Supporting Information

In situ growth of $NiCo_2S_4$ nanosheets on graphene for high-performance supercapacitors

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Materials synthesis

Graphite oxide was prepared from natural graphite (SP-1) by a modified Hummers method.[S1-S3] For the preparation of $NiCo_2S_4$/RGO hybrid 1 mmol of $Ni(NO_3)_2 \cdot 6H_2O$, 2 mmol of $Co(NO3)_2 \cdot 6H_2O$, 4 mmol of thiourea (Tu) and 2 mL of ethylenediamine (En) were added to 30 mg of GO dispersed in 30 ml of H_2O. The mixture was sonicated at room temperature for approximately 60 min until a clear and homogeneous solution was achieved. Then the solution was transferred to a 50 mL Teflon-lined autoclave. It was heated in an oven at 200 °C for 12 h. After being cooled to room temperature, the precipitate was collected by centrifugation, washed with deionized water and ethanol several times, and dried at 60 °C. The $NiCo_2S_4$ hollow spheres were obtained in the absence of RGO sheets, while keeping other experimental conditions unchanged.

Materials characterization

The phase purity and the structure of the as-prepared products were determined by X-ray diffraction (XRD) with Cu Kα radiation (λ = 1.5418 Å) at a scan rate of 0.04º s^{-1}. The morphologies of the products were characterized by field-emission scanning electron microscopy (FESEM, JEOL, JSM-7600F) at an acceleration voltage of 5 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscope (HRTEM) was performed on a JEOL 2100F microscope with an accelerating voltage of 200 kV. The carbon and sulphur elements were measured by a high-frequency infrared carbon-sulphur analyzer (Keguo Instrument, HCS-500P). Raman spectra were obtained by a WITec CRM200 confocal Raman microscopy system at a laser wavelength of 488 nm and a spot size of 0.5 mm.

Electrochemical measurements

The working electrode was prepared by mixing 70 wt% of active material 20 wt% of Super P carbon (Timcal), and 10 wt% of polyvinylidene difluoride (PVDF, Kynar 2801)). This mixture was then coated on the Ni foam electrode and dried at 80 ºC for 12 h. The electrochemical properties and capacitance measurements of the supercapacitor electrodes were investigated in a three-electrode half-cell system in 2 M KOH aqueous electrolyte with Solartron analytical equipment (Model 1470E). A platinum foil electrode and a standard calomel electrode were used as the counter electrode (SCE) and the reference electrode, respectively.

S1 Y. X. Xu, H. Bai, G. W. Lu, C. Li and G. Q. Shi, J. Am. Chem. Soc., 2008, 130, 5856–5857.

S2 W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc., 1958, 80, 1339–1339.

S3 J. X. Zhu, T. Zhu, X. Z. Zhou, Y. Y. Zhang, X. W. Lou, X. D. Chen, H. Zhang, H. H. Hng and Qingyu Yan, Nanoscale, 2011, 3, 1084–1089.

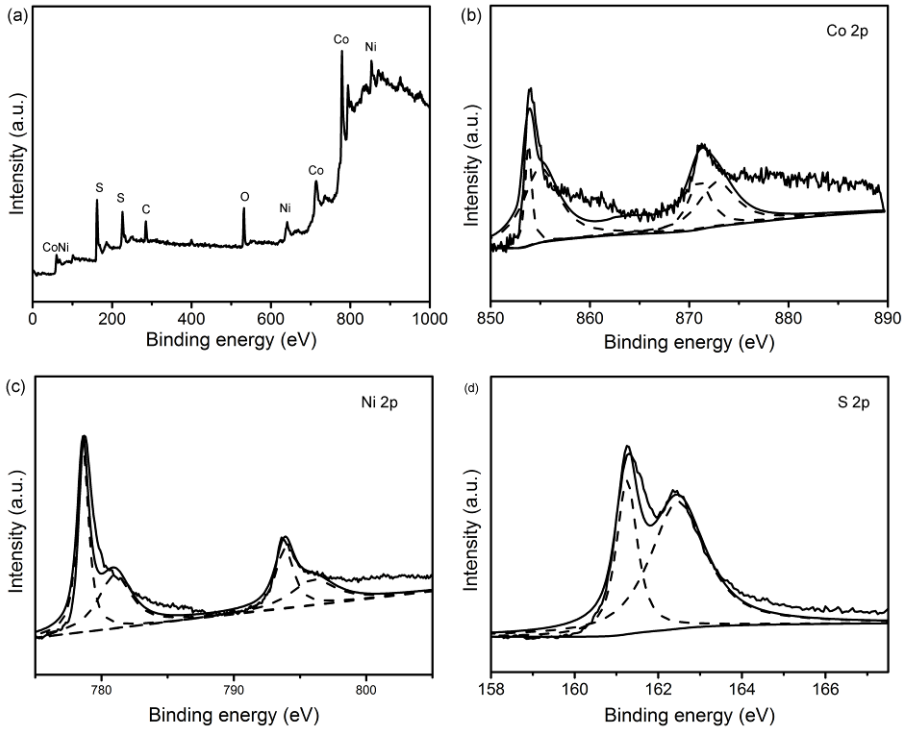

Fig. S1 The XPS survey spectrum (a), the XPS spectrum of Co 2p (b), the XPS spectrum of Ni 2p (c), and the XPS spectrum of S 2p (d) of the $NiCo_2S_4$/RGO hybrid.

