Electronic Supplementary Material (ESI) for CrystEngComm

Electronic Supporting Information

A general synthesis of Co_mS_n (Co_9S_8, Co_3S_4, and $Co_{1-x}S$) hierarchical microspheres with controllable homogeneous phases

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Preparation of NiS, Ni_3S_4, $NiCo_2S_4$, and FeS_2

This facile and general approach was extended by the attempt to prepare other transition metal sulfides with controlled chemical compositions, such as NiS, Ni_3S_4, $NiCo_2S_4$, and FeS_2, etc. The detail was identical to the preparation of cobalt sulfides, and $Ni(OAc)_2{\cdot}4H_2O$ and $FeCl_3$ were taken as metal precursors. Nickel sulfides were prepared under certain molar ratios of Ni/S as 1:1, 1:2 and 1:3, respectively; the synthesis of FeS_2 and $NiCo_2S_4$ respectively corresponded to the molar ratios of Fe/S=1:2.5 and Co/Ni/S=2:1:6. Without specification, all samples were prepared in EG medium at 200 °C for 8 h.

Electrocatalytic experiments

The electrochemical tests were carried out on an AutoLab worksation (μ Autolab III) assembled with a model of ATA-1B rotational system, using a Pt pole as the counter electrode, Ag/AgCl electrode as the reference, the sample-coated glass carbon electrode as working electrode (WE). The WE was prepared by loading 4 μL catalyst's nafion ink (the preparation as follows: 100 μL of 5 wt% Nafion solution was added in 1mL of 4:1 v/v water/ethanol, and then 4 mg of catalyst was dispersed in it and sonicated to form a homogeneous ink). Then the electrode was dried under infrared lamp for 2 minutes. Cyclic voltammetry (CV) was measured in Ar- and O_2-saturated 0.1M KOH measurements electrolyte at room temperture (~20 ℃) with a sweep rate of 20 mV s^{-1}. Linear sweep voltammetries were obtained in O_2-saturated 0.1M KOH with a sweep rate of 20 mV s^{-1}. Catalyst loading was ~0.283 mg cm^{-2} for all samples.

