

Supporting Information

An electrospinning strategy to fabricate integrated electrode with multiple components for highly efficient electrocatalytic water splitting

Jian Cai, Jiace Hao, Shuanglong Lu, Fang Duan, Mingliang Du, Han Zhu*

Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, P. R. China

E-mail: zhysw@jiangnan.edu.cn

Experimental section

Materials

Copper chloride (CuCl_2), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), manganous acetate ($\text{Mn}(\text{CH}_3\text{COO})_2$) were purchased from Aladdin Co., Ltd. Sulfuric acid (H_2SO_4), potassium hydroxide (KOH) and dimethylformamide (DMF, 99.5%) were supplied by Shanghai Civi Chemical Technology Co., Ltd. Polyacrylonitrile (PAN, $M \approx 1.4 \times 10^5$, copolymerized with 10 wt% methyl acrylate) was manufactured by Sinopec Shanghai Petrochemical Co., Ltd. Ultrapure water (Milli-Q) was used in all experiments. All of the reagents were used without purification.

Preparation of CuCoMn salt/PAN precursor nanofibers

First, 3g PAN powder were dissolved in 22g DMF to form a homogeneous solution under stirring for 2h. Then, 0.15g CuCl_2 , 0.15g CoCl_2 and 0.15g $\text{Mn}(\text{CH}_3\text{COO})_2$ were added in the above mixture under stirring for 2h. After that, the prepared mixture was transferred into a syringe, equipping on the injection pump. The speed of the injection was 0.6 mL/h, and the voltage applied was fixed at 16 kV. Under these conditions, the CuCoMn salt/PAN precursor nanofibers were collected on the rotating drum.

Preparation of CuCo-MnO@CNTs/CNFs 3D architecture

The CuCoMn salt/PAN precursor nanofibers were put on a home-built chemical vapor deposition furnace for the NH_3 -assisted graphitization. The temperature was

firstly heated to 280 °C from room temperature and maintained at 280 °C for 3h. Subsequently, the temperature of the furnace was further heated to 1000 °C under Ar atmosphere with heating rate of 5 °C min⁻¹. Finally, the samples were stabilized at 1000 °C under NH₃/Ar atmosphere for 3h. In comparison, the CuCo-MnO@CNTs/CNFs were prepared with different flow rates of NH₃ (0, 1, 3 and 5 sccm). The control CNFs were prepared without metallic salts in the same process.

Instrumentation

Field-emission scanning electron microscope (FE-SEM) images were carried out using a JEOL JSM-6700F with acceleration voltage of 3 kV. Crystal structure and selected-area electron diffraction (SAED) were conducted on a transmission electron microscopy (TEM) with acceleration voltage of 200 kV. Elemental mapping, high-angle annular dark field scanning TEM (HAADF-STEM) and lines-scan energy dispersive X-ray spectroscopy (EDX) were recorded on a STEM (Tecnai G2 F30 S-Twin, Philips-FEI) at an acceleration voltage of 300 kV. X-ray diffraction (XRD) patterns of the samples were performed on a SIEMENS Diffractometer D5000 X-ray diffractometer using Cu K_α radiation ($\lambda=1.5406 \text{ \AA}$) source at 35 kV, with a scan rate of 0.02° 2 θ s⁻¹ in the 2 θ range of 20-60°. In addition, Surface chemical composition of samples were measured by a Kratos Axis Ultra DLD X-ray photoelectron spectrometer (XPS) with an aluminum (mono) K_α source (1486.6 eV).

Electrochemical performance

Electrochemical performance of the as-synthesized catalysts were performed on an IVIUM electrochemical workstation (Ivium Technologies BV Company, Netherlands) at room temperature. The as-prepared catalysts directly used as the working electrodes without binder in a standard three-electrode system. A saturated calomel electrode (SCE) and the graphite rod were used as the reference electrode and counter electrode. Pt/C and RuO₂ were taken as controls and deposited on glassy carbon electrode (GCE) with diameter of 3 mm for measurement. To prepare the electrocatalyst ink, 3 mg of electrocatalyst was dispersed into 1 mL mixed solvent with a volume ratio of V_{isopropanol}:V_{water}=3:1. after 30 min of ultrasonication, 25 μ L nafion 117 solution was added. After another 30 min for ultrasonication, 5 μ L

electrocatalyst ink was casted on GCE and dried in the air naturally. The cyclic voltammetry curves, the polarization curves and the current-time curves were carried out in 0.5 M H_2SO_4 (pH=0) and 1.0 M KOH (pH=14), respectively. In addition, electrochemical impedance spectra (EIS) were performed in acid environment and the frequency range of the EIS from 100 kHz to 0.001 Hz. The time dependent current density (i - t) curves were examined in acid environment at 0.033 V vs. RHE and in alkaline environment at 1.48 V vs. RHE for 50h, respectively.

