Supplementary Information for

Tailoring Non-Stoichiometric Spinel $Mn_{0.5}Co_{2.5}O_4$ via Tunable Microwave Strategy toward Advanced Supercapacitor Application

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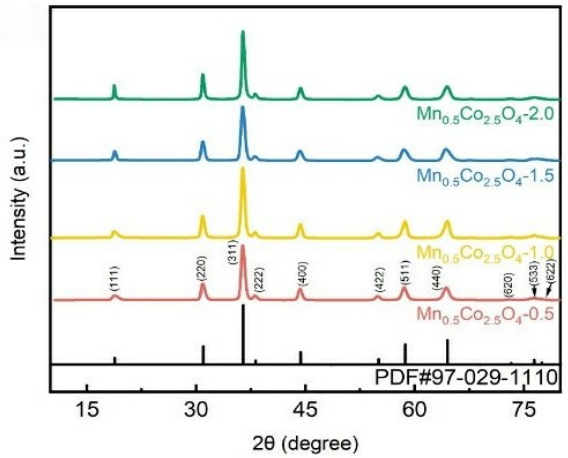

Figure S1. XRD patterns of $Mn_{0.5}Co_{2.5}O_4$ samples synthesized under different reaction time conditions.

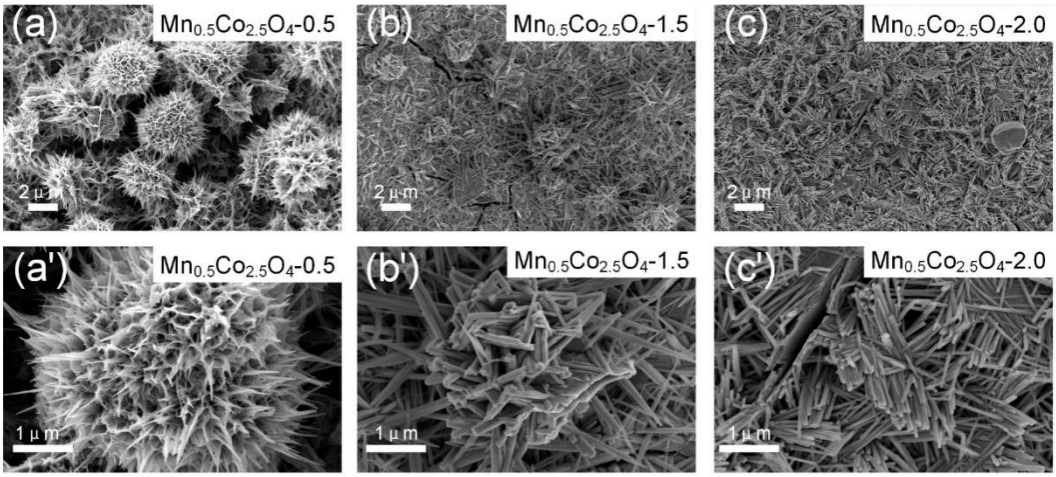

Figure S2. SEM images of (a, a') $Mn_{0.5}Co_{2.5}O_4$-0.5; (b, b') $Mn_{0.5}Co_{2.5}O_4$-1.5; (c, c') $Mn_{0.5}Co_{2.5}O_4$-2.0.

Figure S3. (a) Cyclic voltammograms at 10 mV s^{-1} and (b) galvanostatic charge-discharge curves at 1 A g^{-1}, with the derived specific capacitances, for $Mn_{0.5}Co_{2.5}O_4$ electrodes synthesized with

varied microwave reaction times.

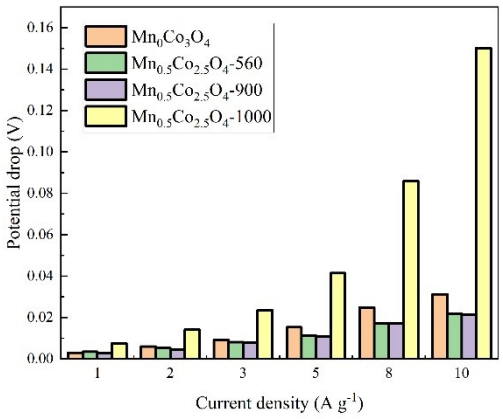

Figure S4. Potential drop at different current density for $Mn_0Co_3O_4$ and $Mn_{0.5}Co_{2.5}O_4$ samples.