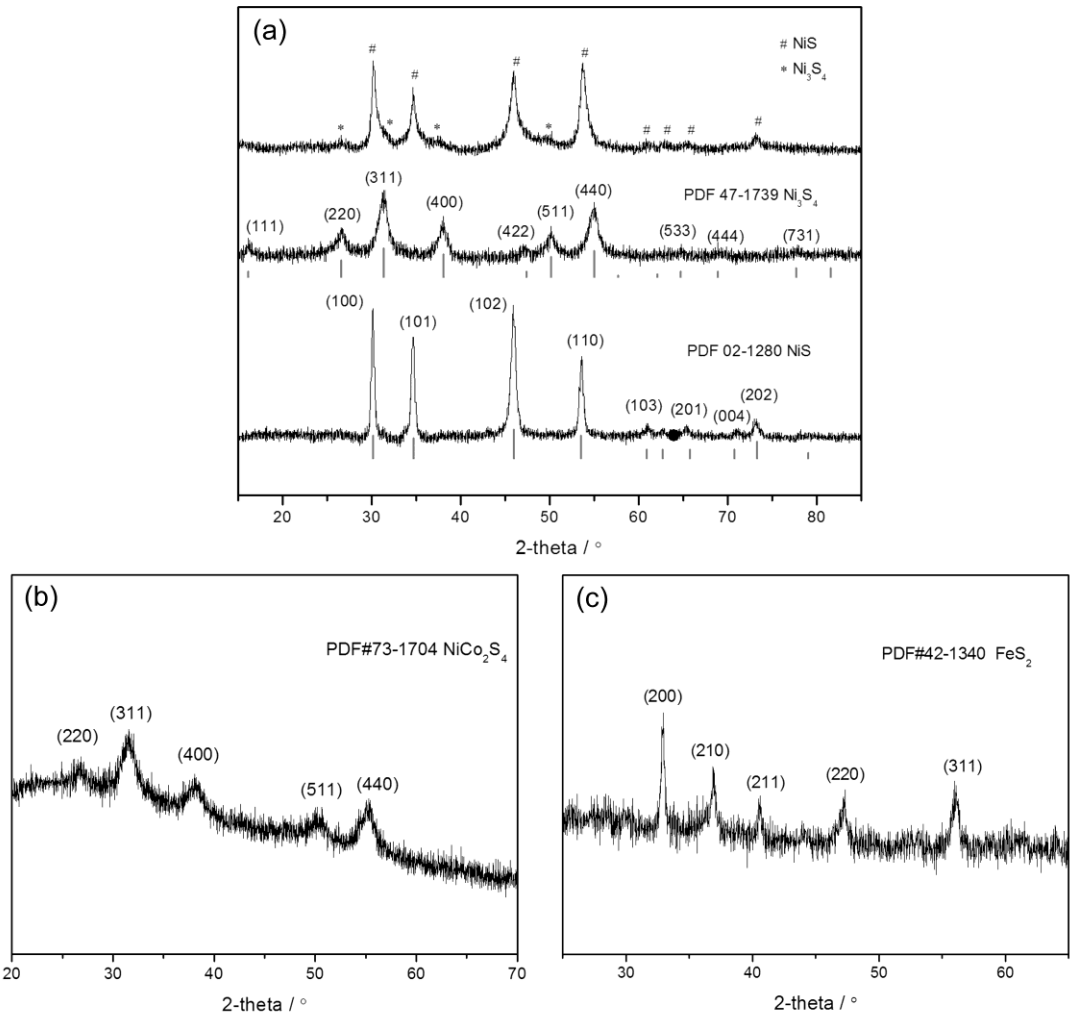

Fig. S1 XRD patterns of (a) nickel sulfides obtained at Ni/S molar ratios being 1:1, 1:2 and 1:3 (down to up), respectively corresponding to NiS, Ni_3S_4, and the mixture of NiS and Ni_3S_4; (b) $NiCo_2S_4$ at Ni/Co/S molar ratio being 1:2:6 and (c) iron sulfide at Fe/S molar ratio being 1:2.5.

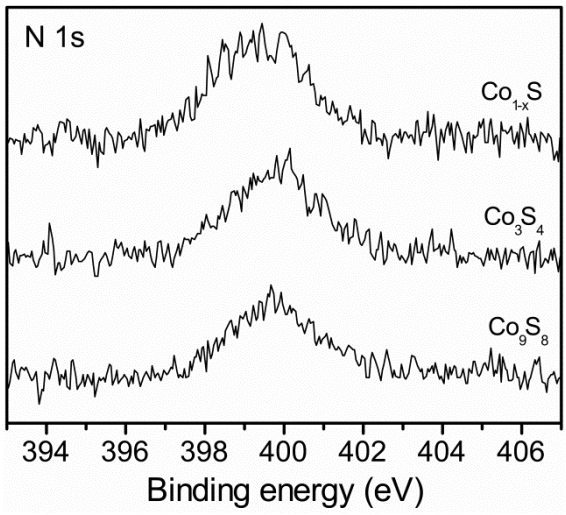

Fig. S2 XPS N 1s spectra of as-prepared Co_9S_8, Co_3S_4, and $Co_{1-x}S$.

