# **Electronic Supplementary Information**

# Ultra-small intermetallic NiZn nanoparticles: a nonprecious metal catalyst for efficient electrocatalysis

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### Materials

All chemicals were used as received and stored in a glove box under nitrogen. Nickel(II) acetylacetonate (95%), oleylamine (OA, 70%), 1-octadecene (90%), trioctylphosphine (TOP, 90%), diethylzinc (DEZ, 1.0 M in hexane), ruthenium(IV) oxide and nafion were purchased from Sigma-Aldrich. Carbon black was obtained from Merck. Potassium hydroxide and isopropanol were procured from Sisco Research Laboratory (SRL), India.

#### Characterization

The morphology of the as-synthesized nanoparticles was characterized by transmission electron microscopy (TEM: FEI TECNAI G2 F20-ST) using an accelerating voltage of 200 kV after dropping the solution containing nanoparticles on a carbon coated copper grid, respectively. High resolution transmission electron microscopy (HRTEM) and Energy dispersive X-ray spectroscopy (EDX) analyses were performed in the above mentioned TEM. Powder X-ray diffraction (XRD) study was carried out on PANalytical X-PERT PRO powder diffractometer using Cu Ka radiation with 45 kV beam voltage and 40 mA beam current. X-ray photoelectron spectroscopy was carried out using a monochromatized Al K $\alpha$  (1486.6 eV) as X-ray source (Omicron Nanotechnology instrument). The energy scale of high-resolution Ni 2p and Zn 2p spectra were calibrated in reference to the adventitious carbon at 284.5 eV in binding energy (BE) scale to compensate the surface charge effects. Based on the straight line background subtraction method, the high resolution Ni 2p and Zn 2p photoelectron peaks were resolved into their respective Gaussian fits after background subtraction. Inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis was also performed using PerkinElmer ICP-OES instrument (PerkinElmer, Inc., Shelton, CT, USA) to estimate the concentration of Ni and Zn in Ni-Zn alloys.



Fig. S1 Histograms of particle size for (A) Ni NPs and corresponding (B) NiZn alloy.



Fig. S2 XPS spectra of Ni 2p in Ni NPs and corresponding NiZn order alloy.

#### Estimation of the electrochemically active surface area (ECSA)

Electrochemically active surface area (ECSA) is a crucial parameter in electrochemistry to determine the electrocatalytic activity of a catalyst. First, we have measured double-layer capacitance ( $C_{dl}$ ) for the calculation of ECSA, as they are proportional to each other. The  $C_{dl}$  was calculated by performing simple CVs at different scan rates, ranging from 10 to 50 mV s<sup>-1</sup>, in the non-Faradaic region in a narrow potential window from 1.1 to 1.2 V vs RHE. By plotting the half of the capacitive current density differences ( $\Delta j = j_{anode} - j_{cathode}$ ) at 1.15 V i.e.;  $\Delta j/2$  against the scan rate and fitting with a linear fit,  $C_{dl}$  can be estimated from the slope. The  $C_{dl}$  value of NiZn and Ni is 1.84 and 0.98 mF cm<sup>-2</sup> respectively. The ECSA was calculated from its  $C_{dl}$  according to this equation: ECSA =  $C_{dl}/C_s$ , where Cs is the specific capacitance for a flat standard with 1 cm<sup>2</sup> of real surface area. The general value for  $C_s$  is between 20 µF cm<sup>-2</sup> and 60 µF cm<sup>-2</sup>. Here, we use 40 µF cm<sup>-2</sup> as the average value (*Angew. Chem. Int. Ed.*, 2014, **53**, 14433; *ACS Appl. Energy Mater.*, 2019, **2**, 1199; *Nat. Commun.*, 2015, **6**, 8668; *J. Am. Chem. Soc.*, 2013, **135**, 16977). The ECSA was estimated to be 46 cm<sup>2</sup> and 24.4 cm<sup>2</sup> for NiZn and Ni respectively.



**Fig. S3** Cyclic voltammograms (CVs) of (A) Ni and (B) NiZn measured at different scan rates from 10 to 50 mV s<sup>-1</sup>.



**Fig. S4** TEM micrographs of NiZn intermetallics after prolonged chronoamperometry analysis at two different magnifications.



Fig. S5 XPS spectra of Ni 2p and Zn 2p of NiZn alloy after chronoamperometry study.



Fig. S6 (A) TEM micrograph of  $Ni_{07}Zn_{0.3}$  alloy. (B) XRD patterns of fcc Ni NPs and corresponding fcc  $Ni_{07}Zn_{0.3}$  and tetragonal NiZn alloys.



**Fig. S7** (A) LSV curves of Ni,  $Ni_{0.7}Zn_{0.3}$  and NiZn at a scan rate of 5 mV s<sup>-1</sup> in 1.0 M KOH solution and their corresponding (B) Tafel slopes indicate much faster OER kinetics of NiZn intermetallics.

Catalysts	Electrolyte	Overpotential (mV)	<b>Tafel Slope</b>	References
		at 10 mA cm <sup>-2</sup>	(mV dec <sup>-1</sup> )	
NiCo LDHs/GC		367	40	1
NiCo <sub>2</sub> O <sub>4</sub> /CNTs		390	68.1	2
NiCo-LDH		335	41	3
NiCo <sub>2</sub> S <sub>4</sub>		337	64	4
Fe-Ni-O <sub>x</sub> /GC		286	48	5
NiFe/CN <sub>x</sub>		360	59	6
Fe-mCo <sub>3</sub> O <sub>4</sub> /GC	H	380	60	7
Ni <sub>30</sub> Fe <sub>7</sub> Co <sub>20</sub> Ce <sub>43</sub> O <sub>x</sub> /GC	KOF	410	70	8
NiMo hollow nanorod	M	310	47	9
NiCo-LDH	1.0	420	113	10
NiCoP NPs		360	82	11
NiCo <sub>2</sub> O <sub>4</sub>		360	60	12
NiS@N/S-C		417	48	13
Ni@C-400 NSs		330	145	14
Ni <sub>x</sub> Fe <sub>3-x</sub> O <sub>4</sub>		402	53	15
NiZn		283	73	This work

Table S1 OER activity of NiZn alloys was compared with the reported Ni based electrocatalysts.

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