S1. Materials

All chemicals were of analytical grade and used without further purification. Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and manganese(II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) were purchased from Aladdin Industrial Co., Ltd. (Shanghai, China); ammonium fluoride (NH_4F) was obtained from Macklin Biochemical Co., Ltd. (Shanghai, China); and urea ($CO(NH_2)_2$) was supplied by Guanghua Chemical Factory Co., Ltd. (Shantou, Guangdong, China). A microwave hydrothermal system (Beijing Xianghu Science & Technology Development Co., Ltd.) and a tubular furnace (Hefei Kemi Instruments Co., Ltd.) were used for sample synthesis and thermal treatment, respectively.

S2. Materials characterization

XRD (X-ray diffraction) analysis was performed using a BRUKER D8 Advance with Cu Kα radiation covering a 2θ range of 10-90° at a scan rate of 5° min^{-1}. This technique was applied to elucidate the crystal structures of both $Mn_0Co_3O_4$ and non-stoichiometric $Mn_{0.5}Co_{2.5}O_4$-*x*. XPS (X-ray photoelectron spectroscopy) with a ThermoFischer ESCALAB 250Xi, utilizing an Al Kα radiation source (*hv* = 1486.6 eV) in a chamber vacuum of 8×10^{-10} Pa, analyzed the elemental composition and oxidation states of the synthesized products. SEM (scanning electron microscopy) with a TESCAN MIRA LMS and TEM (transmission electron microscopy) with an FEI Tecnai F20 documented the microstructures and morphologies of the products.

S3. Electrochemical measurement

Electrochemical characterization was carried out using a typical three-electrode system with 6 M KOH solution as the electrolyte, a CORRTEST CS2350M electrochemical workstation, a saturated calomel electrode (SCE) as the reference electrode, and a platinum mesh electrode as the counter electrode. In this work, all electrode materials were directly grown on pretreated 3D nickel foam substrates through an in-situ microwave-assisted hydrothermal process, forming self-supported binder-free electrodes. The active material loading for the as-prepared samples was approximately 1.5 mg cm^{-2} for $Mn_0Co_3O_4$, 1.6 mg cm^{-2} for $Mn_{0.5}Co_{2.5}O_4$-560, 1.3 mg cm^{-2} for $Mn_{0.5}Co_{2.5}O_4$-900, and 1.5 mg cm^{-2} for $Mn_{0.5}Co_{2.5}O_4$-1000. The active surface area of each electrode was maintained at 1 × 1 cm^2, and the nanowire array films exhibited a uniform thickness of approximately 2-3 μm, ensuring good reproducibility across all samples. The specific capacity was determined using the GCD method (Equation (S1)), while cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were also employed for complementary electrochemical characterization[23–25].

$$C_{sp} = \left(F\ g^{-1}\right) = \frac{I\ \Delta t}{m\ \Delta V} \tag{S1}$$

In the formula, I denotes the current during the discharge process; m refers to the mass of the active material loaded onto the nickel foam; Δt represents the time of discharge; ΔV indicates the voltage (V).

Table S1. Atomic percentages of Mn, Co, and O species in $Mn_0Co_3O_4$ and $Mn_{0.5}Co_{2.5}O_4$ samples.

	$Mn_0Co_3O_4$	$Mn_{0.5}Co_{2.5}O_4$-560	$Mn_{0.5}Co_{2.5}O_4$-900	$Mn_{0.5}Co_{2.5}O_4$-1000
Mn	0	5.95	7.18	6.58
Co	33.89	18.59	18.32	17.41
O	45.6	56.77	55.88	56.91

Table S2. Fitted EIS parameters of $Mn_0Co_3O_4$ and $Mn_{0.5}Co_{2.5}O_4$-900 electrodes.

Sample	Rs（Ω）	Capacitors（F）	Rct（Ω）	Warburg（$S \cdot sec^{0.5}$）
$Mn_0Co_3O_4$	0.677	0.0002	154.49	0.385
$Mn_{0.5}Co_{2.5}O_4$-900	0.485	0.0040	109.26	0.367