Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

One-step synthesis of hierarchical $ZnCo_2O_4$@$ZnCo_2O_4$ core-shell nanosheet arrays on nickel foam for electrochemical capacitors

Fuxi Bao, Ziqing Zhang, Xiaoyang Liu* and Xudong Zhao*

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012 (P. R. China)

*To whom correspondence should be addressed: Tel: (+86) 431-85168316; Fax: (+86) 431-85168316; E-mail: liuxy@jlu.edu.cn; xdzhao@jlu.edu.cn

Experimental details

Synthesis of hierarchical $ZnCo_2O_4$@$ZnCo_2O_4$ core-shell nanosheet arrays

This hierarchical $ZnCo_2O_4$@$ZnCo_2O_4$ core-shell nanosheet arrays was synthesized through a one-step hydrothermal method followed by annealing treatment. All chemicals were analytical grade and used as received without further purification. In a typical procedure, 0.291g of $Co(NO_3)_2$ $6H_2O$, 0.148g of $Zn(NO_3)_2$ $6H_2O$, 0.093g of NH_4F and 0.30g of urea were dissolved in a mixed solution of 60 mL of H_2O and 40 mL of ethanol. After being stirred for half hour, the solution was aged for three days. Then the solution was transferred into a 20 mL of teflon-lined stainless steel autoclave. A piece of Nickel foam ((length × width × thickness = 2 cm × 1 cm × 1mm), after treated with 3M HCl for 15 min and cleaned thoroughly with de-ionized water and ethanol, was immersed into the reaction solution. The autoclave was sealed and heated to and maintained at 120 ℃ for 4 h in an electronic oven, and then cooled to room temperature naturally. After washed with distilled water and acetone repeatedly and dried at 80 ℃ for 2 h, the Ni foam with the Zn-Co precursor was annealed at 350 ℃ for 2 h to obtain hierarchical $ZnCo_2O_4$@ $ZnCo_2O_4$ core-shell nanosheet arrays.

Characterization

The Morphologies and structures of the products were measured by using a scanning electron microscopy (JEOL JSM-6700F microscope, Japan). The Powder X-ray diffraction (XRD) patterns of products were obtained from a Rigaku D/Max2550V/PC with Cu-$K\alpha$ radiation (λ=0.15418 nm). Transmission electron microscope (TEM) images and high resolution transmission electron microscope (HRTEM) images were obtained on a FEI Tecnai G2 F20 s-twin D573 transmission electron microscope working at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250 X-ray photoelectron spectrometer with a Mg-$K\alpha$ excitation source. The nitrogen sorption measurements were examined by a Micromeritics ASAP 2420 surface area analyzer using Brunauer-Emmett-Teller (BET) method at 77 K.

Electrochemical measurements

The electrochemical tests were carried out using a CHI 760D electrochemical workstation in a 2 M KOH aqueous electrolyte with a three-electrode configuration. A platinum plate and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively, and the as-obtained hierarchical $ZnCo_2O_4$@$ZnCo_2O_4$ core-shell nanosheet arrays/Ni foam integrated electrode (1 cm × 1 cm) was directly served as the working electrode. As a comparison, Zn-Co precursor with core-shell nanosheet arrays grown on Ni foam also tested under same conditions.

Table S1. The ratio of Zn(II) and Co(II)/Co(III) in the sample based on the total area of peaks after a Gaussian fitting method.

Composite	Total areas of the fitted peaks	The atom ratio of Co/Zn
Co(II)/Co(III)	90306.66	1
Zn(II)	52812.11	0.44

