Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

In-situ Shape and Phase Transformation Synthesis of Co_3S_4 Nanosheet Arrays for High-Performance Electrochemical Supercapacitors

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1. Experimental section

1.1.Preparation of Co_3S_4 Nanosheet Arrays

The Co_3S_4 nanosheet arrays electrode materials were synthesized on nickel foam *via* an *ion-exchange* reaction by employing Co_3O_4 nanowire arrays as the shape and phase sacrificing template. First, Co_3O_4 nanowire arrays were prepared on nickel foam by a hydrothermal process similar to described previously.[1] In detail, Ni foam (approximately 1 cm×3 cm) substrate was carefully cleaned with 3M HCl solution, de-ionized water and absolute ethanol with the assistance of an ultrasound bath each for 5 min in order to remove the possible NiO layer on the surface. The Ni foam was put in a Teflon-lined stainless steel autoclave with homogeneous aqueous solution containing 4mmol $Co(NO_3)_2·6H_2O$, 8mmol NH_4F and 20mmol urea, respectively. After 5h growth at 120℃, the Ni foam was carefully rinsed several times with de-ionized water and cleaned with the assistance of ultrasonication several seconds to remove the loosely attached products on the surface, and then dried in air. Then, the product was annealed at 250℃ for 2h with a ramping rate of 5℃ min^{-1} in air to completely transform into black Co_3O_4 nanostructures (Co_3O_4 mass loading: ~1.97mg/cm^2). For synthesis the Co_3S_4 products, the pre-grown Co_3O_4 nanowire-Ni foam was put into a Teflon-lined autoclave containing 0.02M Na_2S aqueous solution and maintained at 95℃ for 24h. After the reaction, the converted sample was taken out and rinsed several times with de-ionized water, and finally dried in an oven at 60℃ for 12h. The Co_3S_4 mass loading on Ni foam after conversion is ~2.49mg/cm^2.

1.2.Material Characterization.

The products were characterized by X-ray diffraction (XRD; Bruker D-8 Avance), scanning electron microscopy (SEM, 5.0kV) equipped with an energy dispersive X-ray spectrometer (EDS) and transmission electron microscopy (TEM; JEM-2010FEF, 200kV). N_2 adsorption-desorption measurements were conducted at 77K on a Nove 2200e analyzer.

1.3. Electrochemical Measurements

The electrochemical tests were performed with a electrochemical workstation (CHI660D CH Instruments Inc. Shanghai), using a three-electrode cell, and performed at room temperature in a 2.0M KOH electrolyte within the potential window of -0.2 to 0.5V. Pt foil and Ag/AgCl were served as the counter electrode and the reference electrode, respectively. The nickel foam supported Co_3S_4 nanosheet arrays and Co_3O_4 nanowire arrays (~1cm^2 area) were used as the working electrodes directly. EIS measurements were performed by applying an AC voltage with 5 mV amplitude in a frequency range from 0.01 Hz to 100 kHz at open circuit potential.

2. Figures and Captions

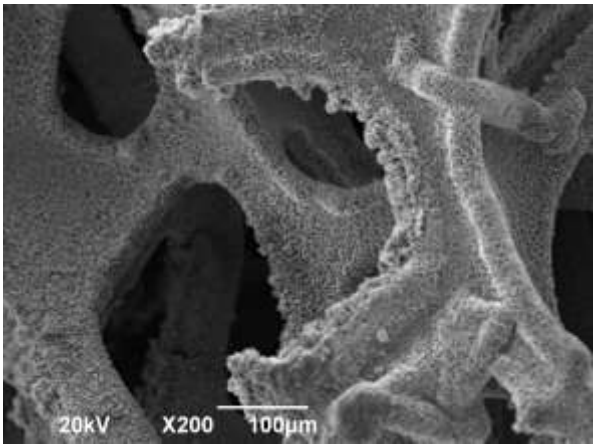

Fig. **S1** Large-scale view of SEM image of the Co_3S_4 nanosheet arrays on Ni foam.

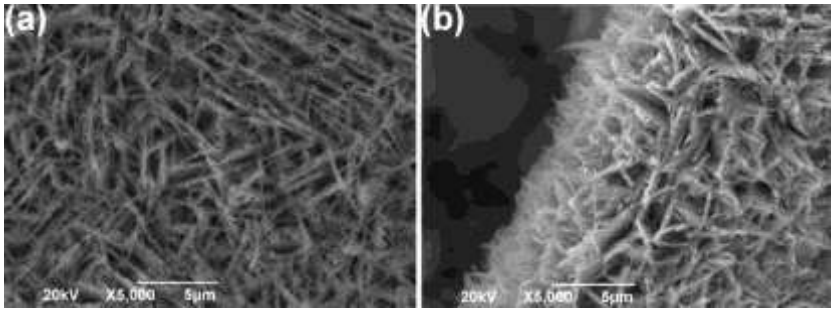

Fig. **S2** SEM images of the sample obtained with the reaction time for 6h under the same condition.

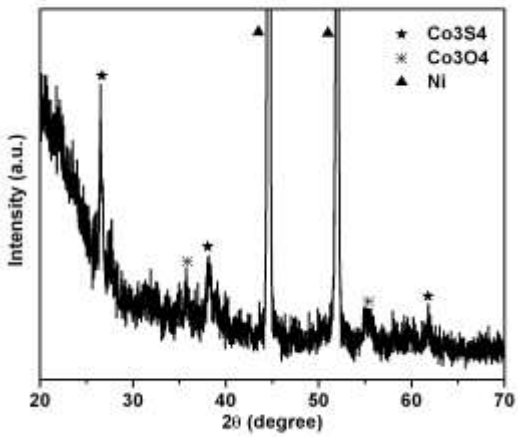

Fig.S3 XRD pattern of the product obtained for 6 h reaction, indicating that the pre-grown Co_3O_4 has been partly converted into Co_3S_4.

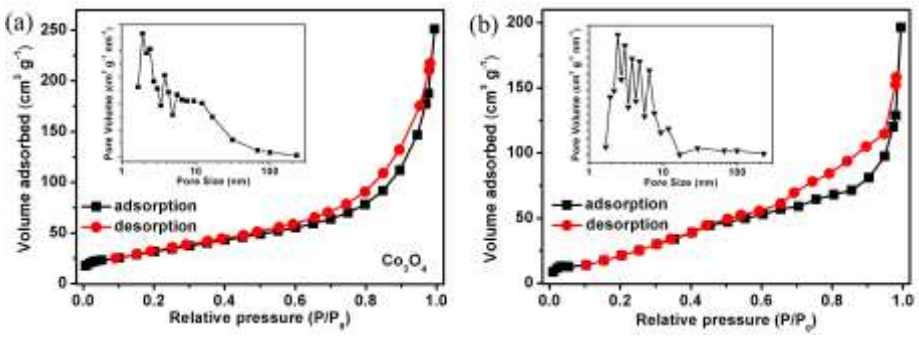

Fig.S4 N_2 adsorption–desorption isotherm and the corresponding pore size distribution (inset) of the pre-grow Co_3O_4 NWs (a) and the Co_3S_4 NSs (b) using BJH method.

Reference

(1) J. Jiang, J. P. Liu, X. T. Huang, Y. Y. Li, R. M. Ding, X. X. Ji, Y. Y. Hu, Q. B. Chi and Z. H. Zhu *Crystal Growth & Design*, **2010**, *10*, 70.