

Hierarchical Porous $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ Nanocubes Obtained by Calcining Prussian Blue Analogous as Anode for Lithium-ion Batteries

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1. Experimental

1.1 Synthesis of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ nanocubes.

All chemicals are of analytical grade and used without further purification. The typical procedures were as follows: Solution A: 0.714 g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 2.262 g $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ were dissolved in 100ml deionized water under agitated stirring to form a transparent solution. Solution B: 0.66 g $\text{K}_3[\text{Fe}(\text{CN})_6]$ was dissolved in 100ml deionized water under magnetic stirring to form another transparent solution. Then, a purple turbid solution was formed when solution B was slowly added into solution A. The mixing process was kept at room temperature (about 25 °C) with agitated stirring. After 5 min, the mixed solution was aged at room temperature for 24 h. Then the resulting purple precipitate was collected by centrifugation and washed several times with water and ethanol, and finally dried in vacuum at 60 °C. The purple Co-Fe-PBA precursors were then collected. After that, the purple precursor was annealed at different temperature (300, 400, 500, 600, 700, 900 °C) in the muffle furnace for 2 h in air at a heating rate of 1 °C·min⁻¹, respectively.

1.2 Materials characterization

The powder X-ray diffraction (XRD) pattern was collected on a Bruker D8 Advance diffractometer equipped with Cu K_α radiation over the 2θ range of 10–80°. Thermogravimetric analysis (TGA) was carried out using a shimadzu-50 thermoanalyser under air flow 10 °C min⁻¹ in the temperature range 27–700 °C. The morphology and structures of the products were characterized by field-emission scanning electron microscopy (SEM) and transmission electron microscopy (HRTEM, JEOL JEM-1011). Specific surface areas were computed from the results of N_2 physisorption at 77 K (Micromeritics ASAP 2020) by using the BET (Brunauer-Emmet-Teller)

and BJH (Barret-Joyner-Halenda). An X-ray photoelectron spectrum (XPS) was performed on an ESCALAB 250 X-ray Photoelectron Spectrometer with Al K_{α} radiation.

1.3 Electrochemical measurements

Electrochemical measurements were carried out using coin cells (CR2025). The composite cathode was formulated with 70% of active materials, 20% conductive material (acetylene black) and 10% CMC (Carboxymethylcellulose) mixed with deionized water. After being stirred for 6 h, the slurry was cast onto Cu foil using a doctor blade, and dried at 60 °C for 12 h under vacuum. The load mass of each electrode was 1.2-1.4 mg. The coin cells were assembled in an argon-filled glove box using lithium as the negative electrodes, Celgard 2500 as the separators, and 1 M LiPF₆ (DEC: DC: EC = 1:1:1, v/v) as the electrolytes. The galvanostatic charge and discharge experiments were carried out at room temperature using a LAND CT-2001A (Wuhan, China) and the cut-off voltage ranged from 0.01 to 3.0 V. Cyclic voltammetry (CV) was conducted on a PARSTAT2273 electrochemical workstation (Princeton Applied Research, USA) at a scanning rate of 0.02 mV s⁻¹ in the potential range of 0.01-3.0 V. Electrochemical Impedance Spectroscopy (EIS) experiments were carried out using a CHI660D electrochemical workstation.

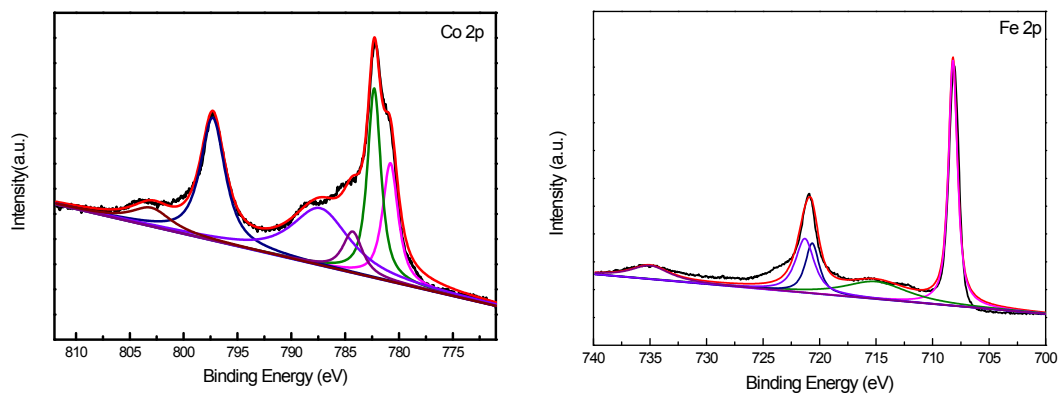


Figure. S1 the XPS spectrum pattern of Co 2p(a) and Fe 2p (b) of Co-Fe-PBA.

