Supporting Information

Co_3S_4 hollow nanospheres grown on graphene as advanced supercapacitor materials

Qinghong Wang, Lifang Jiao,* Hongmei Du, Yuchang Si, Yijing Wang, Huatang Yuan

[a] *Institute of New Energy Material Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (MOE), Nankai University, Tianjin 300071, P.R. China, Tel.: +86 22 23498089; fax: +86 22 23502604; Email: jiaolf@nankai.edu.cn*

Experimental section

Synthesis of Co_3S_4/rGO composites

The preparation of the Co_3S_4/rGO nanocomposite involves two steps: synthesis of a $Co(OH)_2$/GO composite and reaction of the composite with sodium sulfide.

GO was synthesized via a modified Hummers method. In a typical synthesis of the composite, 0.04 g of graphene oxide was dispersed in 50 mL of ethanol by sonication for 2 h to form a homogeneous GO suspension. Then 10 mL of ethanol containing 0.6 g of $CoCl_2{\cdot}6H_2O$ and 10 mL of H_2O containing 2 mL of ammonia solution ($NH_3{\cdot}H_2O$, 25 wt%) were slowly added into the above suspension. After stirring for 10 min, the solution was then sealed in a 100 mL Teflon lined stainless steel autoclave for hydrothermal reaction at 180 °C for 5 h. The $Co(OH)_2$/GO precipitate was collected by centrifugation, washed with water for several times and dried at 60 °C in a vacuum for 10 h. Afterwards, 0.3 g of the as-obtained $Co(OH)_2$/GO was dispersed in 90 mL of ethylene glycol (EG) solution by sonication followed by the addition of 10 mL of H_2O containing 5 g of $Na_2S{\cdot}9H_2O$ under vigorous stirring. Then the black suspension was transferred into a three-neck flask, heated and refluxed at 160 ℃ for 16 h. Finally, the black precipitate was washed with deionized water and ethanol for several times and dried at 60 °C for 10 h in a vacuum oven, and the final Co_3S_4/rGO nanocomposite was obtained. Different amounts of GO were added to adjust the content of rGO in the composites. For comparison, Co_3S_4 hollow nanospheres were also prepared following the same procedure but without adding GO.

Materials characterization

The crystallographic information of samples was gathered by powder X-ray diffraction (XRD) on a Rigaku D/Max-2500 powder diffractometer (Cu Kα radiation, λ=0.15418 nm). The morphologies were characterized by field emission scanning electron microscopy (FESEM; JEOL JSM-6700F), transmission electron microscope (TEM) and high-resolution TEM ((HRTEM; Tecnai G2 F20). The electronic state of the elements of the as-prepared samples was analyzed by X-ray photoelectron spectroscopy (XPS; Kratos Axis Ultra DLD using Al Ka radiation). All the binding energy values were calibrated by using C 1s at 284.6 eV as a reference. The elemental composition was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, USA Themo Jarrel-Ash Corp. instrument). The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method (Micromeritics Tristar-3000 surface area and porosity analyzer).

Electrochemical measurements

The working electrodes were fabricated by mixing the active material (the Co_3S_4/rGO composite or Co_3S_4 HNSs), graphite, acetylene black and polytetrafluoroethylene (PTFE) binder in a weight ratio of 70:10:10:10. The first three components were mixed together in an agate mortar until homogeneous black powder was achieved. PTFE was then added to the mixture with a few drops of ethanol. The formed paste was pressed at 20 MPa to a piece of nickel foam (1.0 cm×1.0 cm), and dried under vacuum at 60 °C for 10 h. Electrochemical measurements were conducted in a three-electrode arrangement in 2 M KOH electrolyte. A bright Pt plate and Hg/HgO electrode were used as the counter electrode and reference electrode, respectively. Cyclic voltammetry (CV) was conducted with a Zahner IM6e electrochemical workstation with voltage scan rates of 5, 10, 20 and 50 mV s^{-1}. The galvanostatic charge-discharge tests were conducted on a LAND battery system at the current densities of 0.5, 1.0, 2.0 and 5.0 A g^{-1}. The specific capacitance is calculated according to the following equation:

$$C = \frac{I\Delta t}{m\Delta V} \tag{1}$$

where C (F g^{-1}) is the specific capacitance, I (A) represents the discharge current, and m (g), ΔV (V) and Δt (s) designate mass of active materials, potential drop during discharge and total discharge time, respectively. Electrochemical impedance spectroscopy (EIS) was performed with a Zahner IM6e electrochemical workstation with 5 mV amplitude in a frequency range from 10^{-2} Hz to 10^{5} Hz at open circuit potential.

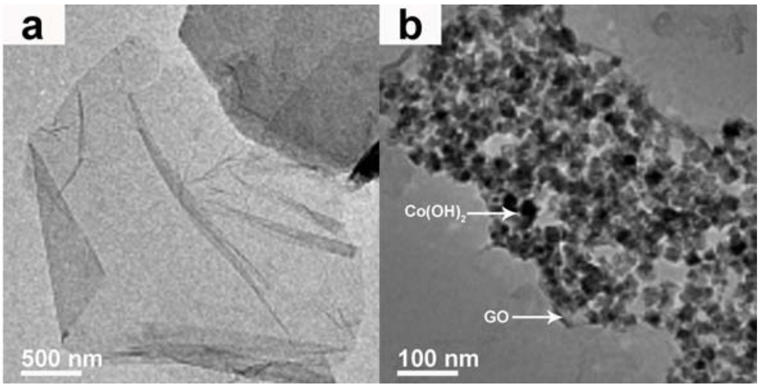

Fig. S1 TEM images of (a) the as-prepared GO sheets and (b) Co(OH)$_2$/GO precursor.