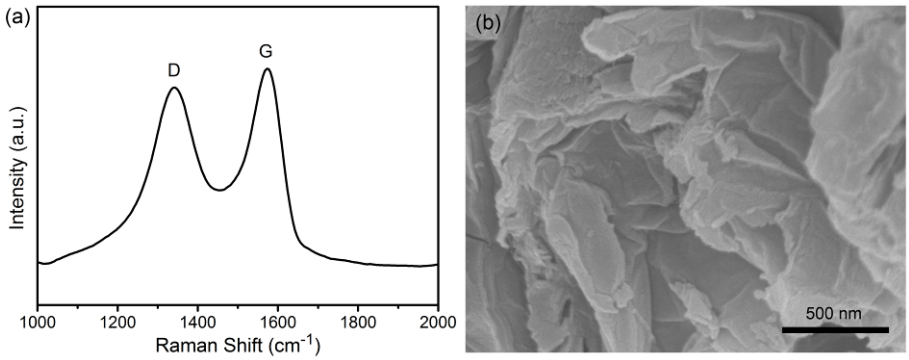

Fig. S2 Raman spectrum (a) and SEM image (b) of the GO.

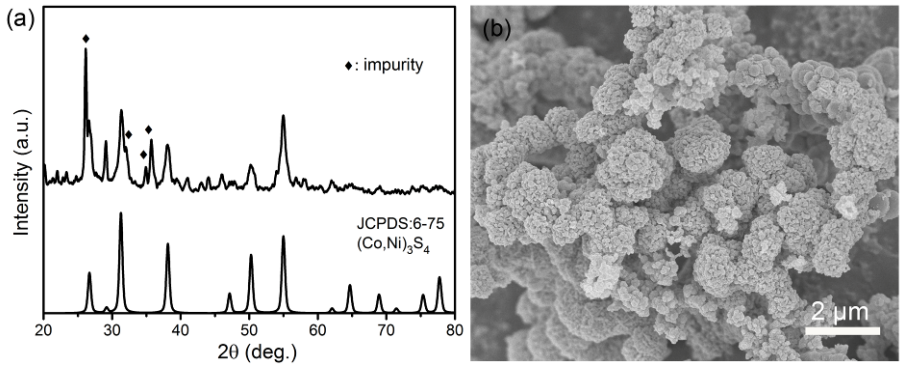

Fig. S3 XRD pattern (a) and SEM image (b) of the product by using 1 mmol of $Ni(NO_3)_2 \cdot 6H_2O$, 2 mmol of $Co(NO_3)_2 \cdot 6H_2O$, and 4 mmol of Tu in the absence of En at 200 °C for 12 h.

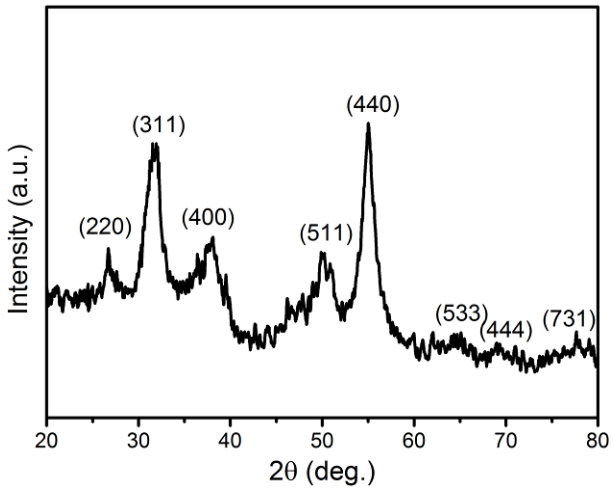

Fig. S4 XRD pattern of the product by using of 1 mmol of $Ni(NO_3)_2 \cdot 6H_2O$, 2 mmol of $Co(NO_3)_2 \cdot 6H_2O$, 4 mmol of Tu and 2 mL of En in the absence of GO at 200 °C for 12 h.

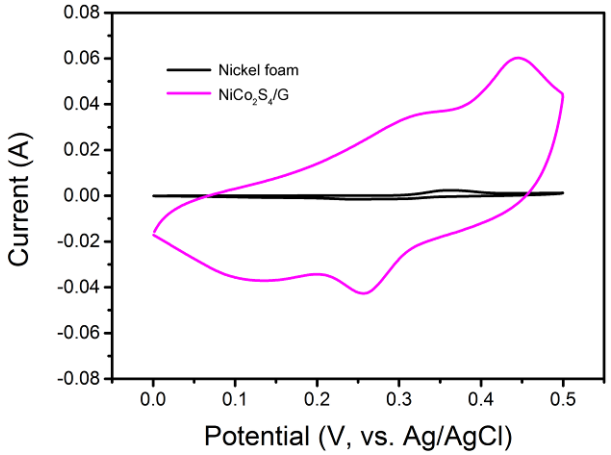

Fig. S5 The CV curves of Ni foam with and without loading of $NiCo_2S_4$/RGO hybrid at a scan rate of 20 mV s^{-1}.

