Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting Information

Pine Cone Mold: A Toolbox for Fabricating Unique Metal/Carbon Nanohybrid Electrocatalysts

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1. The SEM images of the MCNHs

Scanning electron microscopy (SEM) observation was performed using a ZEISS Gemini 500 electron microscope, for which the specimens were split into small pieces and mounted on carbon tape and coated by platinum sputtering (10 mA, 60 s) to prevent charging of the specimens.

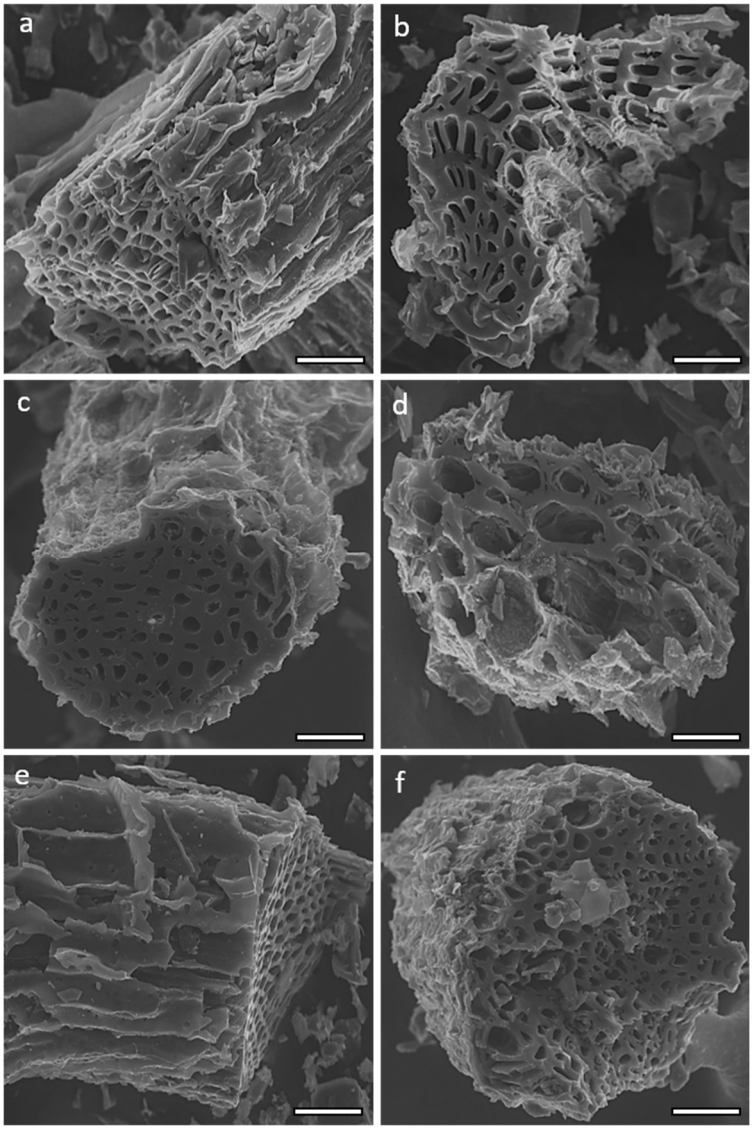

Figure S1. SEM images of the MCNHs at low magnification (scale bar: 1 μm), in which representative two images were provided for the samples: (a, b) M_{Fe}CNH, (c, d) M_{Fe}CNH, and (e, f) M_{Fe}CNH.

