Electronic Supplementary Material (ESI) for RSC Advances.

Electronic supplementary information

Efficient energy storage capabilities promoted by hierarchically $MnCo_2O_4$ nanowires-based architectures

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1. EXPERIMENTAL SECTION

Hydrothermal Synthesis of Flower-like $MnCo_2O_4$ Nanowires: 0.02 M manganese nitrate tetrahydrate [$Mn(NO_3)_2 \cdot 4H_2O$, 97%, Sigma-Aldrich], 0.04 M cobalt nitrate hexahydrate [$Co(NO_3)_2 \cdot 6H_2O$, 99%, ACROS], 0.1 M urea [$CO(NH_2)_2$, 99%, Sigma-Aldrich], and 0.04 M ammonium fluoride (NH_4F, 98%, Merck) were prepared by dissolving an appropriate weight in 50 mL deionized water (DIW). The Ni foam substrate (2 cm×3 cm piece, Kunshan Desike Electronic, China) was ultrasonically cleaned in ethanol for 30 min, immersed in a 10 % vol/vol HCl solution for 5 min to get rid of the possible surface oxide, washed by DIW and finally ultrasonically cleaned by DIW and acetone (30 min of successive sonication for each), before it was put into the top of bottle for reaction, followed by sonication for 45 min. The solution was then transferred into a 100 mL Teflon-lined stainless autoclave where the Nickel foam was kept on top. The autoclave was sealed and maintained at 140 °C for 7 h. After the autoclave cooled down naturally to room temperature, the product was collected, washed, dried, and then thermal-treated at 350 °C for 3 h in air atmosphere.

Instrumentation and Sample Analysis: The crystallographic information of the prepared samples was established by powder X-ray diffraction [XRD, Bruker D2 PHASER XRD Analyzer with Cu Kα radiation (λ = 1.54178 Å)]. Field-emission

scanning electronic microscopy (FESEM, JEOL JSM-6700F) was employed to examine the morphologies of the products. Structural and compositional investigations were carried through transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) using JEM-2100F (JEOL) and Energy Dispersive X-ray Spectrometry (EDS) instruments.

Electrochemical Measurements: The mass loadings of the actual samples for lithium-ion battery and supercapacitor tests were 1.7 ± 0.3 mg cm^{-2}

Li-ion Battery measurement: Electrochemical tests were performed under ambient temperature using two-electrode coin cells (CR 2032) with lithium foil serving as both counter electrode and reference electrode. A piece of the Ni foam mounted by $MnCo_2O_4$ nanowire was directly used as the working electrode without any polymeric binder or carbon black conductive additives involved. Celgard® 2400 polymer separators were also employed. Afterward, 1 M $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) was used as the electrolyte. The cell assembly was carried out in an argon-filled glovebox with both moisture and oxygen content below 1 ppm. Galvanostatic charge/discharge was conducted using a battery tester (AcuTech Systems Co., Ltd., Taiwan) with a voltage window of 0.01 V to 3.0 V at a constant density 200 mA g^{-1}. Cyclic voltammetry (CV) test was carried

out in the potential window of 0.01 V to 3.0 V at a scan rate of 0.5 mV s^{-1} by an electrochemical workstation (AUTOLAB PGST30, Eco Chemie).

Supercapacitor measurement: The electrochemical performance of the prepared $MnCo_2O_4$ nanowires electrode, for symmetric supercapacitor, was investigated using two-electrode coin-type cells (CR 2032) assembled in an argon-filled glove box, A pair of electrodes was assembled with a glass fiber separator (18 mm in diameter, Pall corporation) with 1M $LiClO_4$ in propylene carbonate (PC) organic electrolyte. The electrochemical properties of the supercapacitor were studied using cyclic voltammetry (CV), galvanostatic charge-discharge (GV) and electrochemical impedance spectroscopy (EIS) using 760D (CH Instruments). The CV tests were carried out in the potential range of 0 to 2.5 V at different scan rates ranging from 1 mV s^{-1} to 5000 mV s^{-1}. The galvanostatic charge-discharge measurements were also carried out at different current densities from 0.1 A g^{-1} to 10 A g^{-1} between voltage window 0 and 2.5 V and the EIS measurements were performed in the frequency range of 1 MHz to 1 Hz. The EIS data were analyzed using Nyquist plots.

