Supporting Information for

Design of Ultralong Single-Crystal Nanowire-Based Bifunctional Electrode for Efficient Oxygen and Hydrogen Evolution in Mild Alkaline Electrolyte

Ge Li,[a] *Xiaolei Wang,**[a,b] *Min Ho Seo,*[c] *Sahar Hemmati,*[a] *Aiping Yu,*[a] *and Zhongwei Chen**[a]

[a] Waterloo Institute for Nanotechnology, Department of Chemical Engineering, University of Waterloo, 200 University Avenue West, Waterloo, ON N2L3G1, Canada.

[b] Department of Mechanical and Industrial Engineering, Department of Chemical and Materials Engineering, Concordia University, 1455 De Maisonneuve Blvd. West, Montreal, QC H2G1M8, Canada.

[c] Hydrogen and Fuel Cell Center for Industry, Academy and Laboratories, New & Renewable Energy Research Division, Korea Institute of Energy Research (KIER), 20-41 Sinjaesaengeneogi-ro, Haseo-myeon, Buan-gun, Jellabuk-do, 56332, South Korea.

* The corresponding authors

Email address: xiaolei.wang@uwaterloo.ca (X. Wang) and zhwchen@uwaterloo.ca (Z. Chen)

1. Experimental Section

Chemicals: zinc nitrate hexahydrate, cobalt nitrate hexahydrate, urea, ammonium fluoride, potassium hydroxide were purchased from Sigma-Aldrich. All chemicals were used as received without any further purification.

Synthesis of Co-ZnO/CF Composite Electrode: Carbon fabric (CF) was cleaned by water, acetone and ethanol with ultrasonication for 30 min each to remove impurities before it was surface-functionalized by concentrated HNO_3 (65 wt%) at room temperature overnight and washed with distilled & deionized (DDI) water and dried under vacuum at 80 ^oC for 8 hours. In a typical fabrication of Co-ZnO/CF composite electrode, $Zn(NO_3)_2 \cdot 6H_2O$ (0.446 g), $Co(NO_3)_2 \cdot 6H_2O$ (1.0914 g), urea (0.225 g), and NH_4F (0.056 g) were completely dissolved in DDI water (30 mL) under stirring until the solution turned transparent. One piece of CF (5.0 cm * 5.0 cm) was placed into the solution under ultrasonication for 30 min. Then the solution and CF were transferred together into a 50 mL Teflon-lined autoclave, and kept at 180 ^oC for 10 hr. After the hydrothermal process, the obtained CF was rinsed with DDI water and ethanol repeatedly, and dried in vacuum at 80 ℃ overnight. The loading mass of the Co-ZnO@CF is around 1.0 mg cm^{-2}.

Synthesis of Co_3O_4 nanowires on carbon fibers. All the conditions are same as synthesis of Co-ZnO@CF nanowires, except exclude adding the chemical of $Zn(NO_3)_2 \cdot 6H_2O$. The loading mass of Co_3O_4@CF is around 1.0 mg cm^{-2}.

Materials Characterization. Scanning electron microscopy (SEM) was conducted using an LEO FESEM 1530 microscope. Transmission electron microscopy was performed using JEOL 2010F TEM/STEM field emission microscope equipped with a large solid angle for high X-ray throughput, scanning, scanning-transmission and a Gatan imaging filter for energy filtered imaging. X-ray photoelectron spectroscopy (XPS) spectra were collected on an Axis Ultra (Kratos Analytical, UK) XPS spectrometer equipped with an Al Ka source (1486.6 eV). X-ray diffractometer (XRD) measurements were performed on a Rigaku Miniflex 600 X-Ray Diffractometer (40 kV, 25 mA, Cu Kα radiation λ=1.5406) with the 2θ degree ranging from 5 to 80°.

Electrocatalytic Measurements. All electrocatalytic activity measurements were conducted on an electrochemical workstation (Biological VSP 300) in a three-electrode cell at room temperature. Linear sweep voltammetry with scan rate of 10 mV s^{-1} was conducted in 0.1 M KOH solution using saturated calomel electrode as the reference electrode. A Pt wire was used as the counter electrode. The Co-ZnO@CF and Co_3O_4@CF (1 cm × 1 cm) were directly used as the working electrode, respectively. Commercial 28.8 wt% Pt/C and 20 wt% Ir/C powders were prepared by ultrasonically mixing 4 mg of the catalyst powder with the mixture of 750 ul ethanol and 50 ul 5 wt% Nafion solution for 20 min to form homogeneous catalyst inks. Then, a certain amount of the catalyst ink was dropped onto the polished glassy carbon disk electrode (RDE), leading to 1 mg cm^{-2}. To make a more similar testing system of commercial materials, the catalyst inks were also dropped onto CF paper (1 cm × 1 cm) with a same loading mass 1 mg cm^{-2}. In all experiments, the electrolyte solutions were purged with N_2 for half hour prior to the experiments and during the testing of both hydrogen evolution reaction (HER) and Oxygen evolution reaction (OER) measurements.