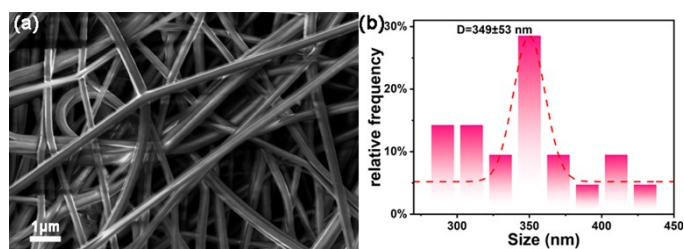


Fig. S1. (a) SEM image and (b) the corresponding diameter distribution of CuCoMn salt/PAN precursor nanofibers.

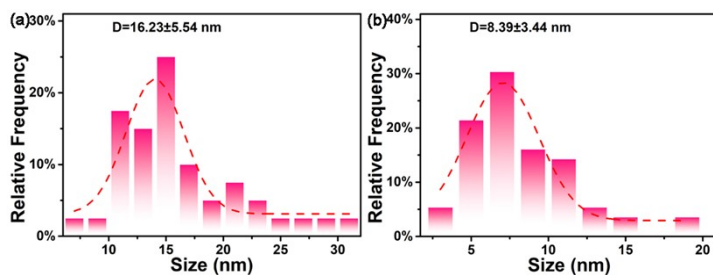


Fig. S2. (a) The inner diameter distribution and (b) the wall thickness distribution of CNTs in CuCo-MnO@CNTs/CNFs.

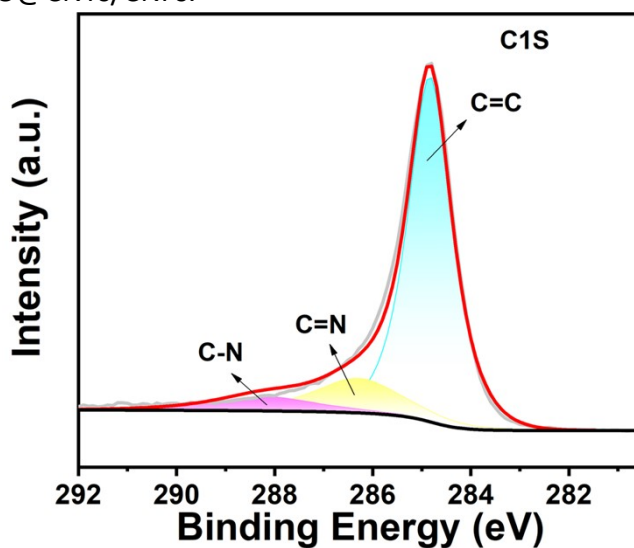


Fig. S3. C 1s XPS spectra of CuCo-MnO@CNTs/CNFs.

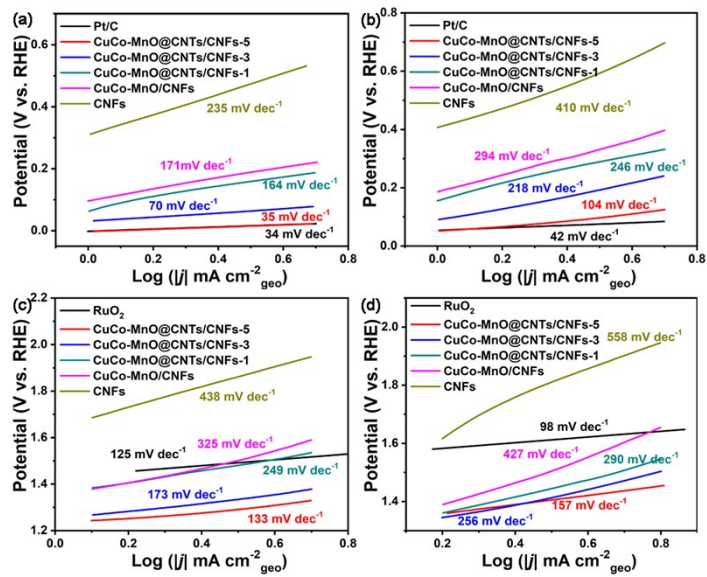


Fig. S4. Tafel slopes of commercial Pt/C, CuCo-MnO@CNTs/CNFs-5, CuCo-MnO@CNTs/CNFs-3, CuCo-MnO@CNTs/CNFs-1, CuCo-MnO/CNFs and CNFs in (a) 0.5 M H₂SO₄ and (b) 1 M KOH for HER. Tafel slopes of various samples in (c) 0.5 M H₂SO₄ and (d) 1 M KOH for OER.