The specific capacitance, (C, F g^{-1}) was then calculated from the CV curves according to the following equation ($C= i / m x\Delta V$) where m (g) is the mass of active materials, ΔV (V s^{-1}) is the potential sweep rate and i (A) is the current response, which is obtained through integrating the area of the CV curve.[1]

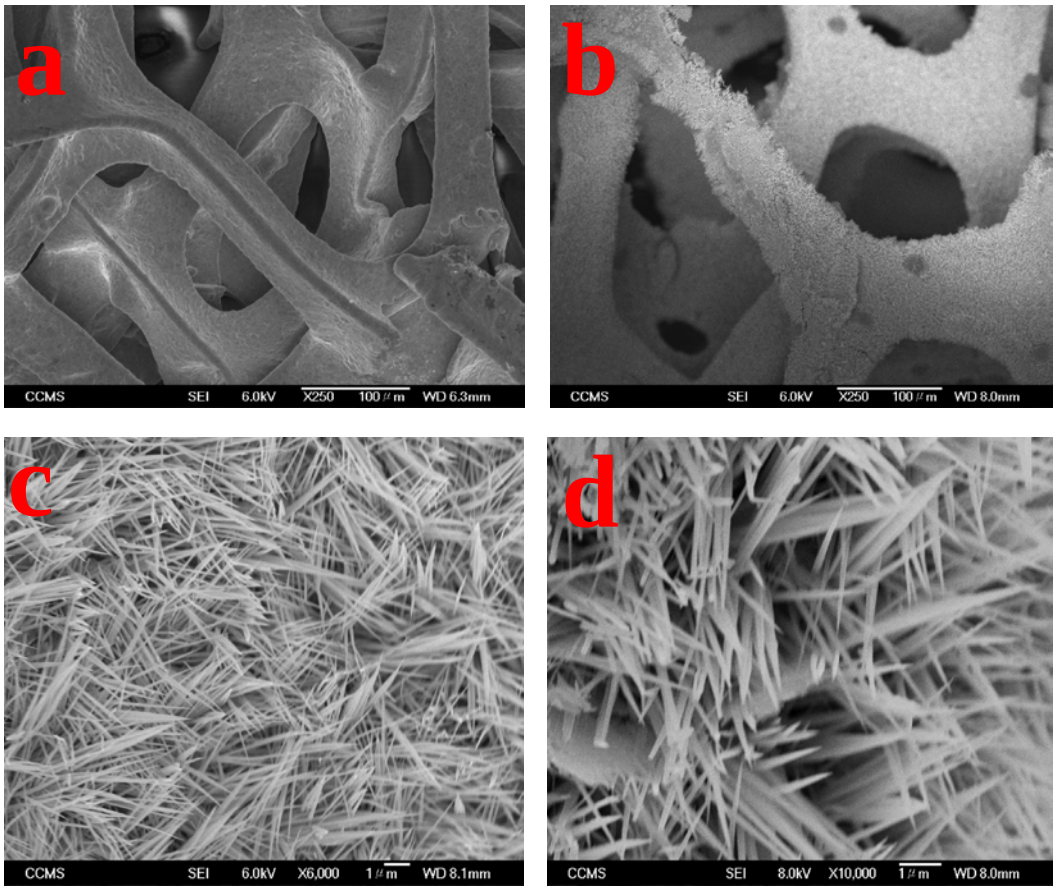

Figure S1 FESEM images of (a) pristine Nickel foam and (b–d) different SEM magnifications the $MnCo_2O_4$ nanowire growing on Nickel foam. Showing a uniform distribution of discrete nanowires onto Ni foam.