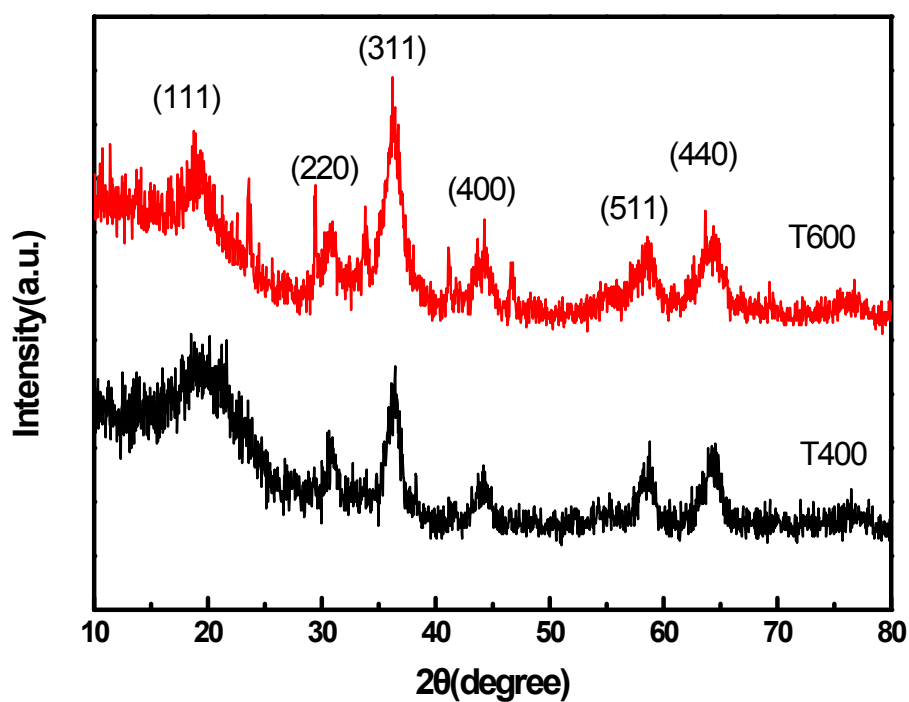


Figure. S2 XRD pattern of T400 and T600.

Table S1 The detailed component information of T300, T500, T700 and T900 confirmed by the EDS.

Temperature (°C)	Element	Atomic (%)
T300	Co	16.53
	Fe	25.63
	O	57.84
T500	Co	16.34
	Fe	26.49
	O	57.17
T700	Co	17.41
	Fe	24.68
	O	57.91
T900	Co	13.17
	Fe	27.35
	O	59.48

