Supporting Information

Thermodynamics driven metal diffusion strategy for controlled synthesis of high-entropy alloy electrocatalysts

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Experimental

Materials

Iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, chromium trichloride hexahydrate ($Cr(Cl_3)_3 \cdot 3H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), manganese acetate tetrachloride ($Mn(CO_2CH_3)_2 \cdot 4H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) , potassium hydroxide (KOH), N,N-dimethylformamide (C_3H_7NO (DMF)), and polyvinylpyrrolidone ((C_6H_9NO)n, M_W= 1 300 000, PAN) were bought from Aladdin Reagent. Ruthenium oxide (RuO_2) and Nafion solution (5 wt%) were obtained from Sigma Aldrich. All chemicals were directly used as received without any further purification.

Synthesis of FeCoNiCrMn high entropy alloy nanocrystals supported on electrospun carbon nanofibers

Initially, 0.1 mmol $Fe(NO_3)_3 \cdot 9H_2O$, 0.1 mmol $CrCl_3 \cdot 3H_2O$, 0.1 mmol $Co(NO_3)_2 \cdot 6H_2O$, 0.1 mmol $Mn(CO_2CH_3)_2 \cdot 4H_2O$, 0.1 mmol $Ni(NO_3)_2 \cdot 6H_2O$, and 1.6 g PAN were dissolved in 14 mL DMF. Then, the mixture was stirred for 12 h to obtain a homogeneous solution at room temperature. In a typical electropinning process, 17 KV high applied voltage and 0.8 KV collect voltage were set at a suitable distance (15 cm) between the syringe and the collector to obtain nanofiber mats. The obtained nanofiber mats were heated to 240 °C at a rate of 2 °C/min and then kept maintained for 3 h in air. After the pre-oxidation process, the mats were heated to 1000 °C (5 °C/min) and then kept maintained for 3 h under Argon atmosphere.

Synthesis of FeCoNi alloy nanocrystals supported on electrospun carbon nanofibers

First, 0.167 mmol $Fe(NO_3)_3 \cdot 9H_2O$, 0.167 mmol $Co(NO_3)_2 \cdot 6H_2O$, 0.167 mmol $Ni(NO_3)_2 \cdot 6H_2O$, and 1.6 g PAN were dissolved in 14 mL DMF. Subsequently, the nanofiber mats were obtained by electrospinning process. The pre-oxidation and carbonization process was same to the FeCoNiCrMn HEA/CNFs.

Synthesis of FeCoNiMn medium-entropy alloy nanocrystals supported on carbon nanofibers

For FeCoNiMn nanofibers, the concentration and species of metal salts were converted to: ($Fe(NO_3)_3 \cdot 9H_2O$ (0.125 mmol, 0.0505 g), ($Co(NO_3)_2 \cdot 6H_2O$) (0.125 mmol, 0.0363 g), ($Mn(CO_2CH_3)_2 \cdot 4H_2O$) (0.125 mmol, 0.0308 g), ($Ni(NO_3)_2 \cdot 6H_2O$)

(0.125 mmol, 0.0363 g) and PAN were dissolved in DMF. Following the same composition steps as above-mentioned programs.

Synthesis of FeCoNiCr medium-entropy alloy nanocrystals supported on carbon nanofibers

For FeCoNiCr nanofibers, (Fe(NO$_3$)$_3$⬩9H$_2$O (0.125 mmol, 0.0505 g), (Co(NO$_3$)$_2$⬩6H$_2$O) (0.125 mmol, 0.0363 g), (CrCl$_3$⬩3H$_2$O) (0.125 mmol, 0.0331 g) , (Ni(NO$_3$)$_2$⬩6H$_2$O) (0.125 mmol, 0.0363 g) and PAN were added into DMF solution. The synthesis process and previously mentioned procedure are the same, only changing species of metal salt.