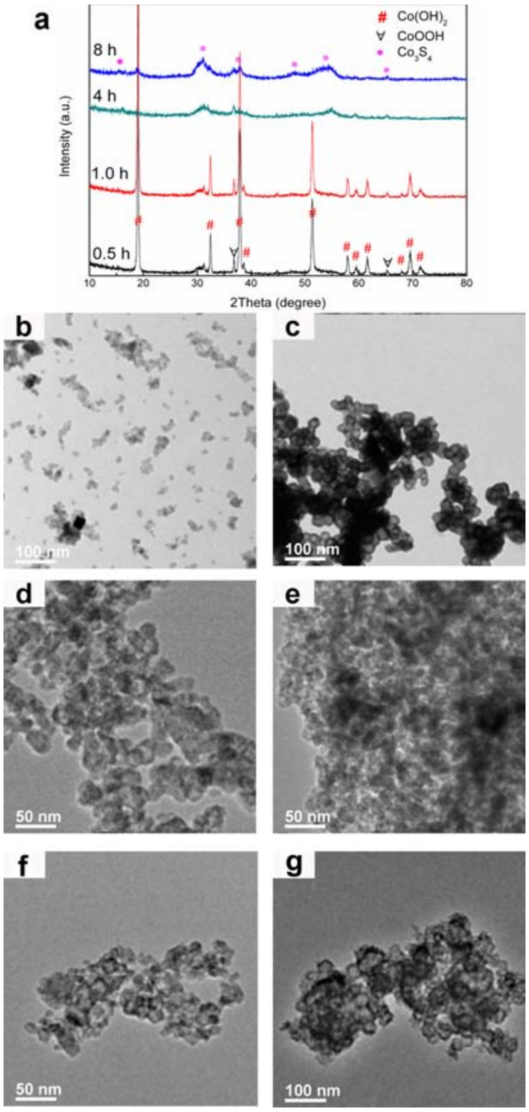

Fig. S2 The formation process of Co_3S_4 hollow nanospheres. (a) XRD patterns of the intermediate products obtained at different reflux time, (b) TEM image of the $Co(OH)_2$ precursor, and TEM images of the intermediate products obtained at reaction time: (c) 1 h, (d) 2h, (e) 4h, (f) 8 h and (g) 12 h.

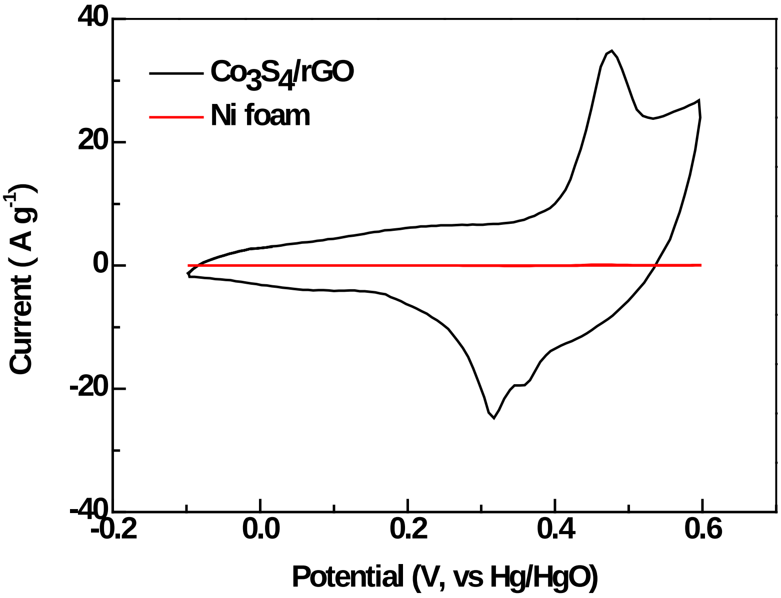

Fig. S3 The CV curves of Ni foam with and without loading of Co_3S_4/rGO composite, 20 mV s^{-1}.

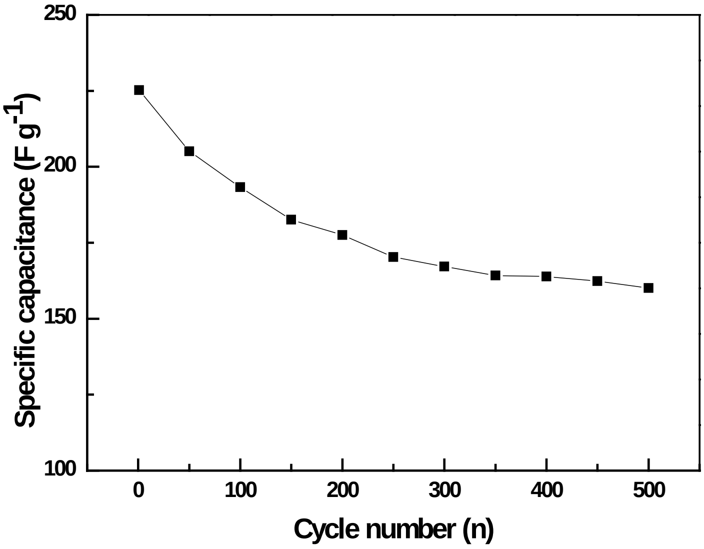

Fig. S4 Cycle life of rGO at 0.5 A g^{-1}.