Supplementary data

Precise preparation of layered $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ micro-sheets for 3.8 V Na-ion batteries

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Experimental

$Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ micro-sheets were synthesized by a polyethylene glycol (PEG)-assisted co-precipitation method. In a typical synthesis, analytical reagent grade $NaCH_3COO{\cdot}3H_2O$, $Ni(CH_3COO)_2{\cdot}4H_2O$, and $Mn(CH_3COO)_2{\cdot}4H_2O$ in the molar ratio of 0.5:0.25:0.75 and in quantities corresponding to 0.40 g of $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ were dissolved in 20 mL of water. The solution was heated to 50 °C and then 2 mL of PEG 400 was added. Under constant magnetic stirring, 1.8 g of tartaric acid was added to the solution. Then the solution was heated to 85 °C to afford a green viscous precursor. The precursor was calcined at 400°C for 5h and 1000°C for 20 h in air to obtain the $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ micro-sheets. We have also prepared a batch of samples by controlling the annealing temperature (700-900 ^oC) for comparison.

Material Characterization

The structures of the as-synthesized samples were characterized by powder X-ray diffraction (XRD, Rigaku MiniFlex600, Cu Kα radiation). The morphologies of the samples were observed by scanning electron microscopy (SEM, JEOL, JSM-7500F). The high-resolution transmission electron microcopy (HRTEM, tecnai G2 F20) equipped with an energy dispersive X-ray detector (EDX) were employed to investigate the particle distribution and surface morphologies of the synthesized samples. X-ray photoelectron spectroscopy (XPS) data were collected using a Perkin Elmer PHI 1600 ESCA system. The inductively coupled plasma-atomic emission spectroscopy (ICP-900, Thermo Jarrell-Ash Corp) was used to check the elemental stoichiometry ratio of $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ micro-sheets. Furthermore, to measure the tap density, a certain amount of the $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ micro-sheet product was placed in a small measuring cylinder and tapped for at least 30 min by hand. The measured volume of the tapped powder and its mass were used to calculate the tap density of $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ micro-sheets.

The working electrodes were made from a mixture of 80 wt. % of the active material, 15 wt. % of the conducting agent (Super P), and 5 wt. % of the polyvinylidene difluoride (PVDF) binder. The counter/reference electrode was sodium metal, and the separator was glass fiber. The electrolyte solution was 1 M $NaClO_4$ dissolved in ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 in volume). The assembled cells were cycled at different charge-discharge rates in the voltage range of 3.2 – 4.3 V on a CT2001A cell test instrument (LAND Electronic Co.). The specific capacity was calculated on the basis of the amount of the active material. The cyclic voltammograms (CV) were performed with a Parstat 263A electrochemical workstation (AMTECT Company).

