Supporting Information

Mn doped Porous Cobalt Nitride Nanowire with High Activity for Water Oxidation under Both Alkaline and Neutral Conditions

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Experimental Section

Reagents. Carbon fiber cloth (CFC) with a thickness of 1 mm (ROCKTEC, Ltd., Hubei, China) were used as the substrate. $Mn(SO_4)_2{\cdot}H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, KOH, Na_2HPO_4, NaH_2PO_4, $CO(NH_2)_2$, NH_4F were purchased from Sinopharm group and used without further purification. All the aqueous solutions were prepared with Milli-Q water with the resistance of 18 MΩ·cm at 25 °C.

Synthesis of the Mn doped $Co_2(OH)_2CO_3$/CFC nanowire arrays. Carbon fiber cloth (CFC) was cleaned using water, acetone and ethanol with ultrasonication for 30 min subsequently to remove impurities. First, $Co(NO_3)_2{\cdot}6H_2O$ (1.2 mmol), $Mn(SO_4)_2{\cdot}H_2O$ (0.4 mmol), 10 mmol urea and 4 mmol of NH_4F were dissolved in 40 mL distilled water and stirred for at least 30 min to form a clear solution. The cleaned carbon fiber cloth was immersed into the reaction solution and heated in an oven at 120 °C for 6 h by a simple hydrothermal process and then cooled to room temperature. After the reaction, the Mn doped $Co_2(OH)_2CO_3$/CFC nanowire arrays were immersed in DI water and ethanol several times, and then dried at 60 °C.

Synthesis of the porous Mn doped CoN/CFC nanowire arrays. The porous Mn doped CoN/CFC nanowire arrays were obtained from Mn doped $Co_2(OH)_2CO_3$/CFC nanowires precursor by a simple nitridation process. In a typical experiment, the as-prepared Mn doped $Co_2(OH)_2CO_3$/CFC nanowires precursor were placed in the tube and heated to 380 °C with a rate of 10 °C min^{-1} under a flowing NH_3 atmosphere. After reacting 3 h at 380 °C, the system was allowed to cool down to room temperature naturally still under a flowing NH_3 atmosphere. Finally, the black

products of Mn doped CoN/CFC nanowire arrays were collected for further characterization. Pure CoN /CFC nanowire arrays were also synthetized under same condition.

Electrochemical Measurements. All electrochemical measurements were carried out using a CHI 760E electrochemistry workstation (CH Instruments, Inc., Shanghai) connected with a standard three-electrode configuration under a room temperature of 25 °C. The porous Mn doped CoN/CFC nanowire arrays sample were used as the working electrode. An Ag/AgCl electrode and a platinum wire electrode were used as the reference and counter electrodes, respectively. All of the potentials were calibrated against the reversible hydrogen electrode (RHE). The electrocatalytic activity of the catalysts was examined via linear-sweep voltammetry in a N_2-purged 1 M KOH solution at 298 K and a scan rate of 2 mV s^{-1}. All potentials and voltages were IR corrected no otherwise specified. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronopotentiometric measurements were also conducted under the same condition.

Characterizations. SEM measurements were performed on a Sirion 200 field emission scanning electron microscope at an accelerating voltage of 10 kV. X-ray diffraction (XRD) were recorded on a Philips X'pert Pro X-ray diffractometer with Cu K_α radiation (λ=0.15419 nm). The transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) were performed on a JEM-2100F field emission electron microscope at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250

photoelectron spectrometer. The XPS data were analyzed and fitted with XPSPEAK 4.1 software. ICP-MS was performed on Thermo Scientific iCAP6300 series instrument.