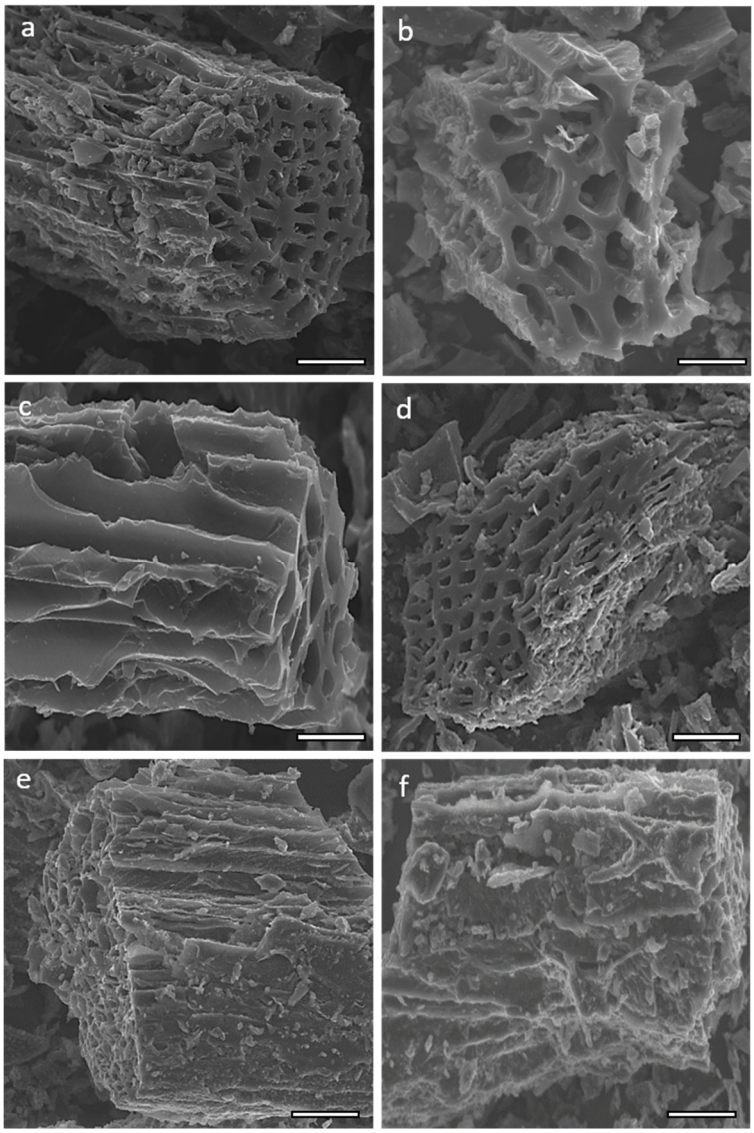

Figure S2. SEM images of the MCNHs at low magnification (scale bar: 1 μm), in which representative two images were provided for the samples: (a, b) M_{FeMn}CNH, (c, d) M_{MnCo}CNH, and (e, f) M_{FeCo}CNH.

2. Particle size distribution of the deposited metal nanoparticles

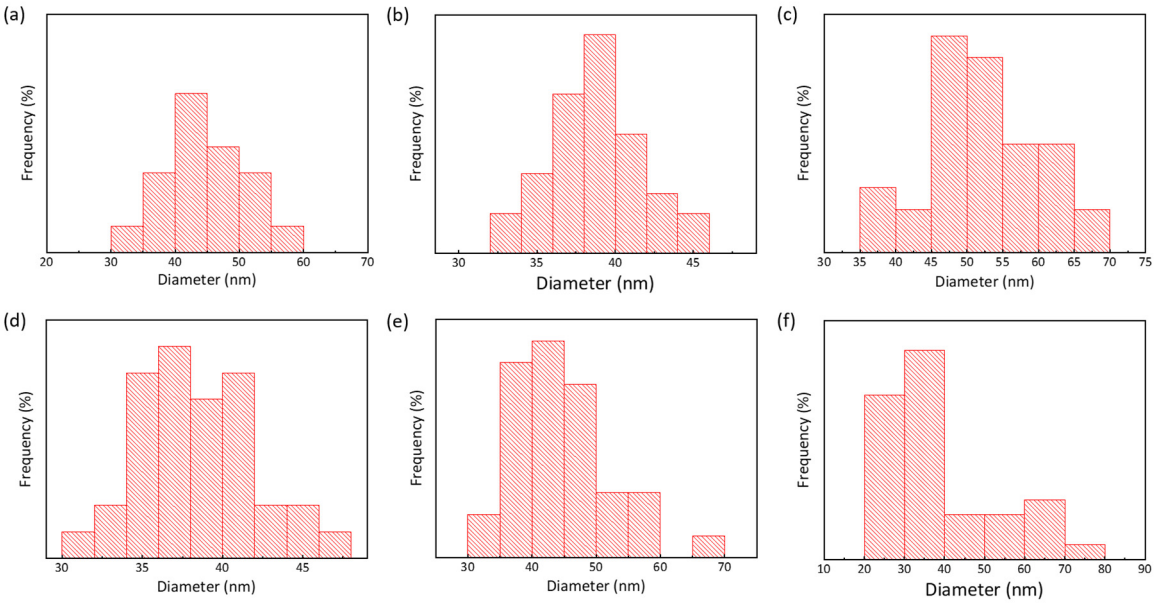

Figure. S3. Histograms showing the size distribution of the deposited metal nanoparticles in Figure 2: (a) M_{Fe}CNH (avg. 45 nm), (b) M_{Mn}CNH (avg. 39 nm), (c) M_{Co}CNH (avg. 53 nm), (d) M_{FeMn}CNH (avg. 38 nm), (e) M_{MnCo}CNH (avg. 44 nm), (f) M_{FeCo}CNH (avg. 40 nm), respectively.

3. Thermal gravimetric analysis

Thermal gravimetric analysis (TGA) was performed for the MCNHs using a TA Instruments Q50.