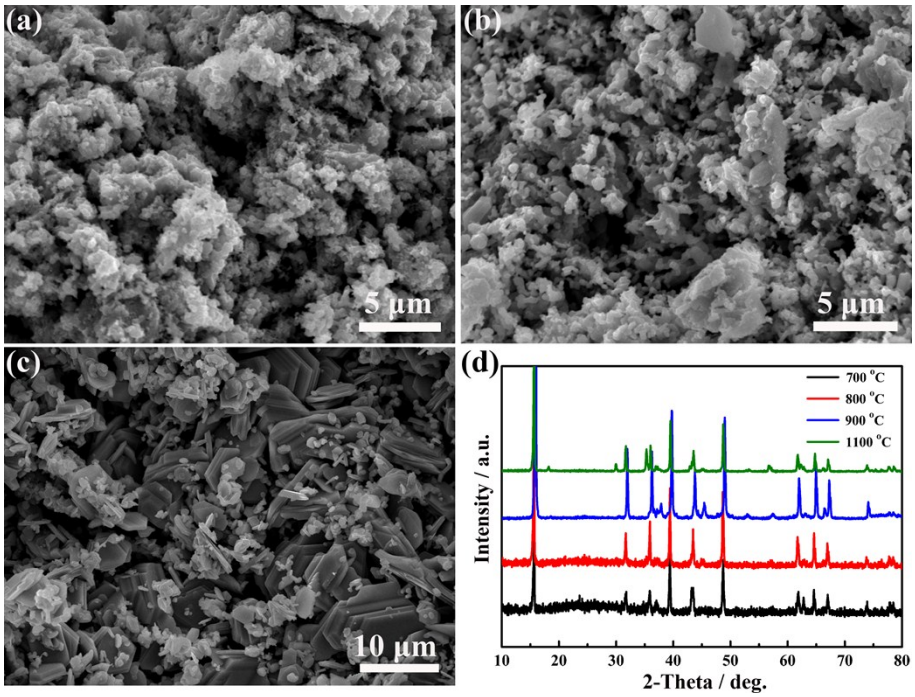

Fig. S1 SEM images (a-c) and XRD patterns (d) of samples prepared with different annealing temperature (a) 700 °C, (b) 800 °C and (c) 900 °C. When annealing temperature below 800 °C, the sample presents in the form of irregular nanoparticles, while the phase is not belong to P2-type $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$. When the calcination temperature is higher than 800 °C, P2-type $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ has form and the crystallinity increases with the annealing temperature. Meanwhile the nanoparticles began to melt into micro-sheets and at calcination temperature of 1000 °C, the sample appears completely in the micro-sheet structure. When the temperature reached 1100 °C, some other diffraction peaks are detected, suggesting the appearance of impurity.

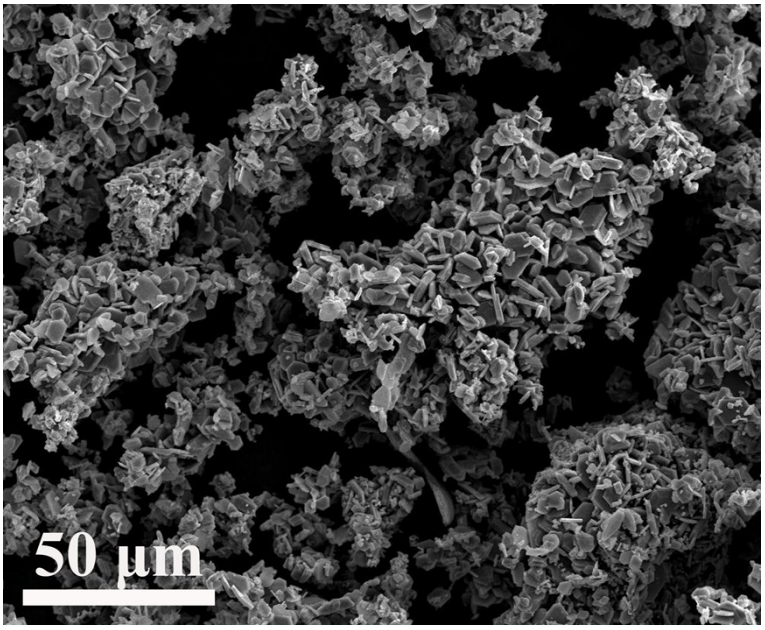

Fig. S2 Low-Resolution SEM image of $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ micro-sheets.