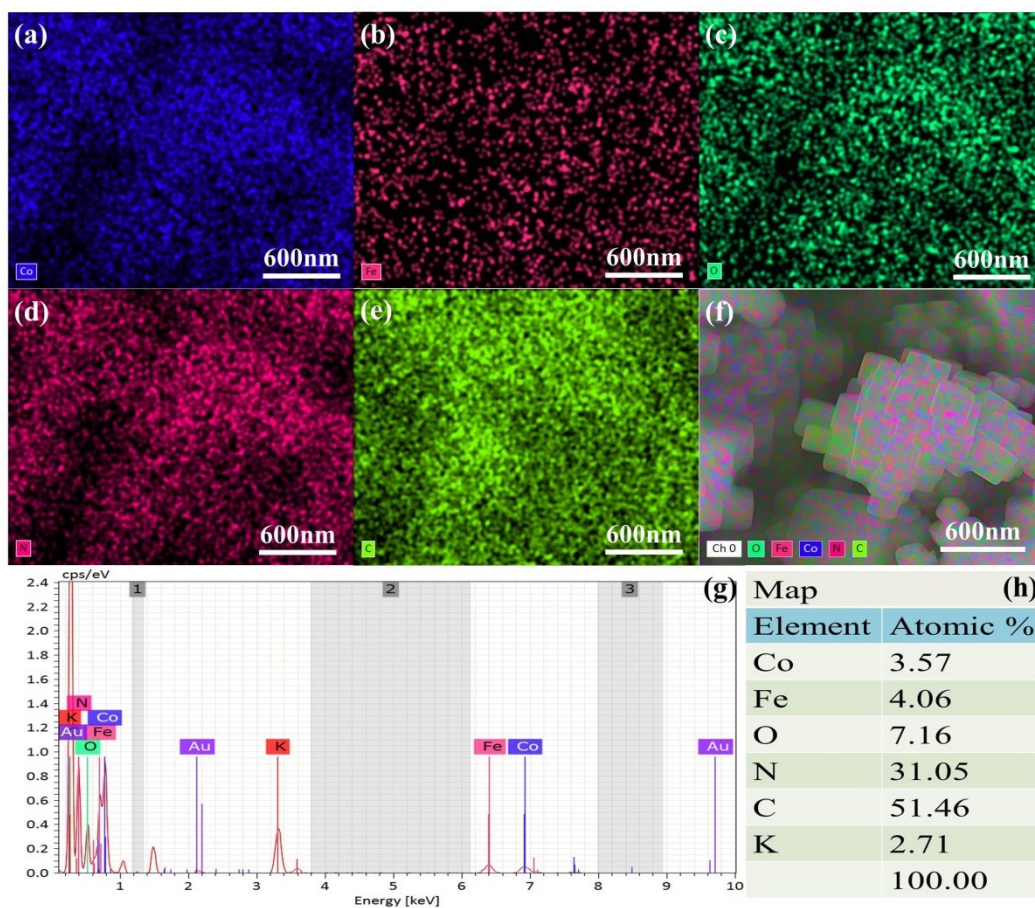


Figure. S3 Element mapping of (a) Co, (b) Fe, (c) O, (d) N, and (e) C; (f) The overlapped element mapping of Co, Fe, O, N, and C; (g) EDX spectrum and (h) the ratio of each element of Co-Fe-PBA.

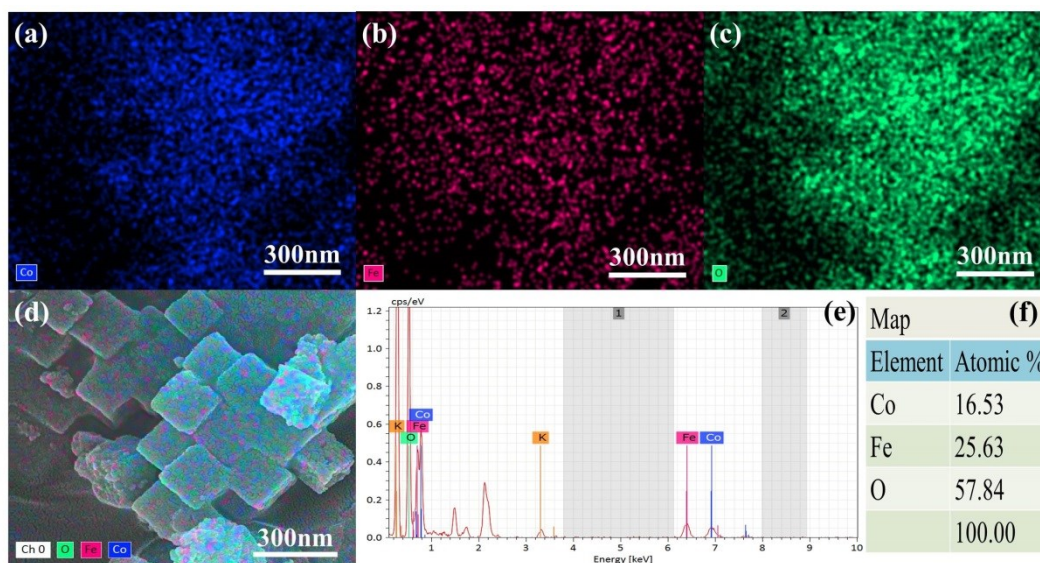


Figure. S4 Element mapping of (a) Co, (b) Fe and (c) O; (d) The overlapped element mapping of Co, Fe and O; (e) EDX spectrum and (f) the ratio of each element of T300.