For overall water splitting including HER and OER tests, the Co-ZnO@CF were used as both anode and cathode electrodes. To comparison, the 28% Pt/C@CF and 20% Ir/C@CF were also used as anode and cathode, respectively. The mass loading of these electrodes were controlled around 1.0 mg cm^{-2}. The potential scan range was from 1.0 to 2.0 V. The durability of the two-electrode system was performed using chronopotentiometric measurements. All currents presented are corrected against ohmic potential drop.

2. Supporting Figures

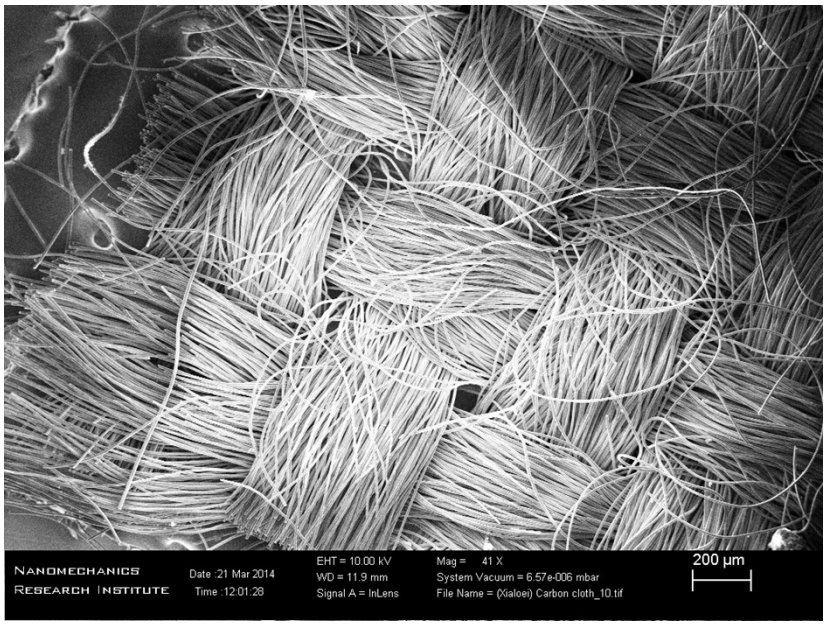

Figure S1. Representative SEM image of carbon fabric.

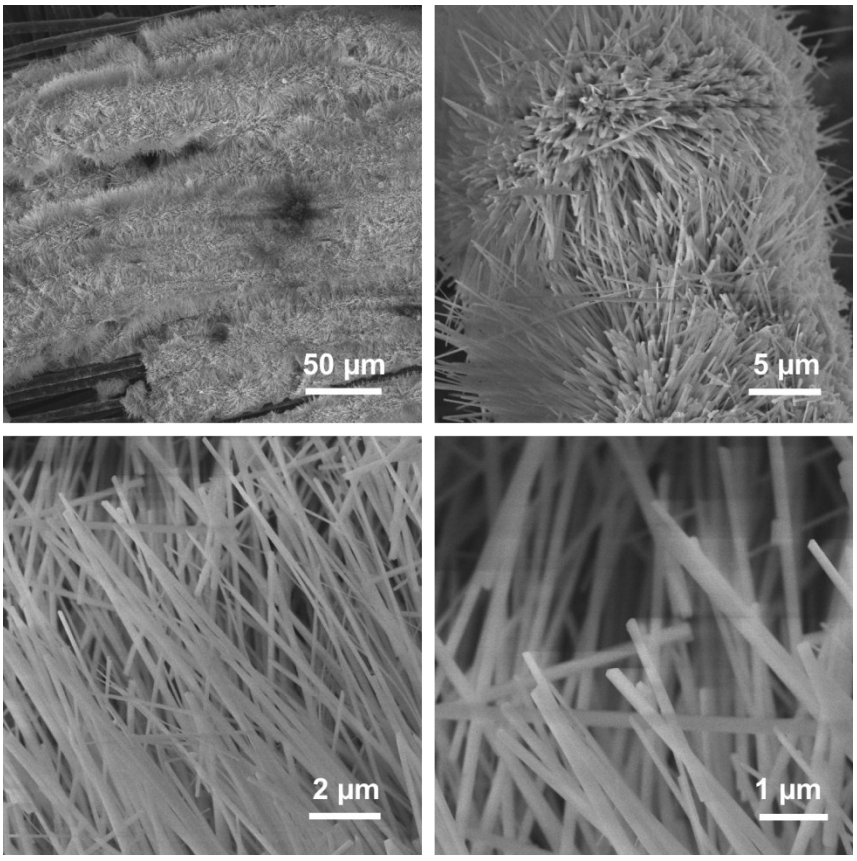

Figure S2. Representative SEM images of Co_3O_4/CF composite electrode at different magnifications.