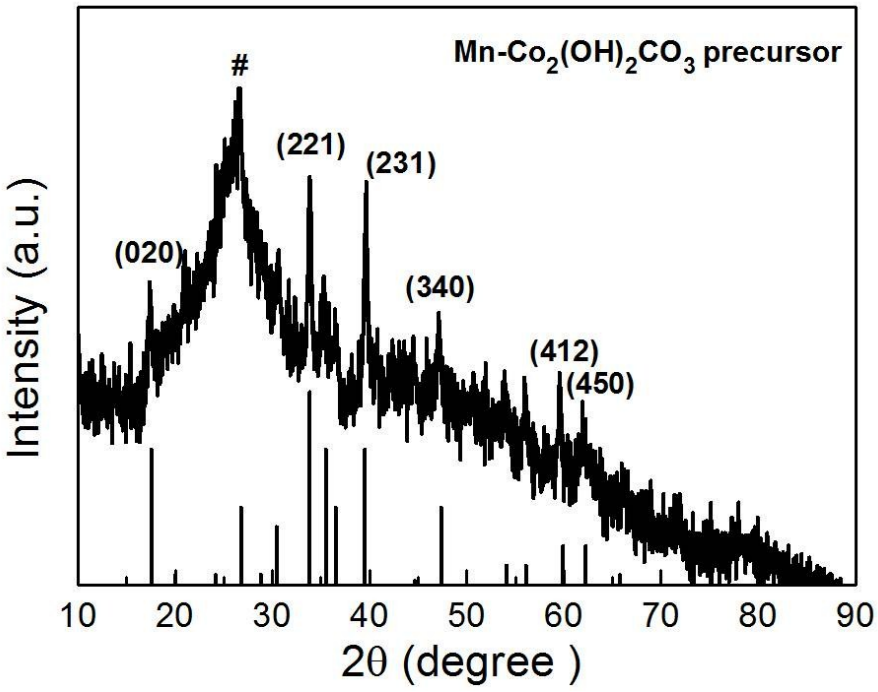

Figure S1. XRD pattern Mn doped $Co_2(OH)_2CO_3$ nanowire arrays precursor. # represent the diffraction peaks from CFC.

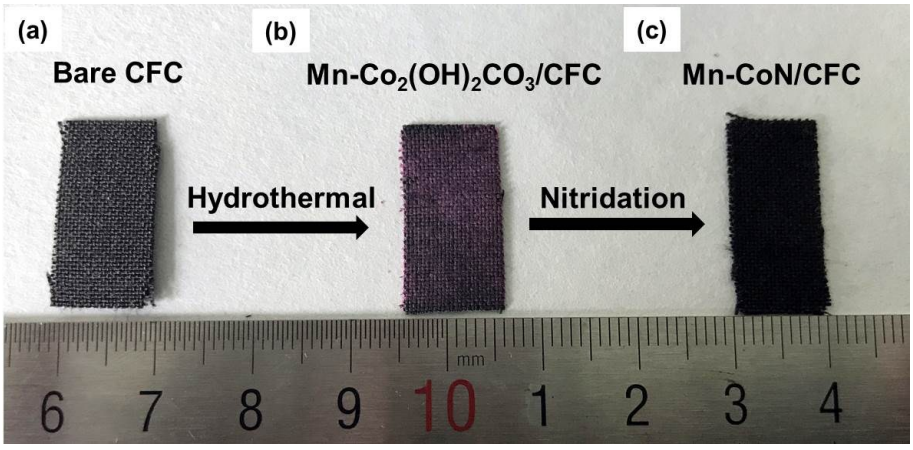

Figure S2. The photographic images of (a) bare CFC, (b) Mn-$Co_2(OH)_2CO_3$/CFC, (c) Mn-CoN/CFC.