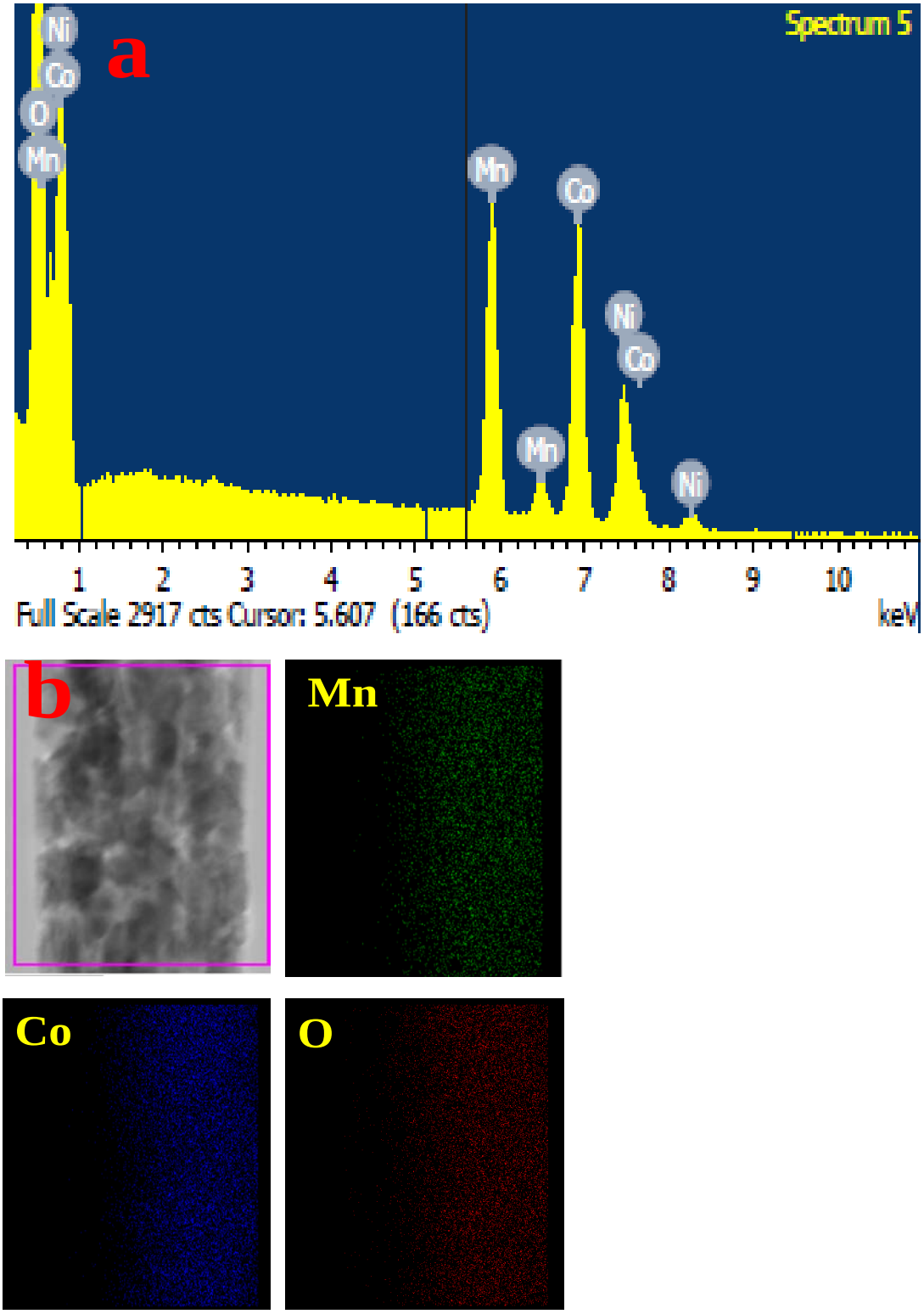

Figure S2 (a) The EDS microanalysis on selected areas and (b) elemental mappings of Mn, Co, and O for the $MnCo_2O_4$ nanowire