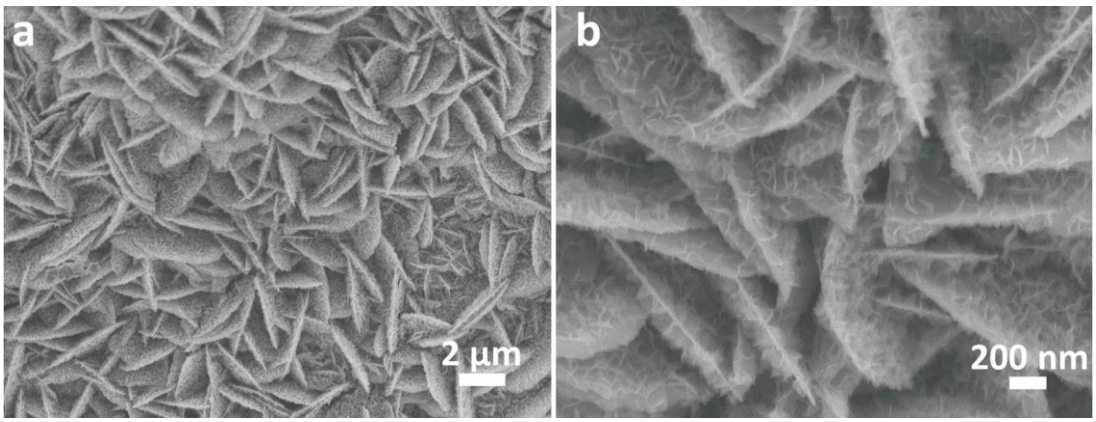

Fig. S1 The SEM of Zn-Co precursor core-shell nanosheet arrays.

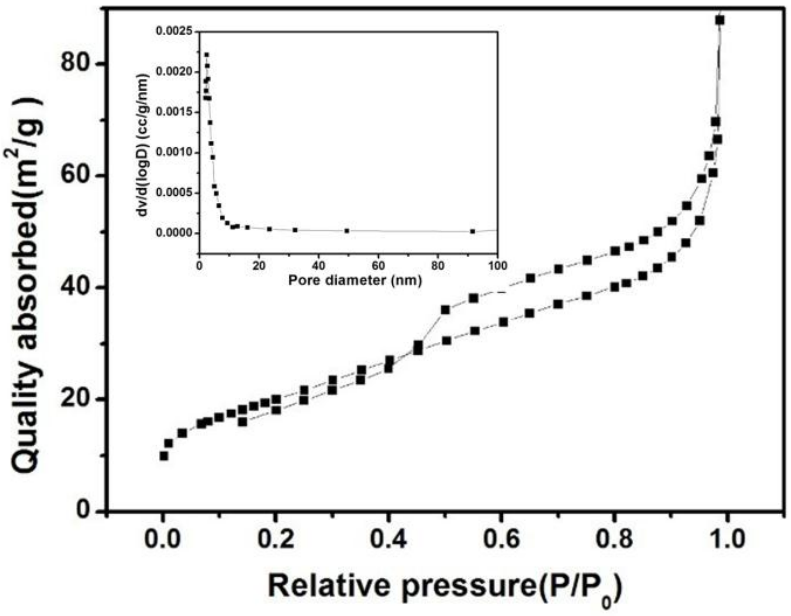

Fig. S2 N_2 adsorption-desorption isotherms of as-prepared $ZnCo_2O_4$@$ZnCo_2O_4$ nanosheet arrays peeled from nickel foam substrate and the inset was the corresponding pore size distribution.