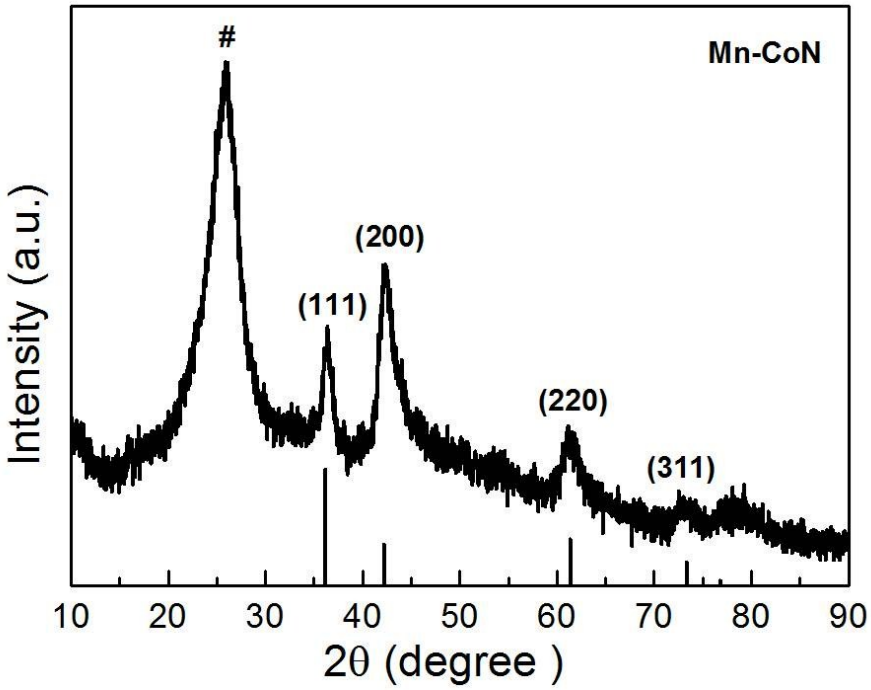

Figure S3. XRD pattern Mn doped CoN nanowire arrays. # represent the diffraction peaks from CFC.

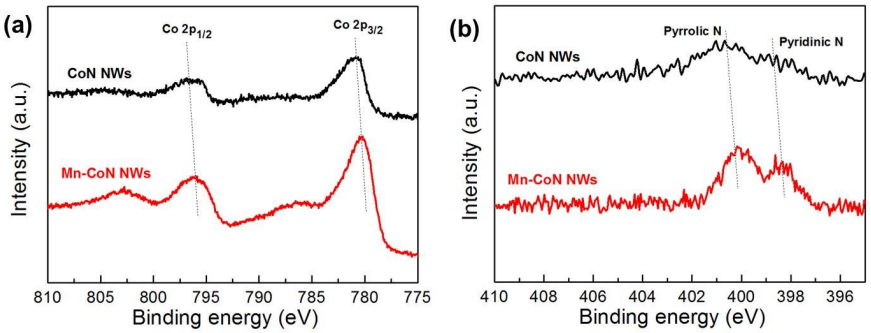

Figure S4. XPS spectra for CoN NWs, and Mn-CoN MWs. (a) The Co 2p region. (b) The N 1s region.

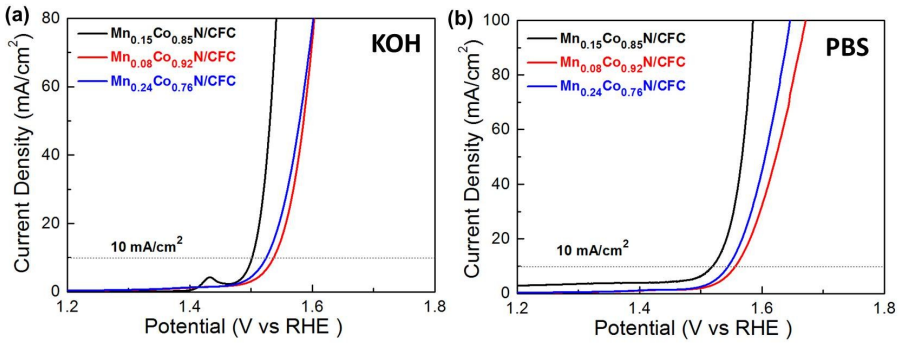

Figure S5. Polarization plots for OER measured with the Mn_xCo_yN nanowire array/CFC with different x, y value samples in (a) 1.0 M KOH and (b) PBS electrolyte at 2 mV s^{-1}.