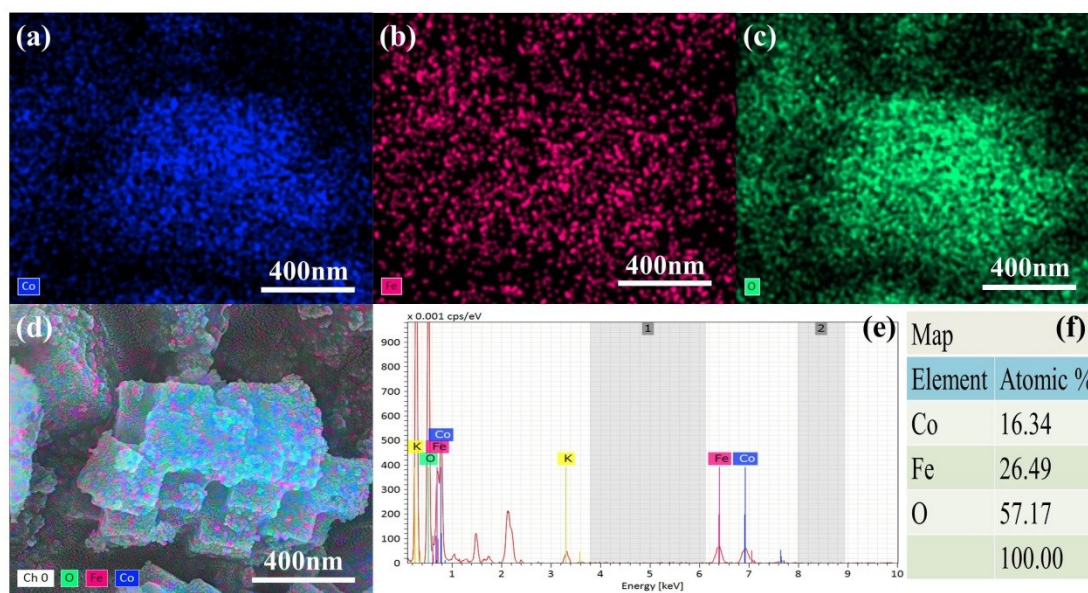


Figure. S5 Element mapping of (a) Co, (b) Fe and (c) O; (d) The overlapped element mapping of Co, Fe and O; (e) EDX spectrum and (f) the ratio of each element of T500.

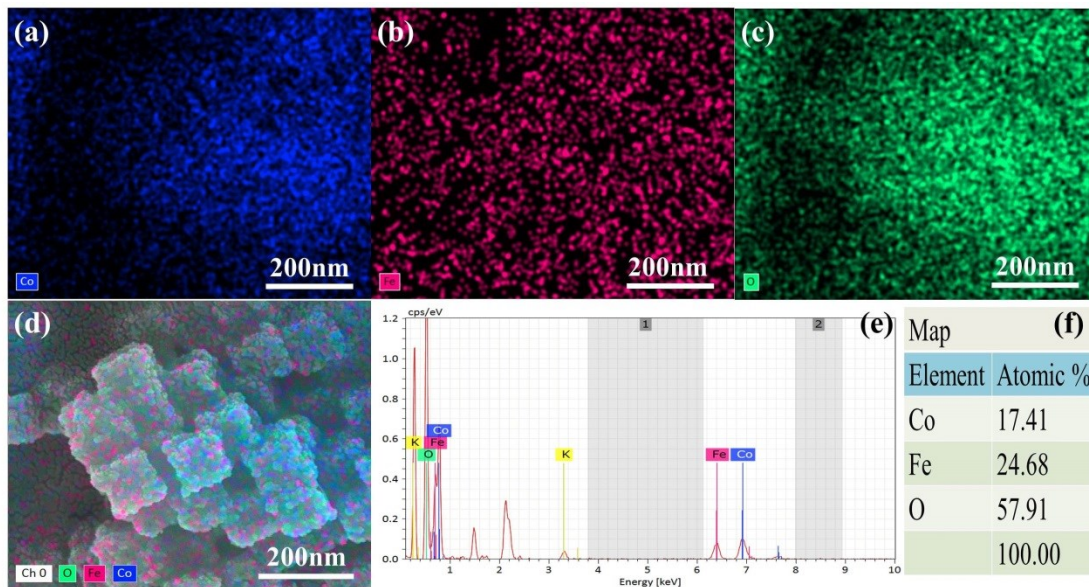


Figure. S6 Element mapping of (a) Co, (b) Fe and (c) O; (d) The overlapped element mapping of Co, Fe and O; (e) EDX spectrum and (f) the ratio of each element of T700.