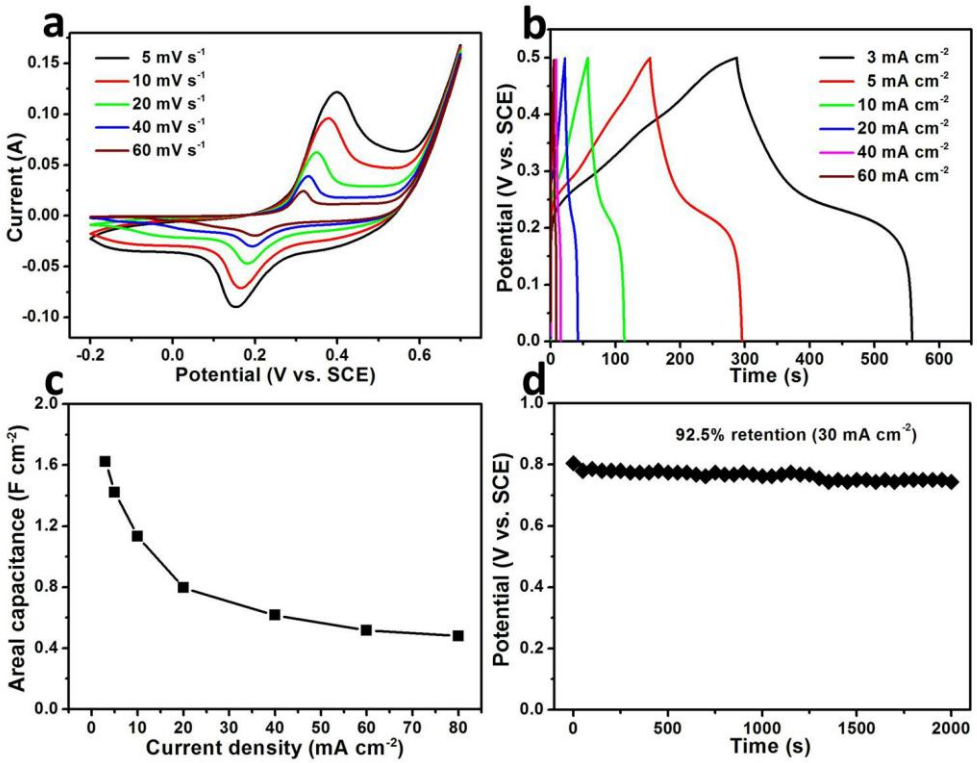

Fig. S3 Electrochemical properties of the Zn-Co core-shell nanosheet arrays grown on Ni foam: (a) CV curves at various scan rates; (b) charge-discharge curves at different current densities; (c) specific capacitance as a function of current density; (d) cycling performance at a constant current density of 30 mA cm^{-2}.

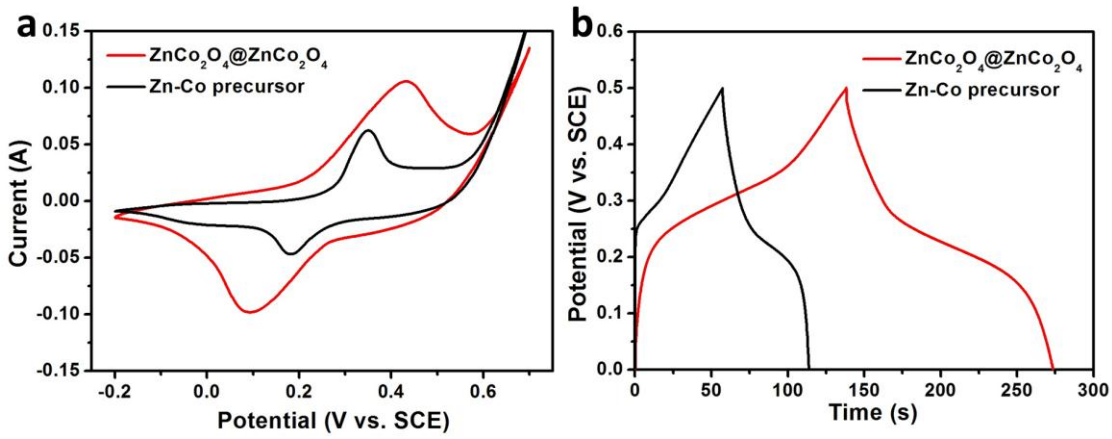

Fig. S4 (a) Comparison of the cyclic voltammetry (CV) curves of the as-synthesized $ZnCo_2O_4$@$ZnCo_2O_4$ core-shell nanosheet arrays and Zn-Co precursor at a scan rate of 20 mV s^{-1}; (b) Comparison of the galvanostatic charge-discharge curves of as-prepared materials at a current density of 10 mA cm^{-2}.