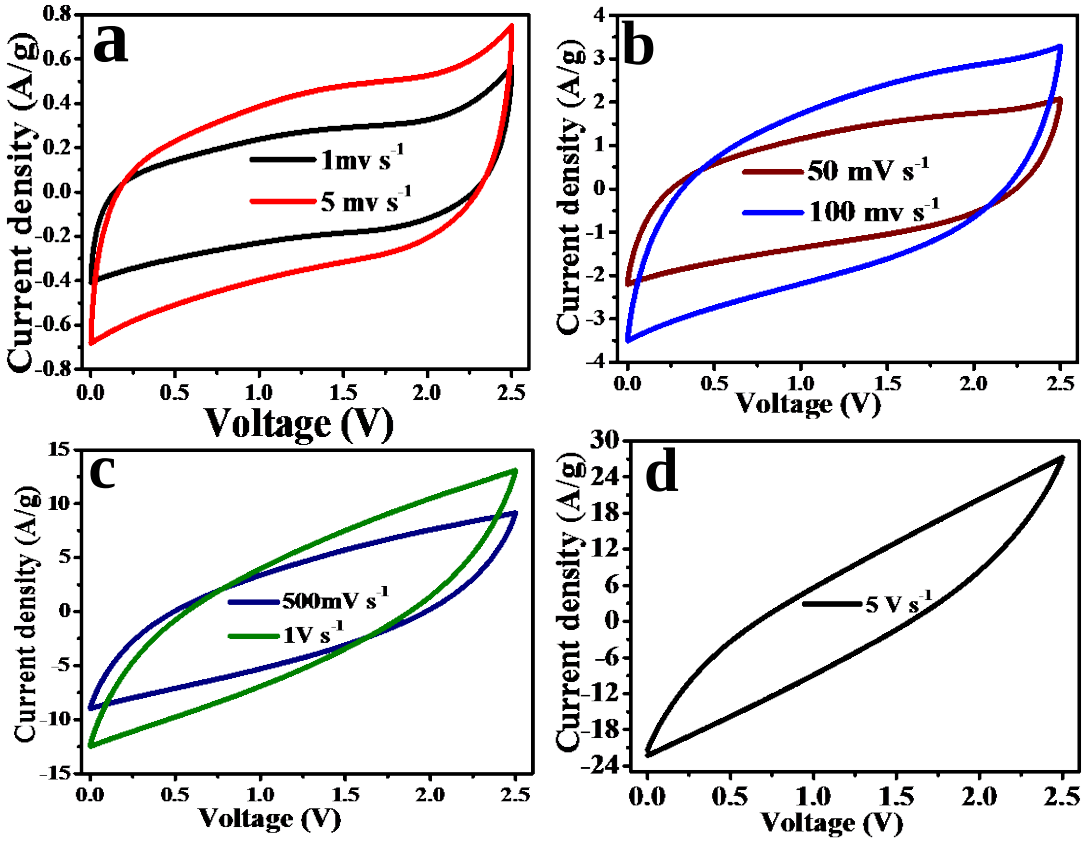

Figure S3 CV curves of symmetrical supercapacitor containing $MnCo_2O_4$/Ni foam electrode in 1 M $LiClO_4$ electrolyte at a voltage scaning rate of (a) 1 and 5 mV s^{-1}, (b) 50 and 100 mV s^{-1}, (c) 500 mV s^{-1} and 1 V s^{-1} and (d) 5 Vs^{-1}. The figure shows that the CV curves are nearly rectangular shape at low scan rate and then deviated to oval shape by increasing the scan rate.

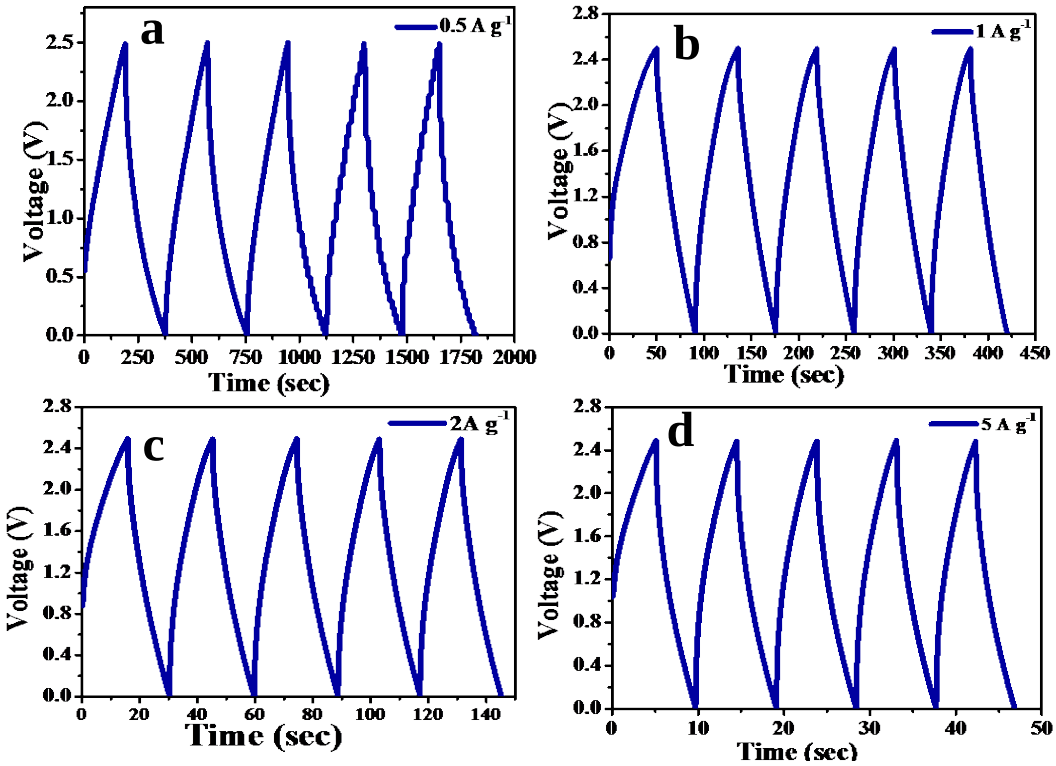

Figure S4 first 5 cycles of galvanostatic charge- discharge of symmetrical supercapacitor containing $MnCo_2O_4$/Ni foam electrode in 1 M LiClO4/PC electrolyte at current density of (a) 0.5, (b) 1, (c) 2 and (d) 4 A g^{-1}. The result showed that the anodic charging segments are symmetric to the corresponding cathodic discharging counterparts (triangular shape) for lower and higher charge-discharge current density.

References for supporting information.

(1) X. Tang, H. Li, Z.-H. Liu, Z. Yang and Z. Wang, *J. Power Sources*, 2011, **196**,855