Electrochemical measurements

Electrochemical measurements were tested through a workstation CHI-660H (Shanghai Chenhua) with a three-electrode cell system at room temperature. The three-electrode cell system is composed of working electrode, count and reference electrode, which are glassy carbon electrode, saturated calomel electrode and a graphite rod, respectively. The FeCoNiCrMn carbon nanofibers (FeCoNiCrMn/CNFs), (FeCoNi/CNFs), (FeCoNiCr/CNFs) and (FeCoNiMn/CNFs) were directly cut into a flake of 1X1 cm^2 in area, respectively, and were utilized as working electrode. All potentials mentioned in this article were denoted by reversible hydrogen electrode (RHE). The calibrated and converted formula was E (RHE) = E (SCE) + 0.242 + 0.059 PH. All OER tests of overpotential (η) were directly calculated from (η = E (RHE) − 1.23 V) without additional ohmic potential drop (iR drop) compensation processing.

The OER tests were operated by linear sweep voltammetry (LSV) techniques between 0 V and 0.8 V vs. RHE in electrolyte solution (0.1M KOH). The LSV has scanned take *X* axis speed of 5 mV s^{-1} in measurements. The OER stability of the catalysts were estimated from chronoamperometric measurements in 1M KOH for 10 h. The Tafel slopes were obtained according to Tafel equation: η = a + b log (j); where η serve as over potential, b is the Tafel slope and j is measured current density, respectively. The EIS was carried out in opening circuit voltage mode in alkaline electrolyte solution. In order to calculate the electrochemical active surface areas (ECSA) of the catalysts, the electrochemical double layer capacitances (C$_{dl}$) with various scan speed were investigated from 0 mV s^{-1} to 120 mV s^{-1}.