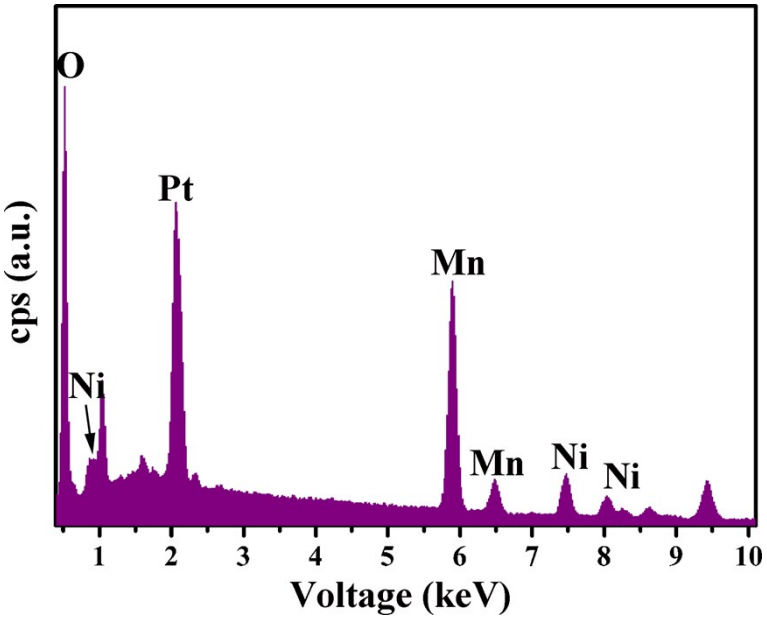

Fig. S3 EDS image of $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ micro-sheets.

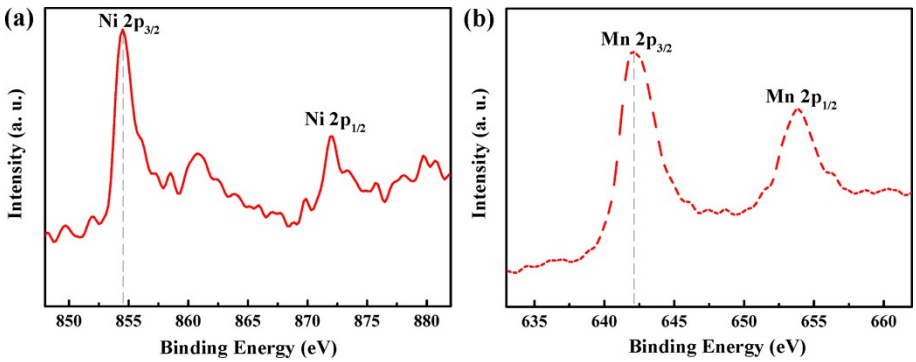

Fig. S4 XPS spectrum of $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ micro-sheets.

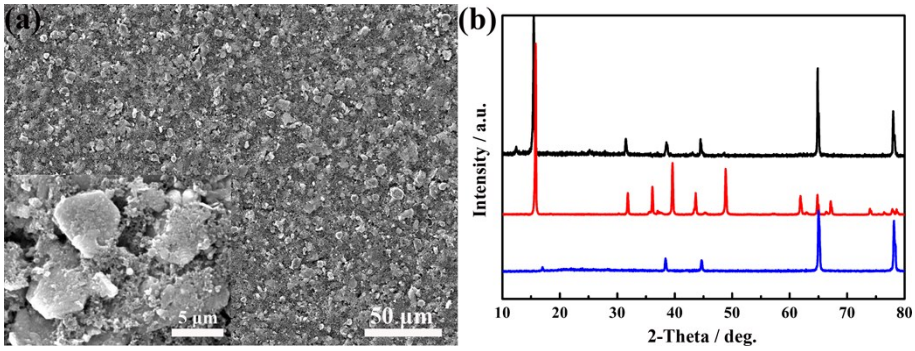

Fig. S5 SEM and XRD of the $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ micro-sheet electrode in full discharged state after 50 cycles at 0.2 C rate. In the XRD pattern, the black line (top) indicates the experimental data of cycled $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ micro-sheet electrode, red line (middle) is as-prepared $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ micro-sheets and blue line (bottom) represents the Al that is the current collector used for the cathode.