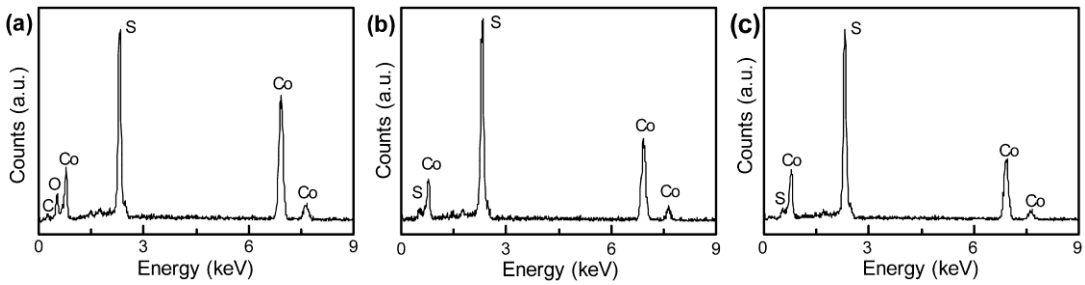

Fig. S3 EDS spectra of Co_9S_8 (a), Co_3S_4 (b), and $Co_{1-x}S$ (c), confirming Co/S ratio in all samples close to their respective stoichiometric values. In the spectrum of Co_9S_8, oxygen element was observed, consistent with XPS result.

Table S1 Atomic concentration of Co and S obtained by XPS and EDS for three cobalt sulfides.

samples	atomic Co/S from XPS	atomic Co/S from EDS	theoretical value
CS-**I**	1.10	1.134	1.125 (Co_9S_8)
CS-**II**	0.740	0.734	0.75 (Co_3S_4)
CS-**III**	0.569	0.564	< 1 ($Co_{1-x}S$)

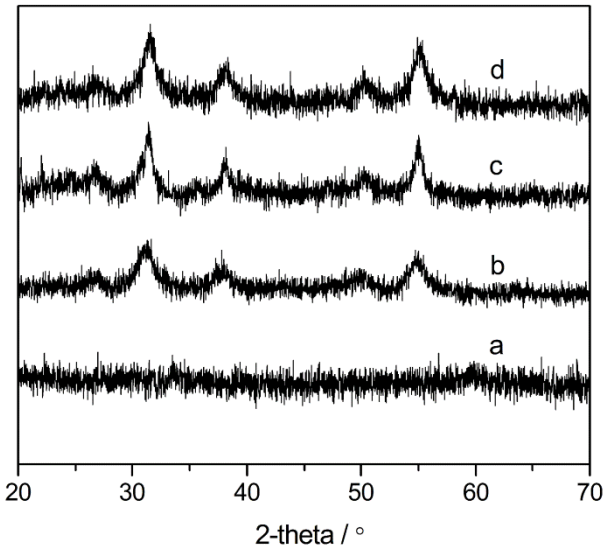

Fig. S4 XRD patterns of Co_3S_4 samples synthesized from different reaction intervals: (a) 1 h, (b) 8 h, (c) 16 h, and (d) 48 h.

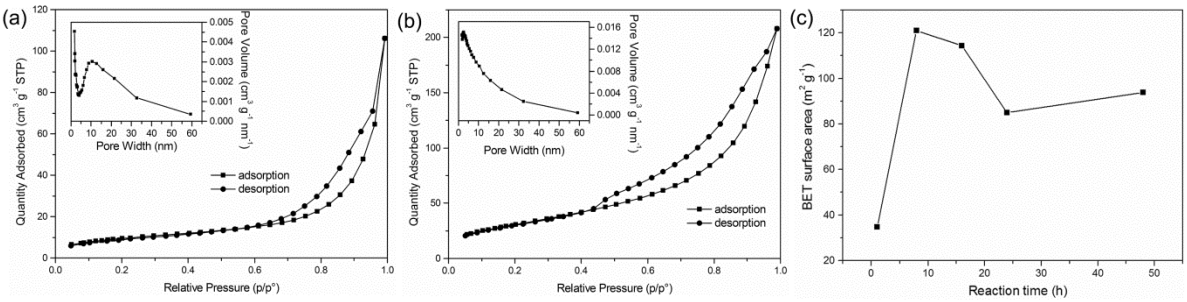

Fig. S5 N_2-sorption isotherms of samples synthesized from Co/S=1:2 at different reaction intervals of 1 h (a) and 16 h (b). (c) The curve of reaction intervals *vs.* BET values of these samples prepared at different reaction intervals. From CS-1 to CS-48, their surface areas are respectively at 120.94, 34.89, 119.40, 85.15 and 93.89 $m^2 g^{-1}$.