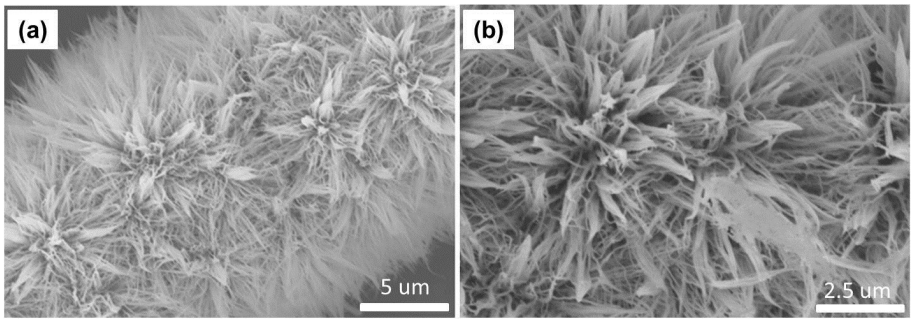

Figure S6. (a) Low-magnification and (b) high-magnification SEM images of pure CoN nanowire arrays/CFC.

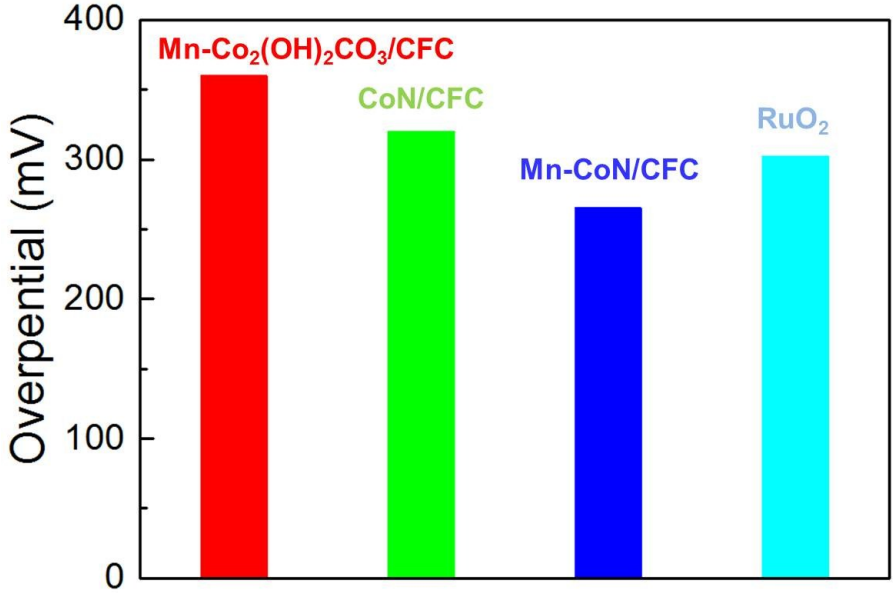

Figure S7. Overpotential required for J=10 mA cm^{-2}.