Materials characterizations

The microstructures of the catalysts were observed via a JEOL Japan field emission scanning electron microscopyunder 3 kV accelerating voltage. The transmission electron microscopy (TEM, JEOL, Japan) was utilized as a tool of observing the microscopic morphology. The mapping images were obtained by energy-dispersive X-ray spectroscopy (EDS) in STEM (Talos F200XG2, acceleration voltage of 200 kV). X-ray diffraction (XRD) patterns were analyzed by a Bruker AXS D8 X-ray diffractometer with Cu K_α radiation (λ = 1.5406 Å) at a scan speed of 5° min^{-1} in the range of 20 to 90. X-ray photoelectron spectra of the catalysts were observed by an X-ray photoelectron spectrometer (Kratos Axis Ultra DLD) with an Al (mono) K_α source (1486.6 eV). The Al K_α source was ranning at 15 kV and 10 mA.
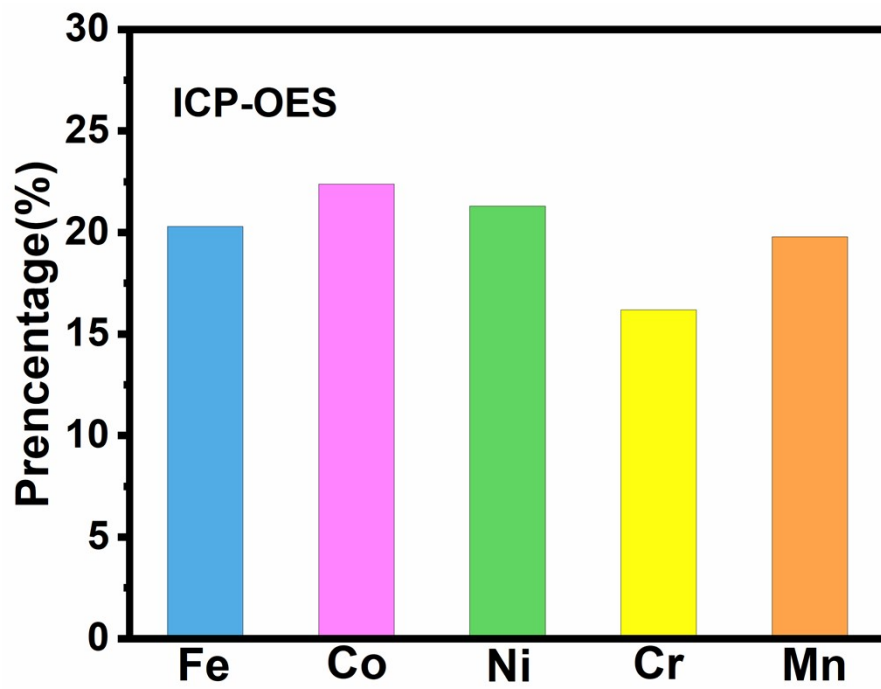
Figure S1. Inductively coupled plasma optical emission spectrometry (ICP-OES) of FeCoNiCrMn/CNFs prepared at 1000 °C.
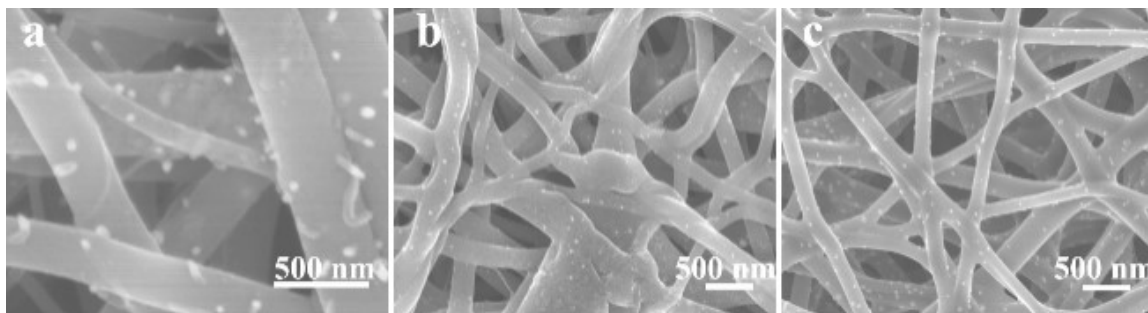
Figure S2. FE-SEM images of (a) FeCoNi/CNFs, (b) FeCoNiMn/CNFs and (c) FeCoNiCrMn/CNFs, respectively.
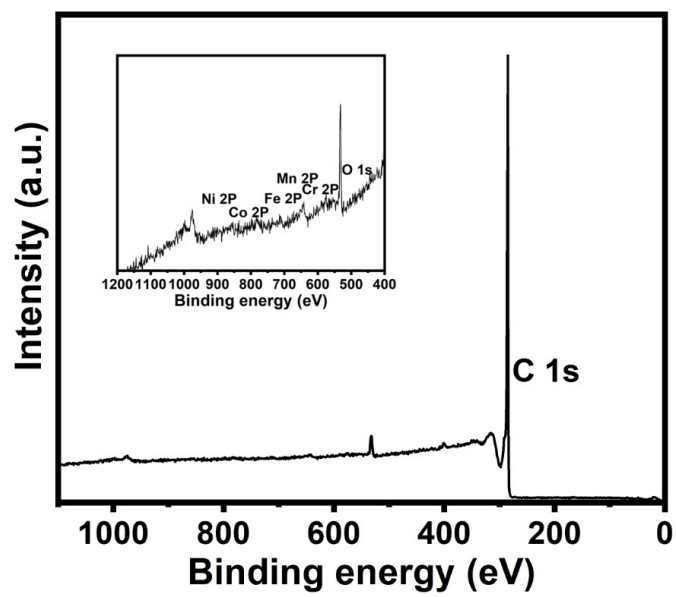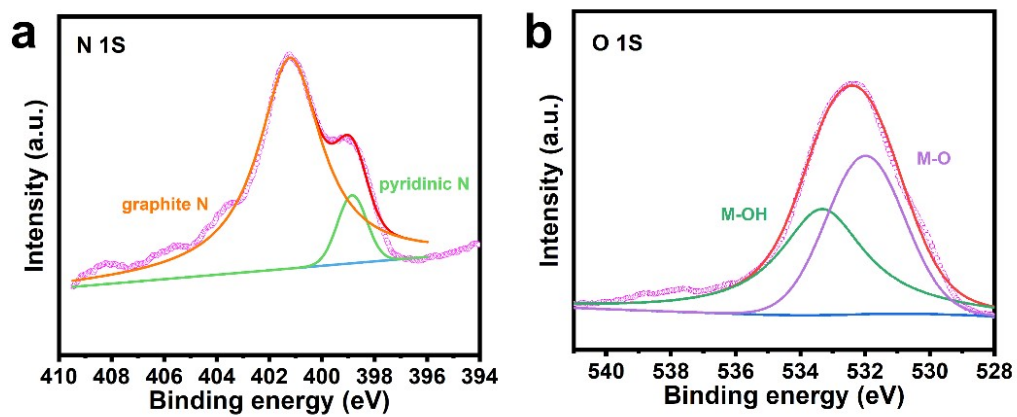
Figure S3. XPS survey spectrum of FeCoNiCrMn/CNFs.

