## **Electronic Supplementary Information**

## $Co_{3}O_{4}/MnCO_{3}\ heterojunction\ on\ three-dimensional\ nickel\ foam\ for$

## enhanced oxygen evolution reaction

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Figure S1.a-f) SEM images of the Co<sub>3</sub>O<sub>4</sub>@NF, Co/Mn-0.5@NF, Co/Mn-1@NF, Co/Mn-1.5@NF, Co/Mn-2@NF and MnCO<sub>3</sub>@NF at same low-magnifications, respectively.



Figure S2. Wettability test of the Co/Mn-1.5@NF electrode in environment temperature.

A sequence of digital photographs of the Co/Mn-1.5@NF electrode surface gradually moving up to the water droplet clinging to the syringe tip, just touching the water droplet with the electrode surface, then gradually moving down and departing from the water droplet. The arrows indicate the moving direction of the Co/Mn-1.5@NF electrode surface. The droplet could infiltrate into the pore canal on account of the porous nature of the three-dimensional NF, which is beneficial to the diffusion of electrolyte.



Figure S3. a) XRD patterns of samples. b) TGA images of the MnCO<sub>3</sub>@NF from room temperature to 700 °C under Ar atmosphere.

The XRD results of the Co/Mn-0.5@NF, Co/Mn-1@NF and Co/Mn-2@NF was also shown in Figure S4a. The diffraction peak of MnCO<sub>3</sub> gradually increased from bottom to top, indicating that the content of MnCO<sub>3</sub> in the sample increased with the increase of Mn source. At the same time, it did not appear other phases except MnCO<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub>. The TGA result of MnCO<sub>3</sub>@NF was tested at pure Ar atmosphere to verify whether MnCO<sub>3</sub> can exist stably at the annealing temperature of 350 °C. As expected, MnCO<sub>3</sub> can be stably present more than 420 °C.



Figure S4. The polarization curves of samples in 1 M KOH electrolyte with a scan rate of 5 mV/s.



Figure S5. a, b, c) CV curves of the Co<sub>3</sub>O<sub>4</sub>@NF, Co/Mn-1.5@NF and MnCO<sub>3</sub>@NF in 1 M KOH electrolyte at a scan rate from 10 to 50 mV/s, respectively. d) Temperature dependent polarization curves of the Co/Mn-1.5@NF from room temperature to 60 °C in a constant temperature water system.



Figure S6. The XPS spectra of sample Co/Mn-1.5@NF before and after the stability tests: a) Survey spectrum, High resolution scan of b) Co 2p and c) Mn 2p.

The XPS spectrum of the Co/Mn-1.5@NF before and after the stability tests were shown in Figure S6. It can be seen from the full spectrum that there is no new phase appeared on the surface of the sample after stability tests during 40 h. Moreover, the high resolution XPS spectra of Co 2p and Mn 2p are almost completely consistent before and after the stability test, which further show that no phase changes occur on the surface of the sample after the stability tests, as shown in Figure S6 b and c. Results revealed that sample Co/Mn-1.5@NF can be stably existed during the reactions in the alkaline environment.