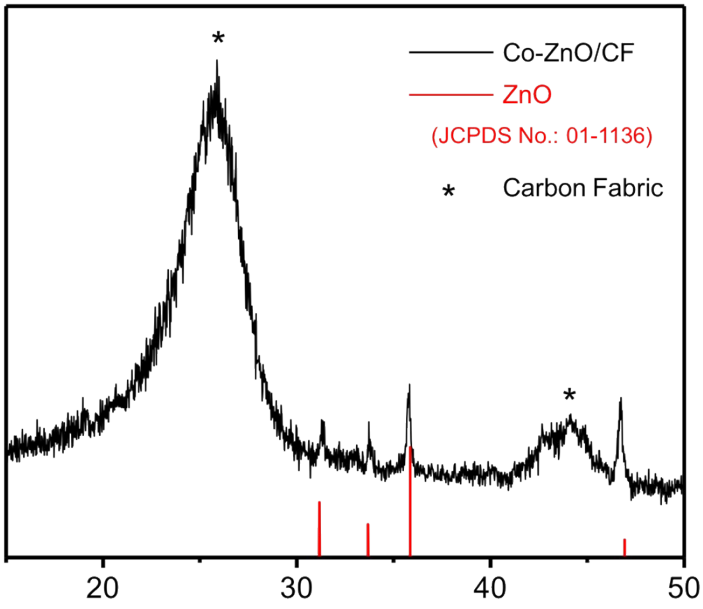

Figure S3. XRD pattern of the Co-ZnO/CF composite electrode.

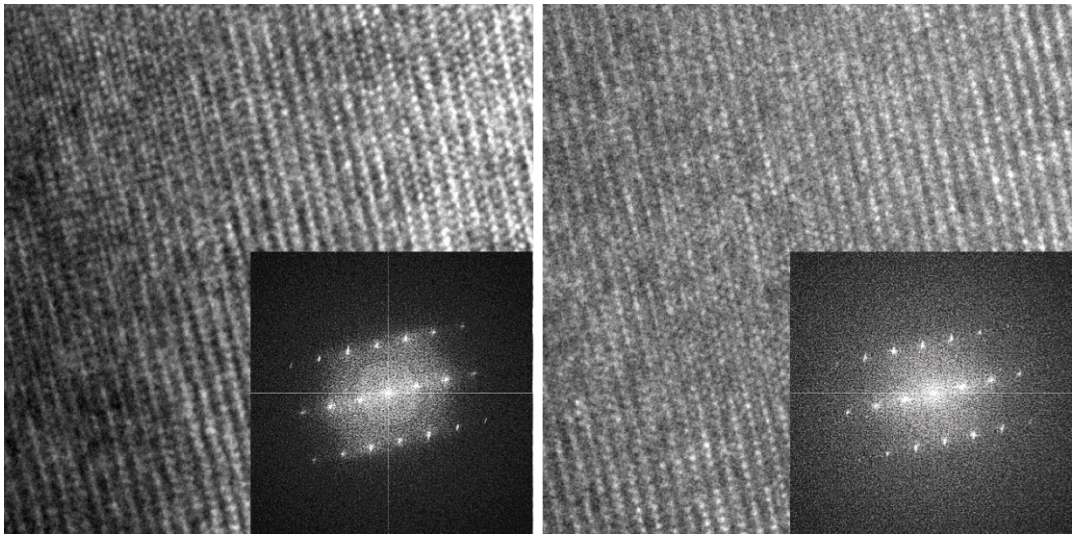

Figure S4. HRTEM images of the Co-ZnO nanowire and corresponding SAED patterns.

