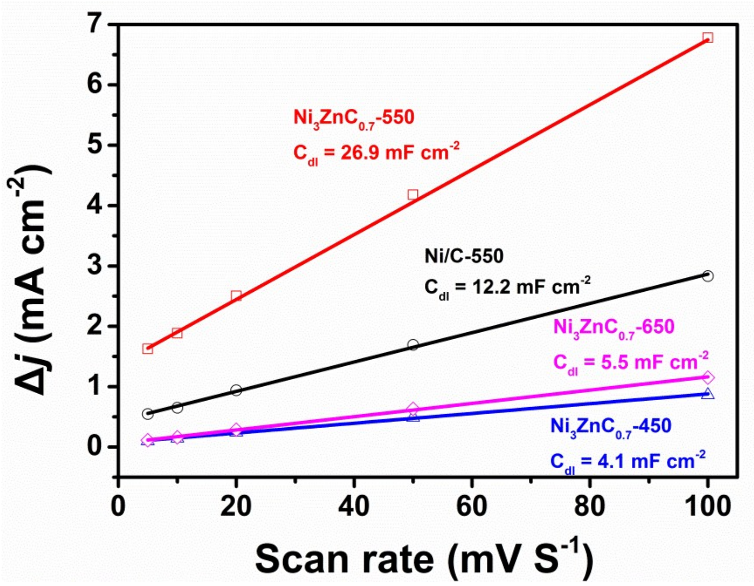

Fig. S8 The plots of Δ*j* with different scan rates. The double layer capacitance (*C*dl) was estimated from the linear slope.

The ECSA normalization electrocatalytic performance was calculated by setting the ECSA of $Ni_3ZnC_{0.7}$-650 as 1, so the ECSA of $Ni_3ZnC_{0.7}$-550 is 4.8. Before ECSA normalization, the needed potential to deliver 5 mA cm^{-2} of current density for $Ni_3ZnC_{0.7}$-650 (-300 mV) is 5 times more negative than that for $Ni_3ZnC_{0.7}$-550 (-60 mV). This narrowing gap after ECSA normalization (required -153 mV to deliver 5 mA cm^{-2} of current density for $Ni_3ZnC_{0.7}$-550) after ECSA normalization highlighs the role of ECSA in enhancing electrocatalytic performance.

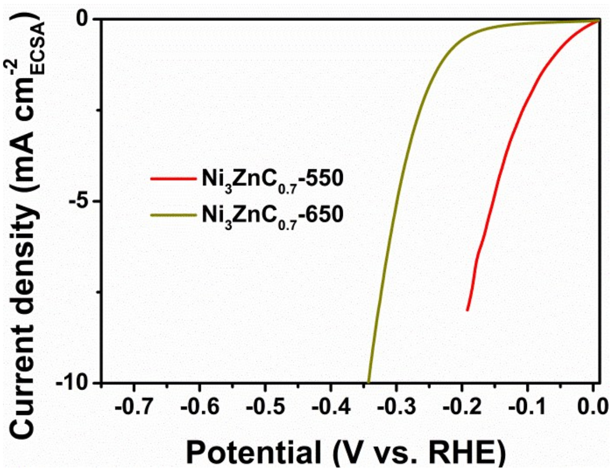

Fig. S9 Polarization curves of $Ni_3ZnC_{0.7}$-550 and $Ni_3ZnC_{0.7}$-650 normalized by the electrochemical active surface area (ECSA).

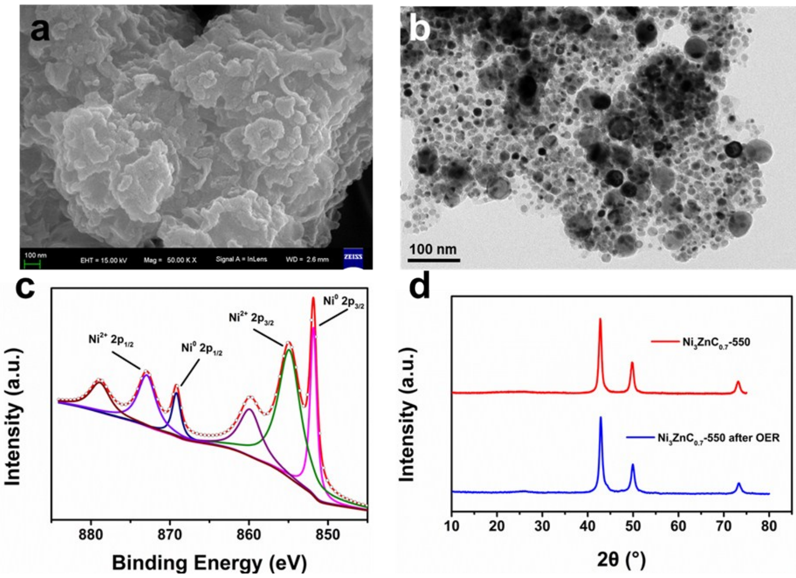

Fig. S10 (a) SEM and (b) TEM images of $Ni_3ZnC_{0.7}$-550 after long-term OER stability measurement. (c) XPS result of Ni 2p spectra of $Ni_3ZnC_{0.7}$-550 after long-term OER stability measurement. (d) XRD patterns of $Ni_3ZnC_{0.7}$-550 before and after long-term OER stability measurement.