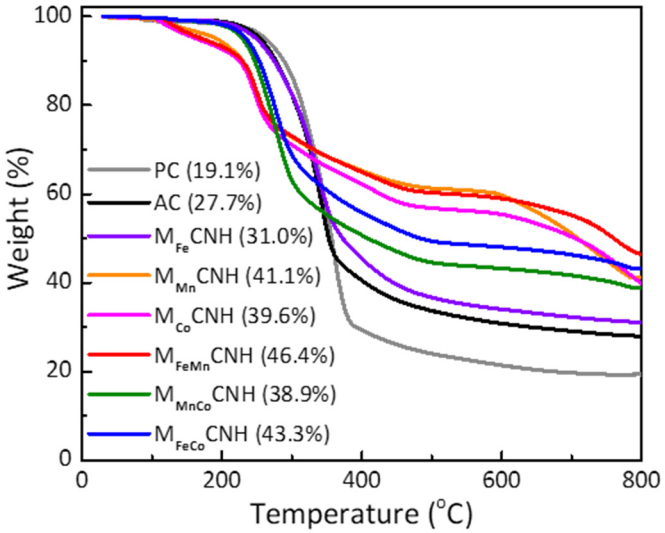

Figure S4. TGA curves of the MCNHs recorded at a heating rate of 3 °C min^{-1} under nitrogen atmosphere using a TA Instruments Q50 analyzer. The weight percentage of the residue is provided in the sample label.

4. X-ray photoelectron spectroscopy

The chemical composition of the MCNHs were examined using X-ray photoelectron spectroscopy (XPS). In the case of using manganese precursors, the main spin-orbit components (Mn $2p_{3/2}$ and $2p_{1/2}$) were observed at 642 and 653 eV. The splitting of the Mn 2p doublet was 11 eV, which is indicative of the presence of MnO_2 as the formed metal phase. In the case of using iron precursors, the main spin-orbit components (Fe $2p_{3/2}$ and $2p_{1/2}$) were observed at 711 and 725 eV. The splitting of the Fe 2p doublet was 14 eV, which is indicative of the presence of Fe_2O_3 as the formed metal phase. Additionally, Fe(0) peak was also observed at 720 eV. Lastly, in the case of using copper precursors, the main spin-orbit components (Co $2p_{3/2}$ and $2p_{1/2}$) were observed at 782 and 797 eV. The splitting of the Co 2p doublet was 15 eV, which is indicative of the presence of Co_3O_4 as the formed metal phase. Additionally, CoO satellite peaks were observed at 782 and 797 eV.

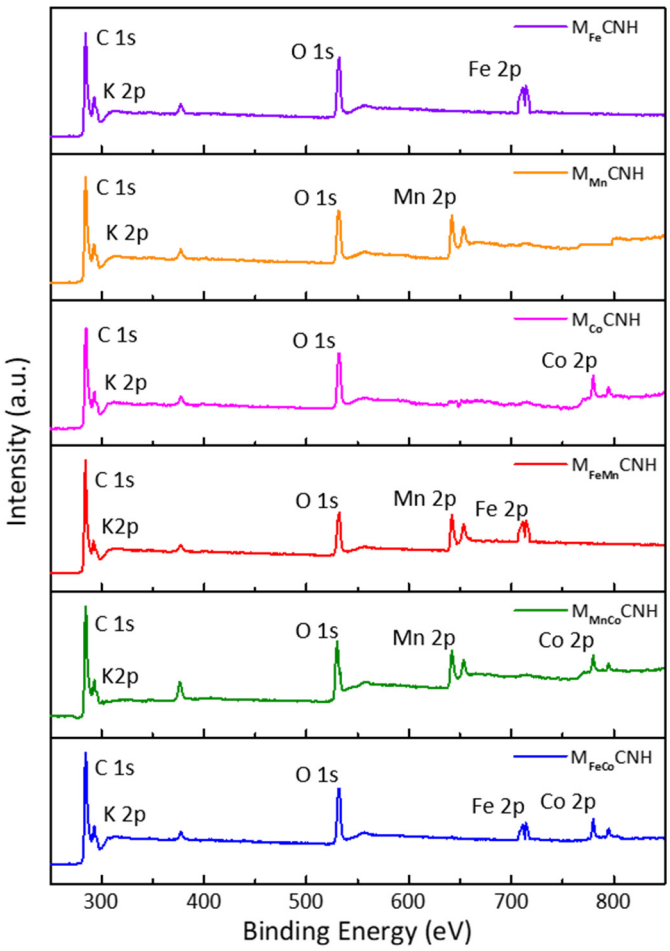

Figure S5. Full XPS spectra of the MCNHs.