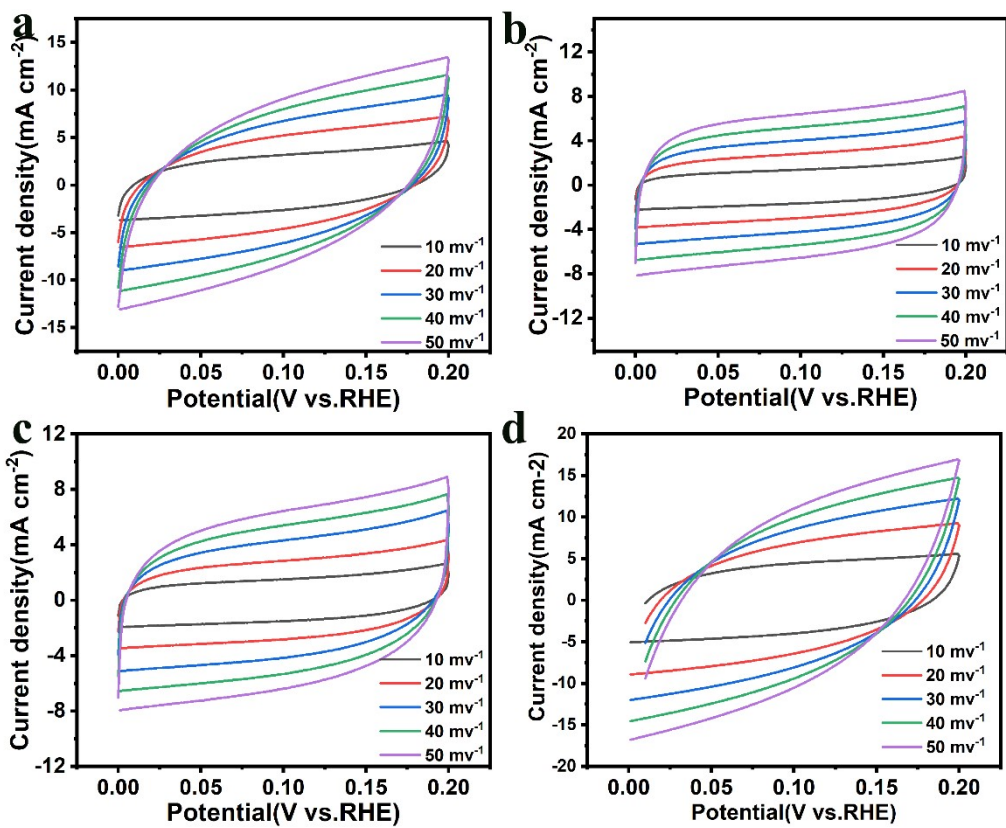**Figure S4**. (a) N1 s and (b) O 1 s XPS spectra of the FeCoNiCrMn/CNFs.

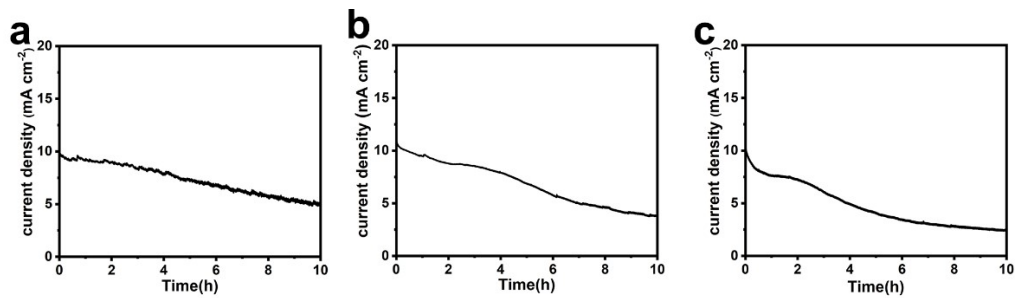**Figure S5**. (a-d) CV curves of the FeCoNi/CNFs, MnFeCoNi/CNFs, FeCoNiCr/CNFs and FeCoNiCrMn/CNFs, respectively.