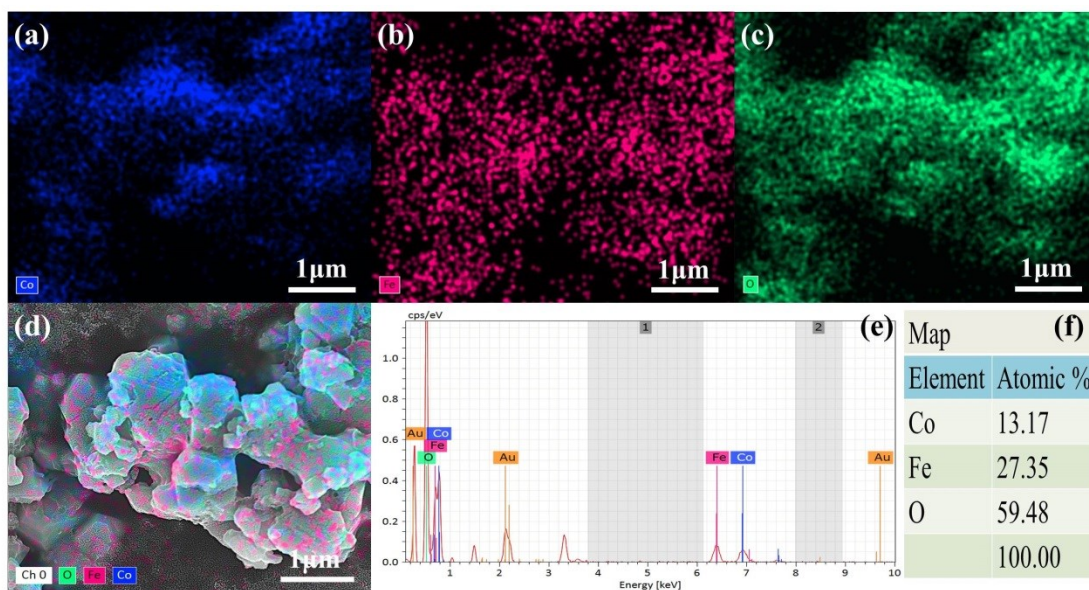


Figure. S7 Element mapping of (a) Co, (b) Fe and (c) O; (d) The overlapped element mapping of Co, Fe and O; (e) EDX spectrum and (f) the ratio of each element of T900.

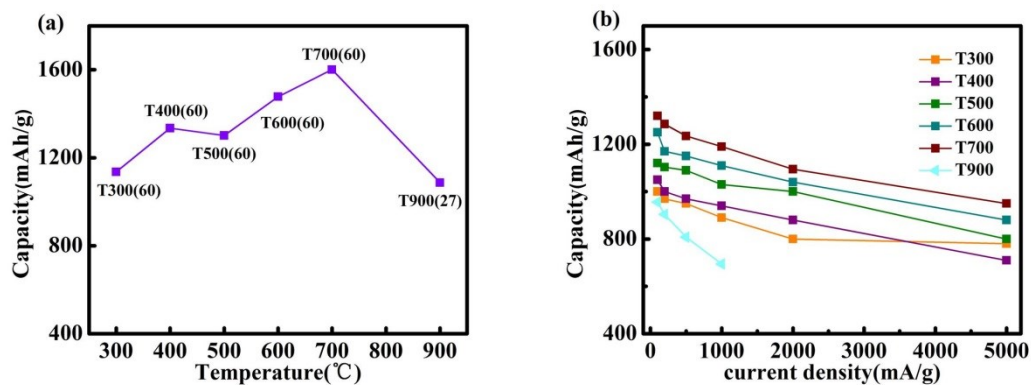


Figure. S8 (a) The comparison of the discharge specific capacity after 60 cycles, and (b) is a comparison graph of discharge specific capacity at different current densities.