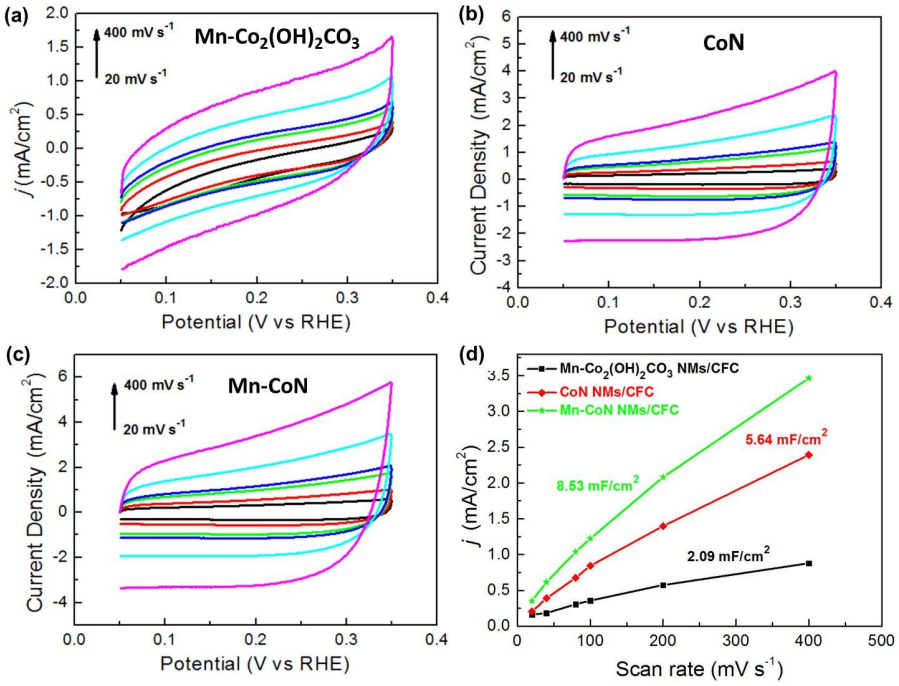

Figure S8. Cyclic voltamogram curves in double layer region at scan rates of 20, 40, 80, 100, 200 and 400 mV s^{-1} of (a) Mn-$Co_2(OH)_2CO_3$ nanowires/CFC, (b) pure CoN nanowires/CFC, (c) Mn-CoN nanowires/CFC, and (d) Plots showing the extraction of the double-layer capacitances allows the estimation of the electrochemically active surface area.

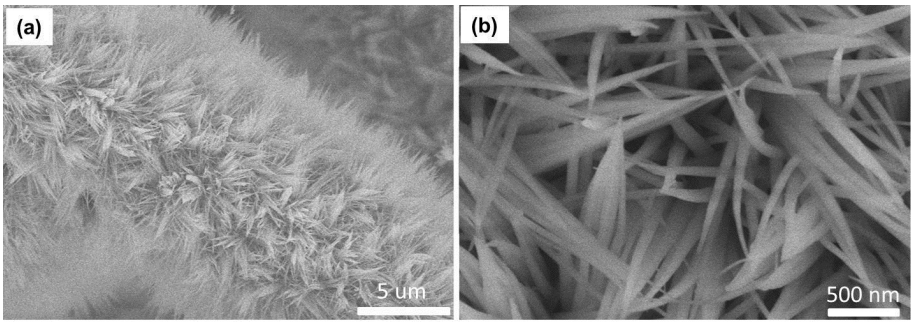

Figure S9. (a) Low-magnification and (b) high-magnification SEM images of Mn-CoN nanowires/CFC after long-term stability tests.