Fig. S11 Photography of the electrolyte after overall water splitting for 24 h.

Table S1. Chemical and texture properties of NiZn-MOF and $Ni_3ZnC_{0.7}$-550

Sample	S_{BET} (m^2 g^{-1})	D (nm)	V (cm^3 g^{-1})	C (Atomic %)	N (Atomic %)	Ni (Atomic %)	Zn (Atomic %)
NiZn-MOF	1107	1.8	0.51	-	-	-	-
$Ni_3ZnC_{0.7}$-550	140	7.1	0.26	70.5	3.9	7.8	2.5
$Ni_3ZnC_{0.7}$-650	-	-	-	57.2	6.8	15.9	5.1

Table S2. Particle sizes of $Ni_3ZnC_{0.7}$ calculated by Scherrer equation[a]

Samples	Particle sizes (nm)
$Ni_3ZnC_{0.7}$-550-2	10.5
$Ni_3ZnC_{0.7}$-550-6	17.1
$Ni_3ZnC_{0.7}$-650-2	16.5
$Ni_3ZnC_{0.7}$-650-6	28.8
$Ni_3ZnC_{0.7}$-750-2	17.6

[a] The particle sizes are estimated from $Ni_3ZnC_{0.7}$ (111) peaks using the Scherrer equation: $D = K\lambda / \beta cos\theta$, where λ is the wavelength of the X-ray (λ = 0.154 nm), K is the Scherrer constant and a value of 0.9 is adopted, β is the full width at the half maximum (FWHM) of 2θ peaks.

Table S3. Comparison of the electrocatalytic activity of $Ni_3ZnC_{0.7}$-550 to recently reported catalysts for HER in basic solution

Catalyst	**Catalyst loading (mg cm^{-2})**	**Electrolyte**	**η at j = 10 mA cm^{-2} (mV)**	**Tafel slope (mV dec^{-1})**	**Reference**
$Ni_3ZnC_{0.7}$-550	~0.24	1 M KOH	93	48	this work
CoO_x@CN	0.12	1 M KOH	232	115	*J. Am. Chem. Soc.* **2015**, 137, 2688
Co-NRCNTs	0.28	1 M KOH	370	-	*Angew. Chem., Int. Ed.* **2014**, 53, 4372
Ni/CeO_2-CNT	0.14 (based on the mass of Ni)	1 M KOH	91	-	*Nano Lett.* **2015**, 15, 7704
NiO/Ni-CNT	0.28	1 M KOH	80	82	*Nat. Commun.* **2014**, 5, 4695
Co-P/NC	0.28	1 M KOH	191	51	*Chem.Mater*. **2015**, 27, 7636
CP/CTs/Co-S	0.32	1 M KOH	190	131	*ACS Nano*. **2016**, 10, 2342
CoP/rGO	0.28	1 M KOH	150	38	*Chem. Sci.* **2016**, 7, 1690
Hierarchical $NiCo_2O_4$ hollow microcuboids	1	1 M NaOH	110	49.7	*Angew. Chem., Int. Ed.* **2016**, 55, 1
Ni_3FeN	0.35	1 M KOH	158	42	*Adv. Energy Mater.* **2016**, 6, 1502585
Ni/NC	0.20	1 M KOH	219	101	*ACS Catal.* **2016**, 6, 580

Table S4. Comparison of the electrocatalytic activity of $Ni_3ZnC_{0.7}$-550 to recently reported catalysts for OER in basic solution

Catalyst	Catalyst loading (mg cm^{-2})	Electrolyte	ŋ at j = 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Reference
$Ni_3ZnC_{0.7}$-550	~0.24	1 M KOH	320	52	this work
CoO_x@CN	1	1 M KOH	260	-	*J. Am. Chem. Soc.* **2015**, 137, 2688
$Zn_xCo_{3-x}O_4$	1	1 M KOH	320	51	*Chem. Mater.* **2014**, 26, 1889
Co-P/NC	0.28	1 M KOH	354	52	*Chem.Mater*. **2015**, 27, 7636
Zn-Co-LDH	0.28	0.1 M KOH	520	-	*J. Am. Chem. Soc.* **2013**, 135, 17242
CP/CTs/Co-S	0.32	1 M KOH	306	72	*ACS Nano*. **2016**, 10, 2342
CoP/rGO	0.28	1 M KOH	340	66	*Chem. Sci.* **2016**, 7, 1690
Hierarchical $NiCo_2O_4$ hollow microcuboids	1	1 M NaOH	290	53	*Angew. Chem., Int. Ed*. **2016**, 55, 1
Ni_3FeN	0.35	1 M KOH	280	46	*Adv. Energy Mater*. **2016**, 6, 1502585
$Ni_{0.9}Fe_{0.1}$/NC	0.20	1 M KOH	330	45	*ACS Catal.* **2016**, 6, 580