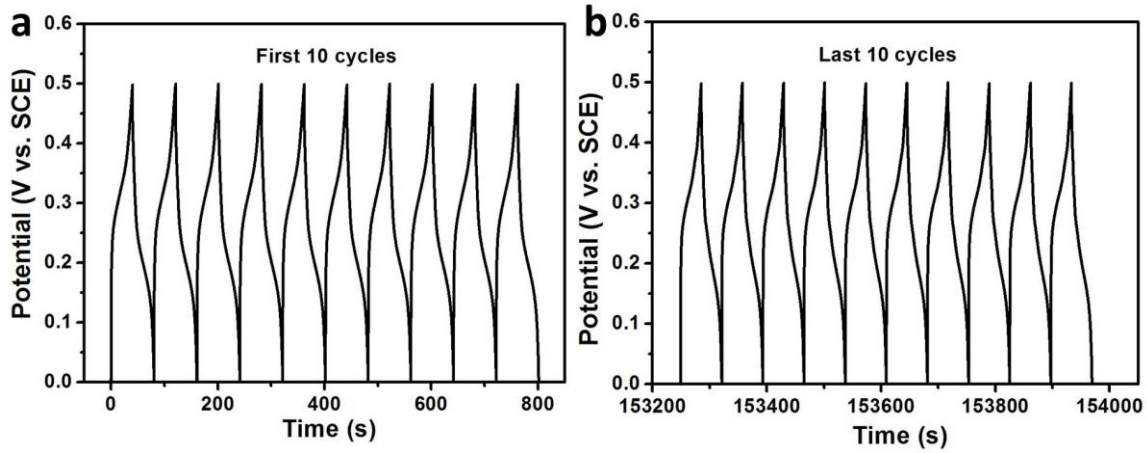

Fig. S5 (a) The charge-discharge curves of the first 10 cycles for the as-synthesized $ZnCo_2O_4$@$ZnCo_2O_4$ core-shell nanosheet arrays; (b) The charge-discharge curves of the last 10 cycles.

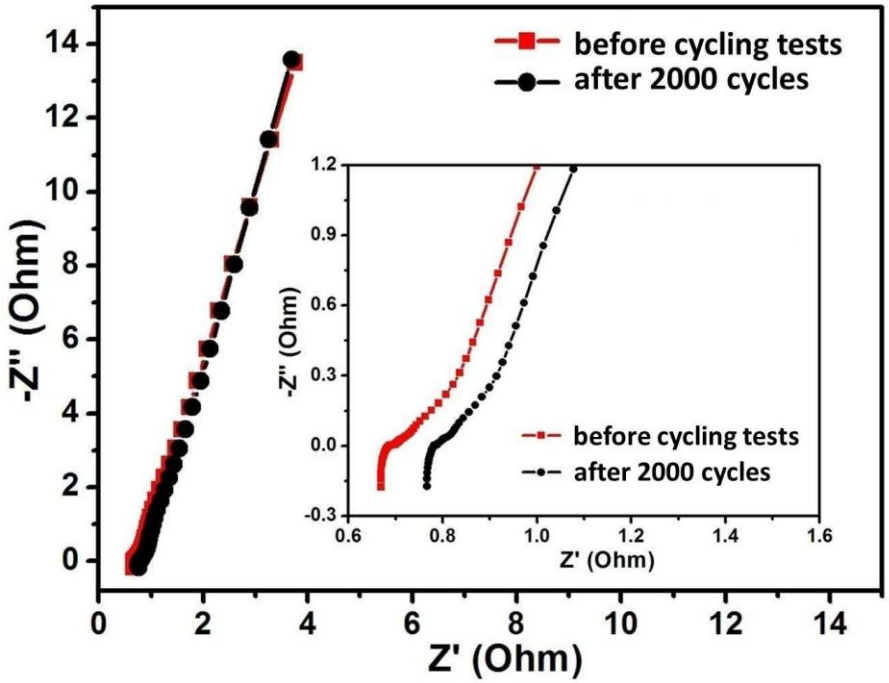

Fig. S6 Impedance Nyquist plots of $ZnCo_2O_4$@ $ZnCo_2O_4$ core-shell nanosheet arrays/Ni foam integrated elecrode before and after 2000 cycles at open circuit potential (insert is impedance plot in high frequency region).