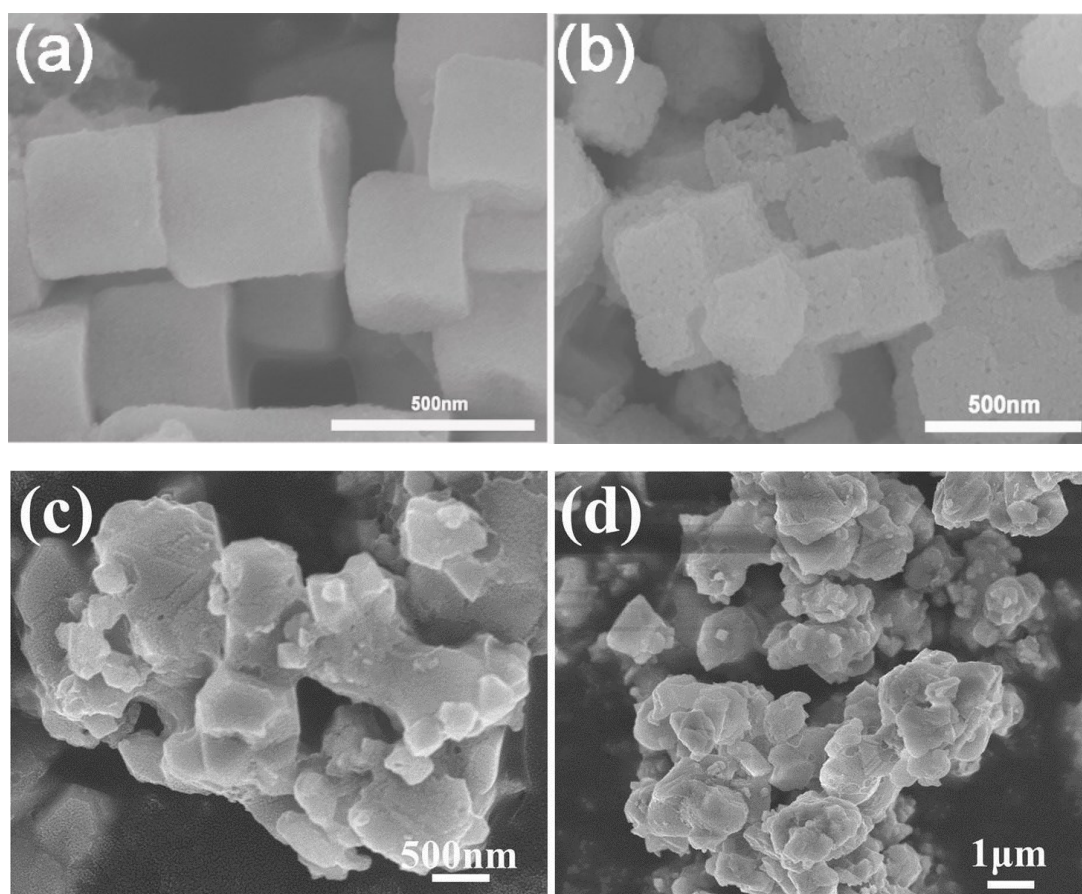


Figure. S9 SEM images of (a) T400 , (b) T600, (c, d) T900, respectively.

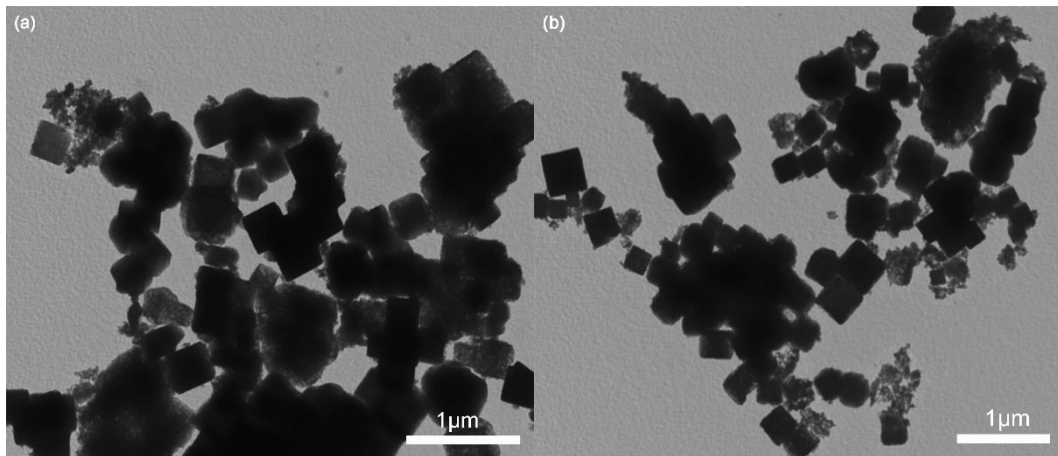


Figure. S10 TEM images of: (a) T400 and (b) T600.