Figure S6. The chronopotentiometry of (a)FeCoNi/CNFs, (b)FeCoNiMn/CNFs and (c)FeCoNiCr/CNFs in 1 M KOH.
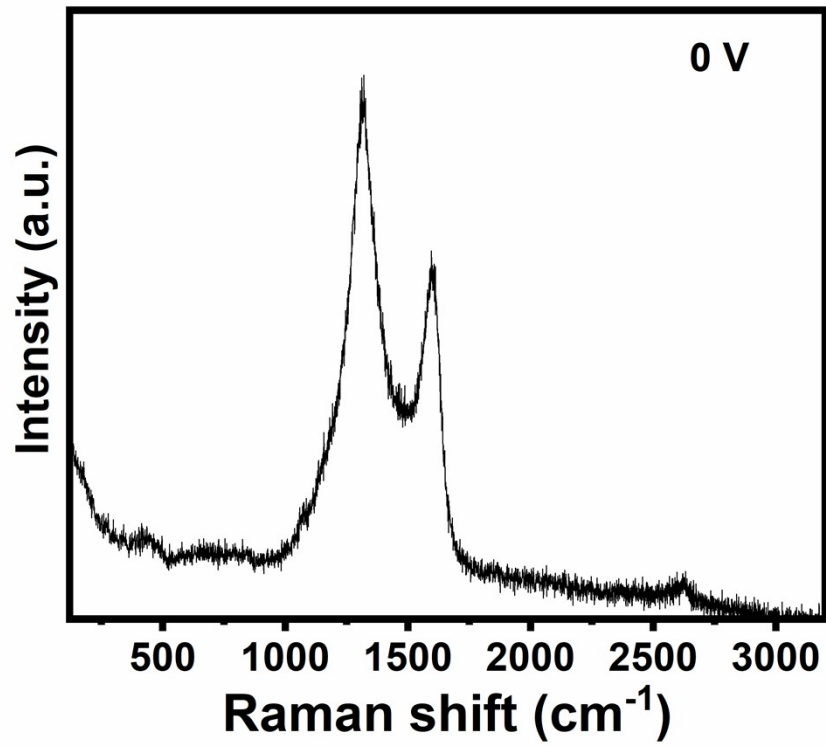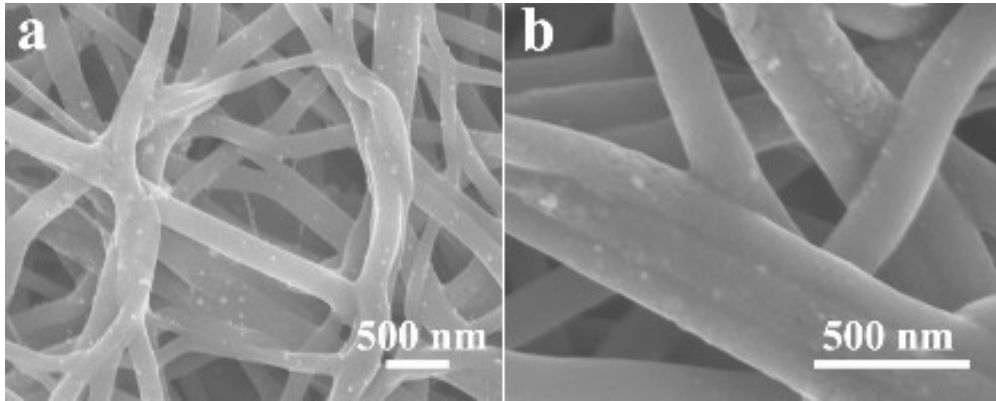
Figure S7. Raman spectra of FeCoNiCrMn/CNFs-1000.