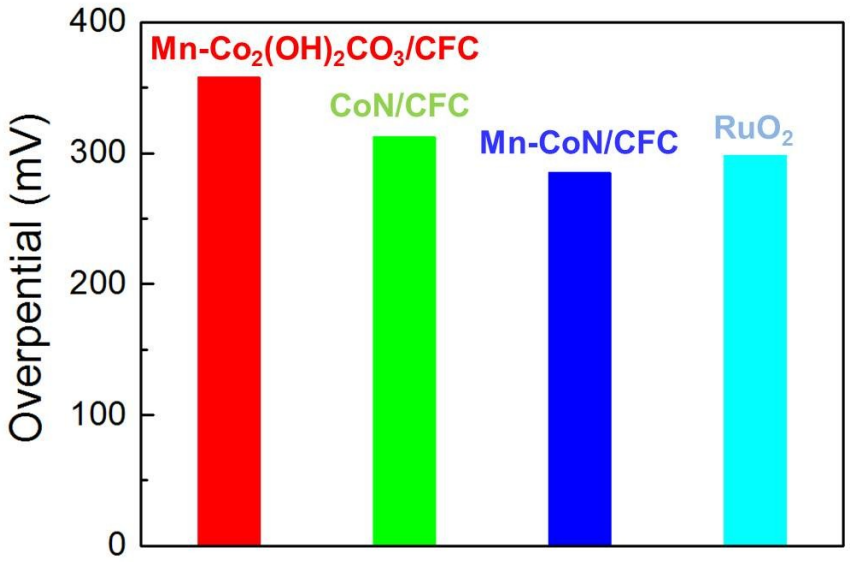

Figure S10. Overpotential required for J=10 mA cm^{-2} in neutral condition.

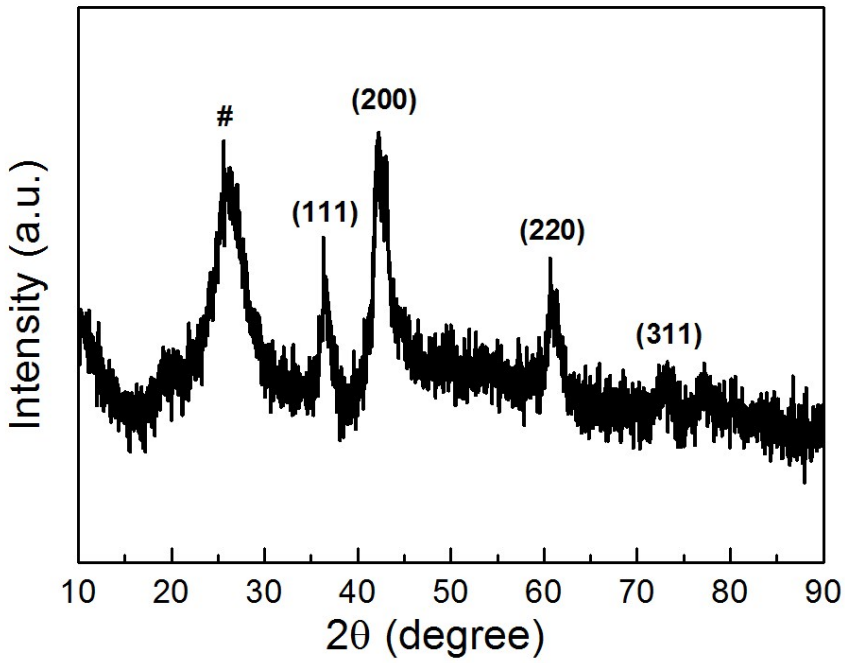

Figure S11. XRD pattern of the Mn-CoN nanowires/CFC after durability test for OER in neutral condition.

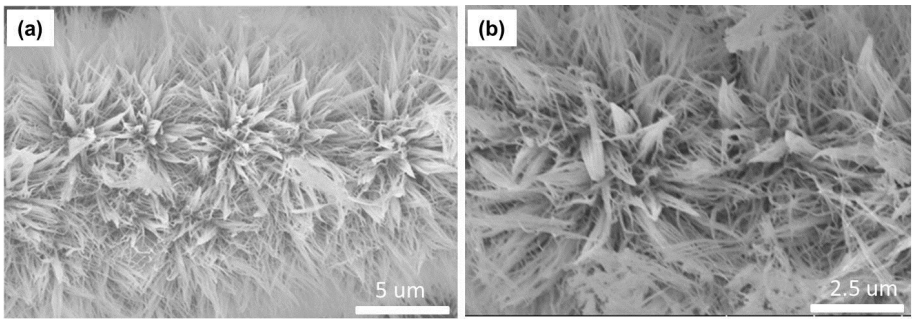

Figure S12. (a) Low-magnification and (b) high-magnification SEM images of Mn-CoN nanowires/CFC after long-term stability tests in neutral condition.