Table S2. The surface-related data of experiment sample

Experiment number	Calcination temperature(°C)	Specific surface area(m ² /g)	The pore volume (cm ³ /g)
1	300	33.121	0.108
2	500	29.195	0.208
3	700	22.130	0.229

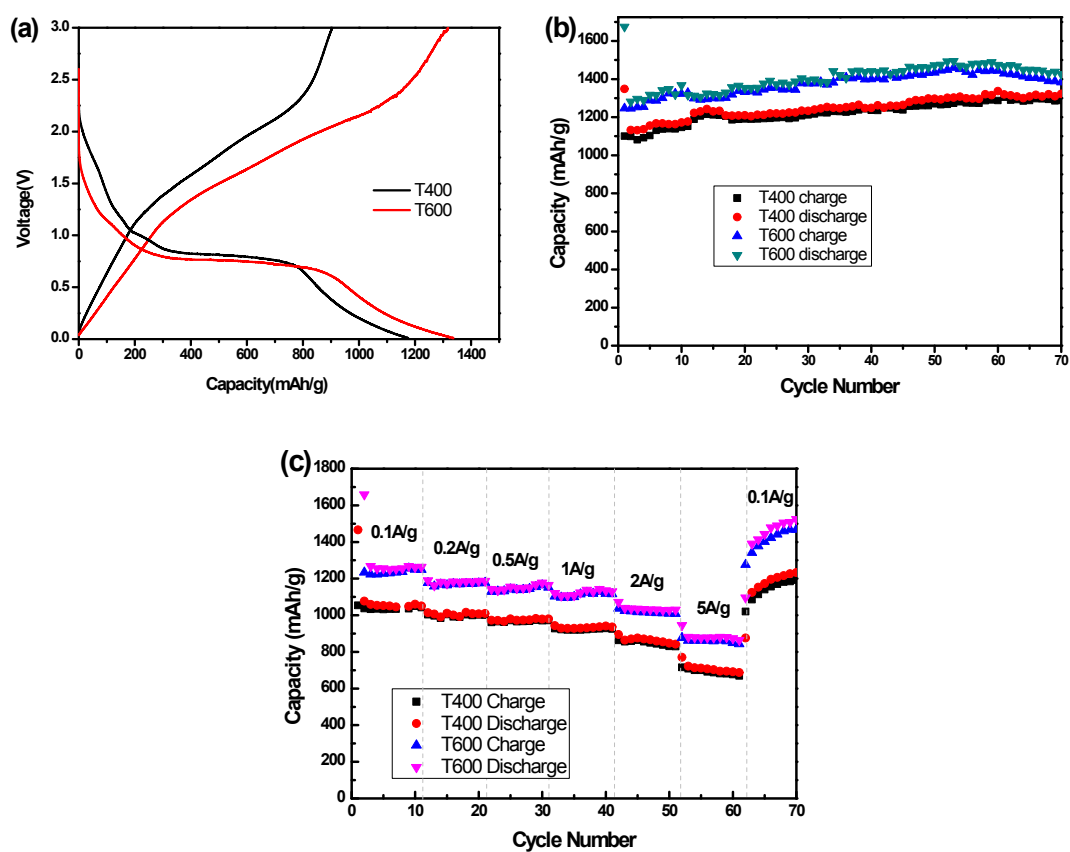


Figure. S11 (a) charge and discharge curves of T400 and T600 respectively; (b) Cycling performance and (c) rate capability, All the galvanostatic tests in (a) and (b) are performed at a constant current density of 100 mA g⁻¹ between 0.01 and 3 V.