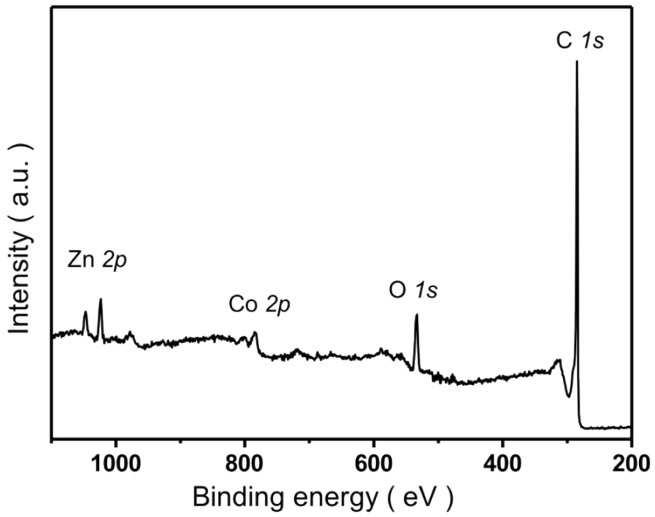

Figure S5. Survey-level XPS result of Co-ZnO/CF composite electrode.

Table S1.

Comparison of electrocatalytic OER activity of various non-precious catalysts in alkaline media.

Catalysts	Mass Loading (mg cm^{-2})	Overpotential at 10 mA cm^{-2} (mV)	Tafel slop (mV dec^{-1})	Electrolyte	Reference
C-Co NPs	0.2	390	/	0.1 M KOH	*J. Am. Chem. Soc*. **2015**, 137, 7071-7074
$Co_3O_4/NiCo_2O_4$ DSNCs	1.0	340	88	1 M KOH	*J. Am. Chem. Soc*. **2015**, 137, 5590-5595
Mn_1Ni_1	~0.28	420	/	0.1 M KOH	*Adv. Funct. Mater.* **2015**, 25, 393-399.
Co-P/NC	1.0	319	52	1 M KOH	*Chem. Mater*. **2015**, 27, 7636-7642
Co-ZnO@CF	~1.0	362	70	0.1 M KOH	*This work*

Table S2.

Comparison of electrocatalytic HER activity of various non-precious catalysts in alkaline media.

Catalysts	Mass Loading (mg cm^{-2})	Overpotential at 10 mA cm^{-2} (mV)	Tafel slop (mV dec^{-1})	Electrolyte	Reference
Mn_1Ni_1	~0.28	-360	/	0.1 M KOH	*Adv. Funct. Mater.* **2015**, 25, 393-399.
Mesoporous Co_3O_4	~0.13	-525	/	0.1 M KOH	*Nano Res.* **2013**, 6(1), 47-54
N,P-graphene	~0.20	<-600	145	0.1 M KOH	*ACS Nano*. **2014**, 8, 5290-5296
MoS_{2+x}/FTO	/	-310	/	1 M KOH	*Angew. Chem. Int. Ed.* **2015**, 54, 664.
Co-NRCNTs	~0.28	-370	/	1 M KOH	*Angew. Chem. Int. Ed.* **2014**, 53, 4372.
Co-ZnO@CF	~1.0	-270	160	0.1 M KOH	*This work*

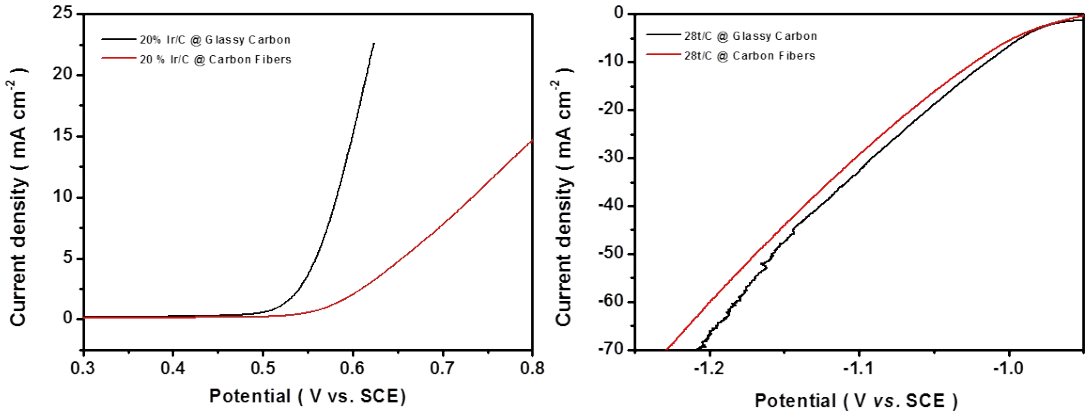

Figure S6. Performance comparison of 20% Ir/C and 28% Pt/C commercial catalyst on various substrate with same mass loading of 1 mg cm^{-2}.