Figure S8. (a-d) SEM images of FeCoNiCrMn/CNFs-900 and FeCoNiCrMn/CNFs-1100, respectively.
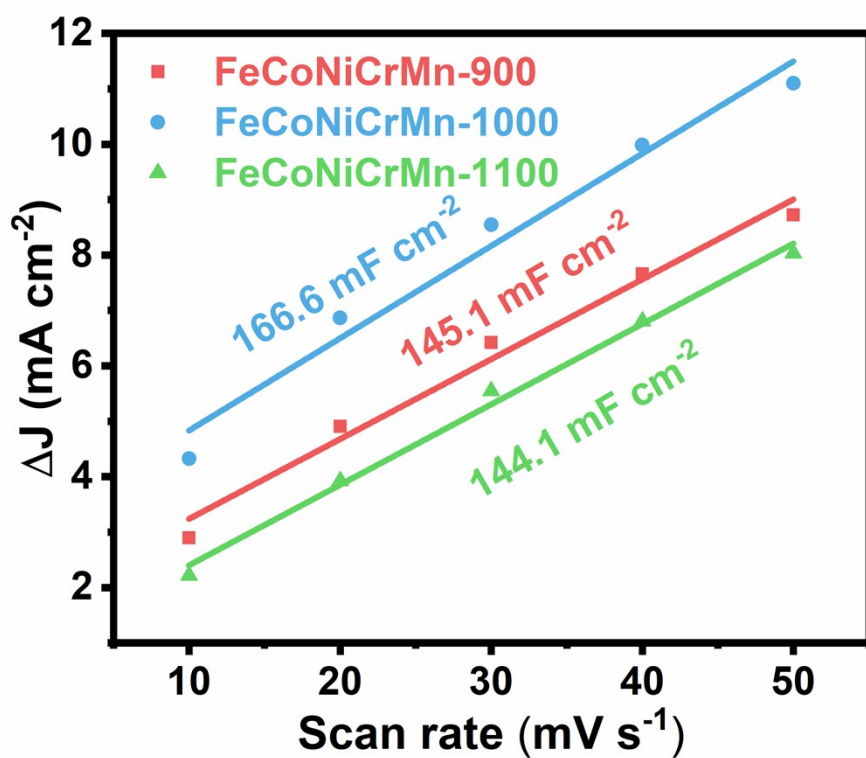
Figure S9. C_{dl} values of FeCoNiCrMn/CNFs-900, FeCoNiCrMn/CNFs-1000 and FeCoNiCrMn/CNFs-1100.
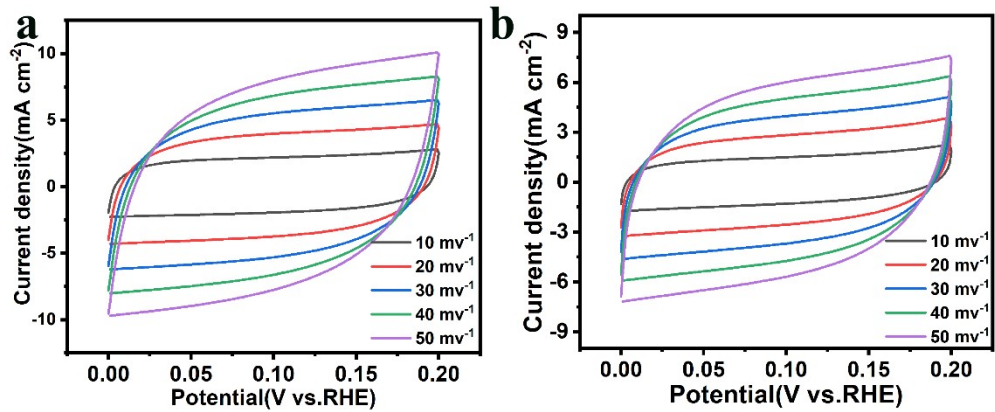
Figure S10. (a-d) CV curves of the FeCoNiCrMn/CNFs-900 and FeCoNiCrMn/CNFs-1100, respectively.