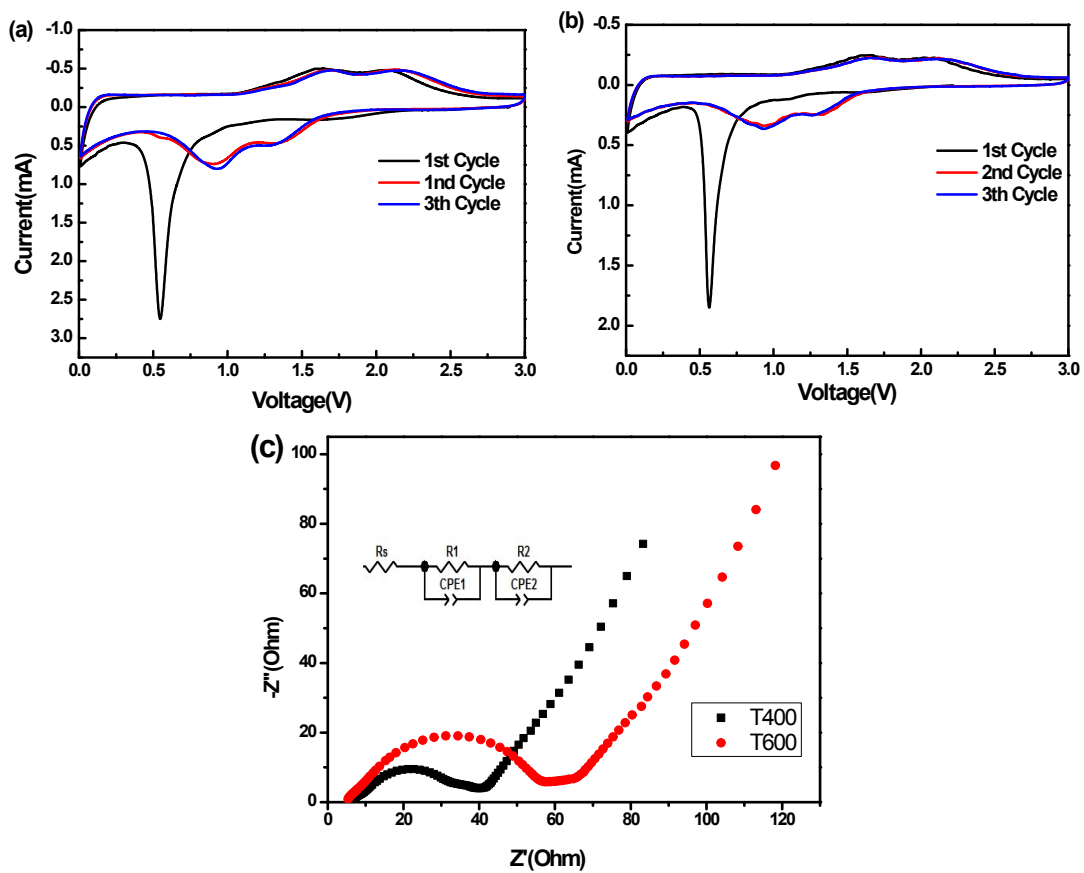


Figure. S12 The first three CV curves of (a) T400, and (b) T600 at a scan rate 0.02 mV s^{-1} , (c) Equivalent circuit and electrochemical impedance spectra after the 1st cycle.

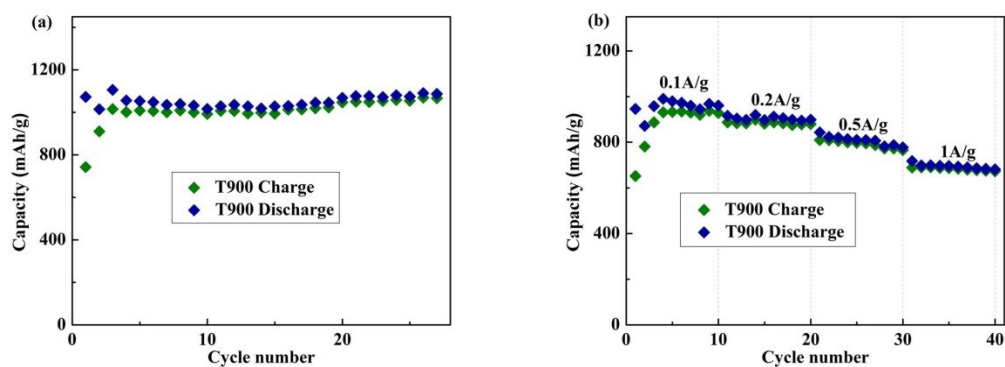


Figure. S13 (a) Cycling performance and (b) rate capability of T900.