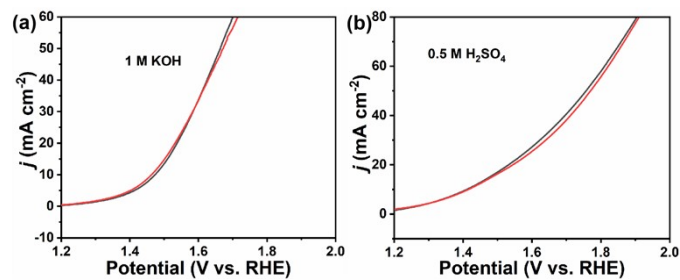


Fig. S5 LSV curves of CuCo-MnO@CNTs/CNFs-5 tested at different times in (a) 1 M KOH and (b) 0.5 M H₂SO₄ for OER.

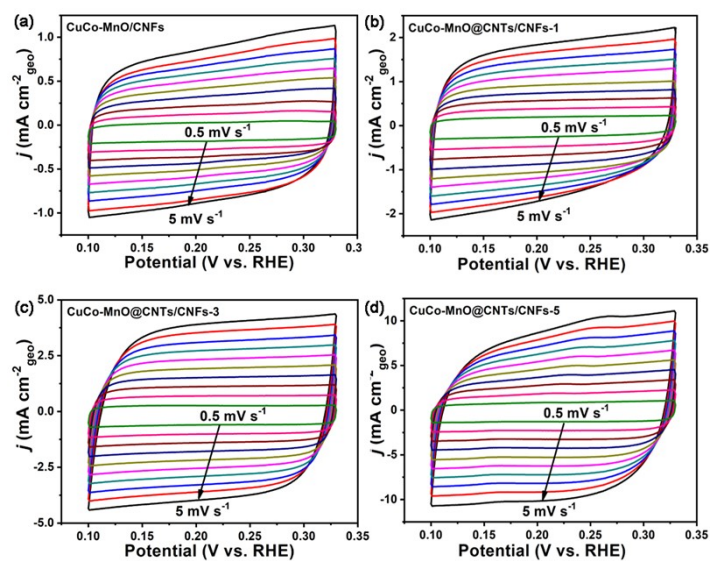


Fig. S6. CV curves of (a) CuCo-MnO/CNFs, (b) CuCo-MnO@CNTs/CNFs-1, (c) CuCo-MnO@CNTs/CNFs-3, (d) CuCo-MnO@CNTs/CNFs-5 at different scan rates.

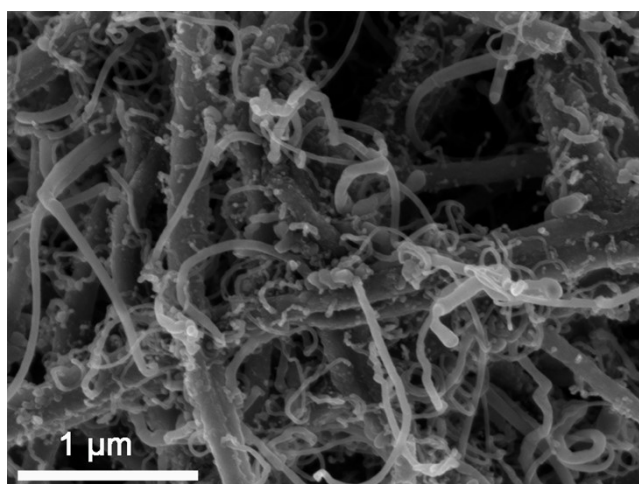


Fig. S7 SEM image of CuCo-MnO@CNTs/CNFs-5 after i-t test.

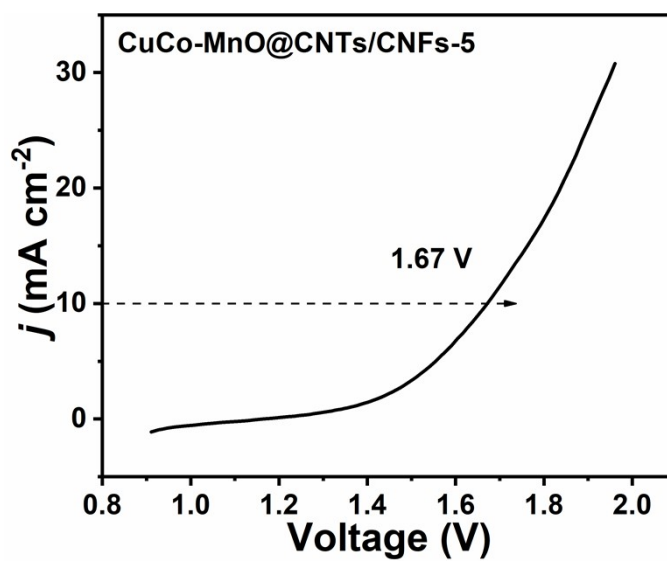


Fig. S8. LSV curve of CuCo-MnO@CNTs/CNFs-5||CuCo-MnO@CNTs/CNFs-5 electrode for water splitting in 1M KOH.