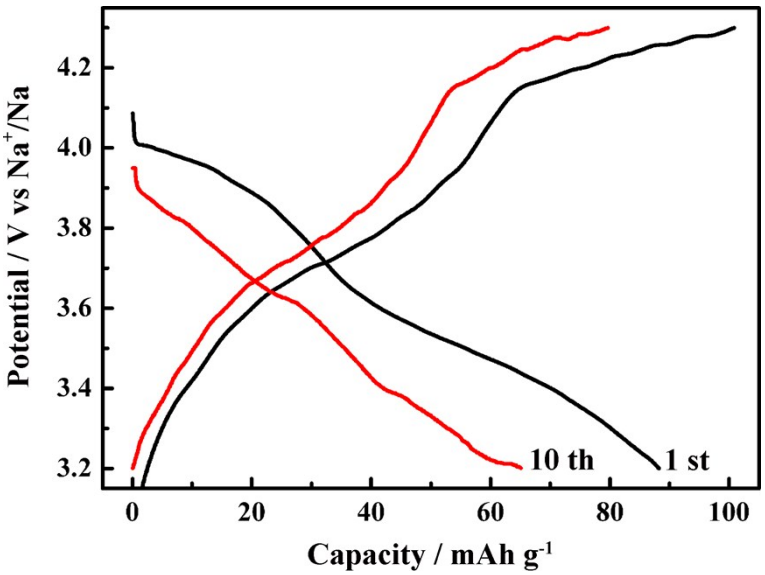

Fig. S6 Typical charge–discharge curves and cycling performance of $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ granular materials (mixed nanoparticles and micro-particles, at annealing temperature of 800 ^oC) at 0.2 C.

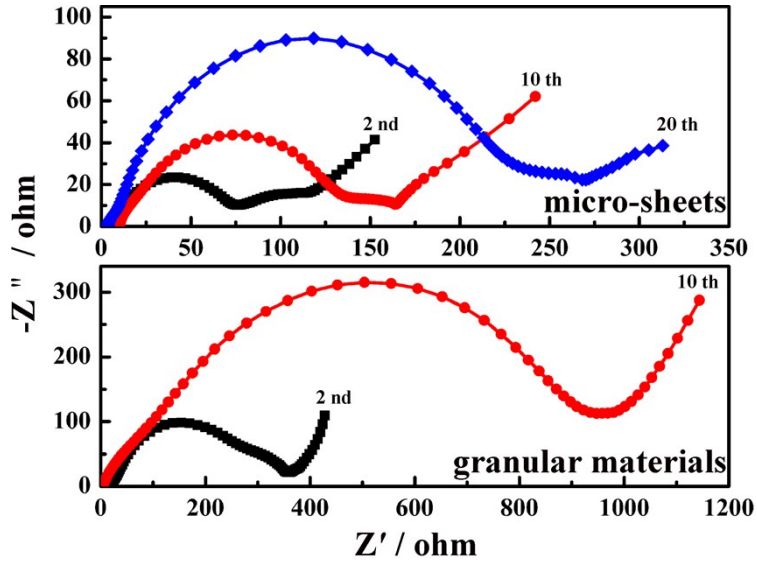

Fig. S7 EIS of the $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ micro-sheets (1000 ^oC) and granular materials (800 ^oC) electrodes collected in part discharged state at about 3.9 V after different cycles at 0.2 C.

Table S1 Electrochemical properties of $Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$ micro-sheets and other current cathode materials.

Materials	**Average Potential**	**Capacity (mAh g^{-1})**	**Capacity retention**	**Reference**
$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$	2.75 V	190 (13 mA g^{-1}, 1.5−4.2 V)	~79 % (30 cycles)	Ref 3
$Na_{1.5}VPO_{4.8}F_{0.7}$	3.8 V	134 (12.9 mA g^{-1}, 1.5−4.6 V)	~95 % (100 cycles)	Ref 6
$NaMnO_2$	2.7 V	190 (10 mA g^{-1}, 2.0−4.2 V)	76 % (100 cycles)	Ref 7
$NaFe_{1/2}Co_{1/2}O_2$	3.1 V	160 (12.1 mA g^{-1}, 2.5–4.0 V)	89 % (40 cycles)	Ref 8
$Na_{0.61}Ti_{0.48}Mn_{0.52}O_2$	2.9 V	86 (20 mA g^{-1}, 1.5–4.0 V)	81% (100 cycles)	Ref 9
$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$	2.6 V	134.5 (13 mA g^{-1}, 1.5−4.0 V)	69 % (40 cycles)	Ref 10
$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$	2.6 V	~195 (26 mA g^{-1}, 1.5−4.2 V)	90 % (80 cycles)	Ref 11
$Na_{0.5}Ni_{0.25}Mn_{0.75}O_2$	3.8 V	121 (26.8 mA g^{-1}, 3.2−4.3 V)	80 % (50 cycles)	This work