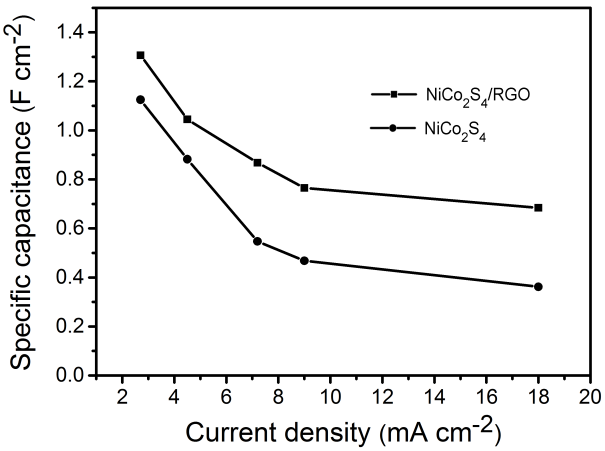

Fig. S6 Areal capacitances of the $NiCo_2S_4$/RGO hybrid and bare $NiCo_2S_4$ electrodes measured as a function of current density.

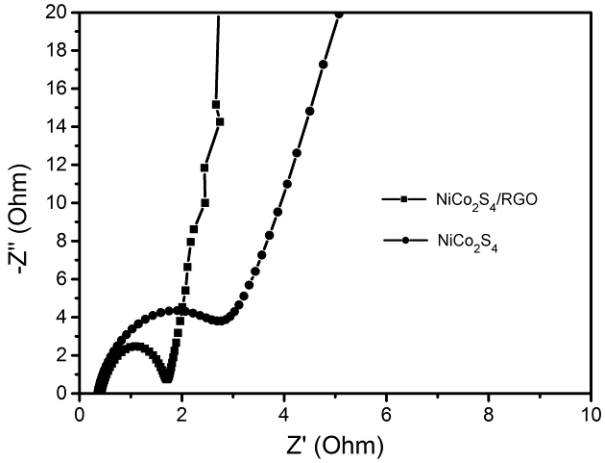

Fig. S7 Electrochemical impedance spectra (EIS) of the $NiCo_2S_4$/RGO hybrid and bare $NiCo_2S_4$ electrodes.

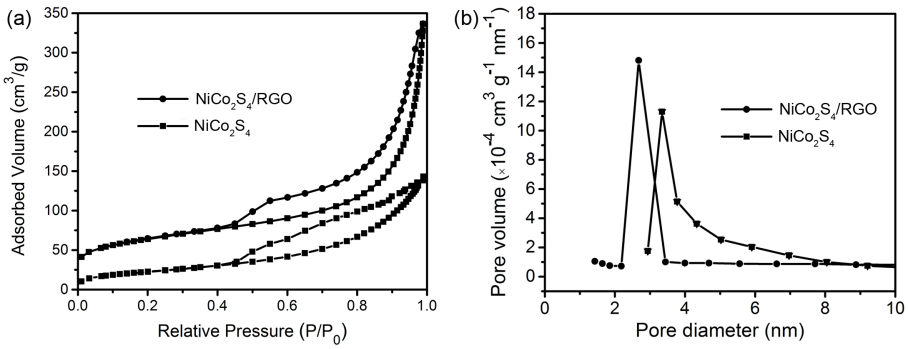

Fig. S8 N_2 adsorption isotherms (a) and pore size distributions (b) of $NiCo_2S_4$/RGO and $NiCo_2S_4$ samples, respectively.

The surface areas of $NiCo_2S_4$/RGO and $NiCo_2S_4$ samples are 172.3 and 79.1 $m^2\ g^{-1}$, respectively.

Table S1 Specific capacitance of sulfides/carbon composites.

Hybrid samples	Specific capacitance (F g^{-1})	Electrolyte	References
$NiCo_2S_4$/RGO	1161 (5 A g^{-1})	2 M KOH	This work
Sn_3S_4/G	123 (2 A g^{-1})	0.1 M NaCl	1
NiS_2/CNT	514 (4 A g^{-1})	2 M KOH	2
Nickel sulfides/G	1169 (5 Ag^{-1})	2 M KOH	3
CuS/CNT	122 (1.2 Ag^{-1})	2 M KOH	4
Co_3S_4/G	675.9 (0.5 Ag^{-1})	2 M KOH	5
CoS_2/G	314 (0.5 A g^{-1})	6 M KOH	6
CoS/CNT	2140 (10 mV s^{-1})	1 M KOH	7
Cobalt sulfide/G	1535 (2 A g^{-1})	2 M KOH	8

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