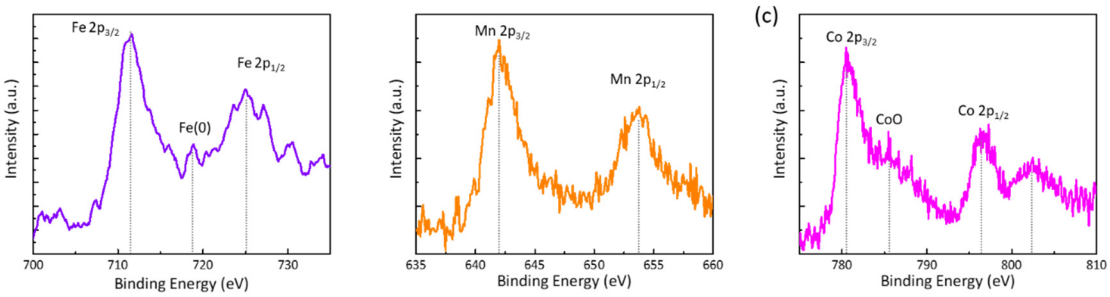

Figure S6. High-resolution XPS spectra of the metal phases in the MCNHs: (a) Fe 2p, (b) Mn 2p, and (c) Co 2p.

5. Electrochemical properties

Table S1. Integrated areas of the CV curves given in Figure 6.

Sample	CV area (V A g^{-1})
PC	0.27
AC	1.06
M_{Fe}CNH	8.49
M_{Mn}CNH	5.24
M_{Co}CNH	4.65
M_{FeMn}CNH	14.5
M_{MnCo}CNH	2.03
M_{FeCo}CNH	4.89

Table S2. Discharge capacitance values calculated from the charge/discharge curves given in Figure 7.

Sample	Capacitance (F g^{-1})
PC	10.2
AC	156
M_{Fe}CNH	539
M_{Mn}CNH	390
M_{Co}CNH	329
M_{FeMn}CNH	1124
M_{MnCo}CNH	242
M_{FeCo}CNH	330

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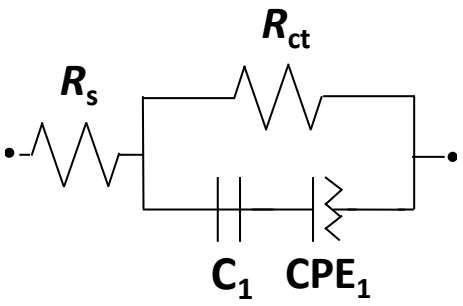
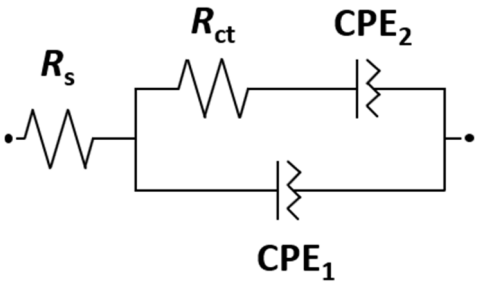
Table S3. Equivalent-circuit component values calculated through the fitting of the Nyquist plots given in Figure 7.

Sample	R_s (Ω)	R_{ct} (Ω)	C_1 (μF)	CPE_1 (Ω^*s^{-n1})	n_1	CPE_2 (μF)	n_2
PC	1.14	23862	17.4	37.6×10^{-5}	0.59	-	-
AC	1.10	571	15.3	126.9	0.58		
M_{Fe}CNH	1.18	110.6	-	0.85×10^{-2}	0.70	33	0.92
M_{Mn}CNH	1.25	207	30.3	0.84×10^{-2}	0.52	-	-
M_{Co}CNH	1.24	238	17.6	0.65×10^{-2}	0.50	-	-
M_{FeMn}CNH	1.17	50.3	-	6.4×10^{-2}	0.84	57	0.91
M_{MnCo}CNH	1.11	291	19.1	0.61×10^{-2}	0.54	-	-
M_{FeCo}CNH	1.30	255	20.5	0.62×10^{-2}	0.52	-	

PC



$M_{Fe}CNH$, $M_{FeMn}CNH$



AC, $M_{Mn}CNH$, $M_{Co}CNH$, $M_{MnCo}CNH$, $M_{FeCo}CNH$

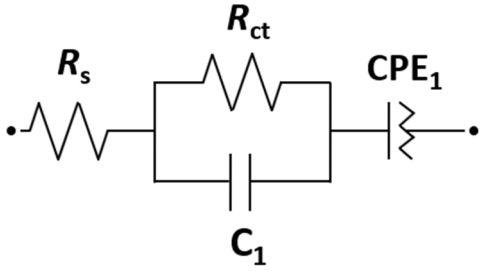


Figure S7. Equivalent-circuit models obtained through the fitting of the Nyquist plots given in Figure 7, where R_s, R_{ct}, C, and CPE note solution resistance, charge transfer resistance, capacitance, and constant phase element.