Supporting information

Facile synthesis of silk-cocoon cobalt polysulfide as an efficient catalyst for hydrogen evolution reaction

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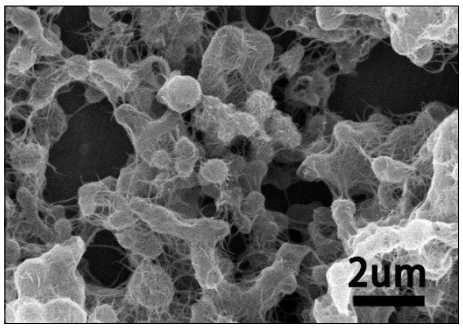

Figure S1 SEM image of the CoS_x composite after hydrothermal for 12 hours with the using of 200 mg sulfur and 100 mg cobalt acetate.

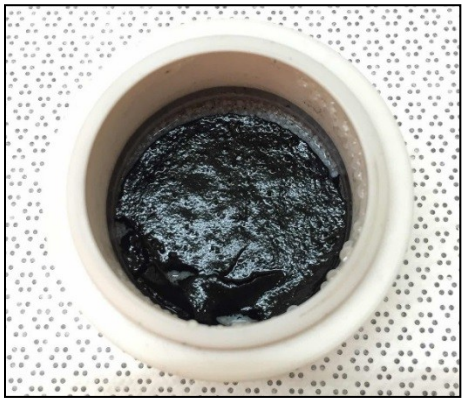

Figure S2 Photograph of the CoS_x after removing water in the PTFE hydrothermal container.

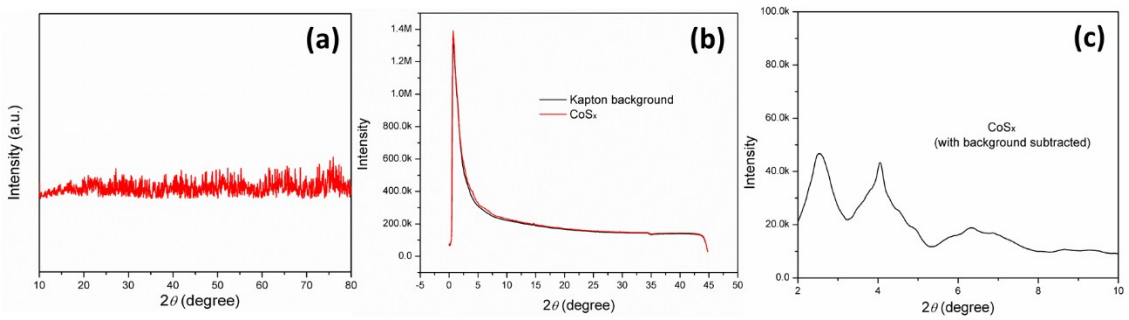

Figure S3 XRD pattern of the CoS_x composite after hydrothermal for 12 hours with the using of 200 mg sulfur and 100 mg cobalt acetate. (a) PANalytical X'Pert Pro using Cu Kα radiation at 45 kV and 40 mA (wavelength = 0.15406 nm), (b) Kapton background and CoS_x composite with Kapton background and (c) Kapton background subtracted using synchrotron XRD at Argonne national lab with a wavelength=0.01173 nm.

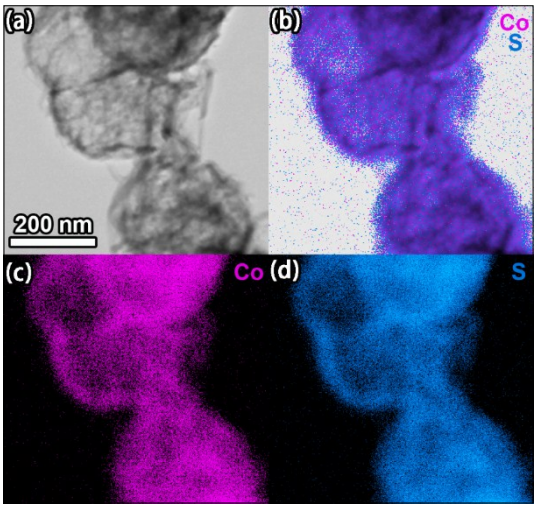

Figure S4 STEM images of silk-cocoon structured CoS_x composite (a) and the corresponding EDX elemental mapping (b) overlap of element Co, S and N, (c) Co, (d) S.

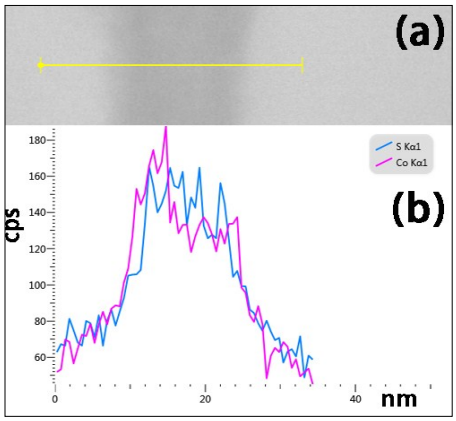

Figure S5 STEM image of the CoS_x nanofiber (a) and its EDX linear sweep (b).

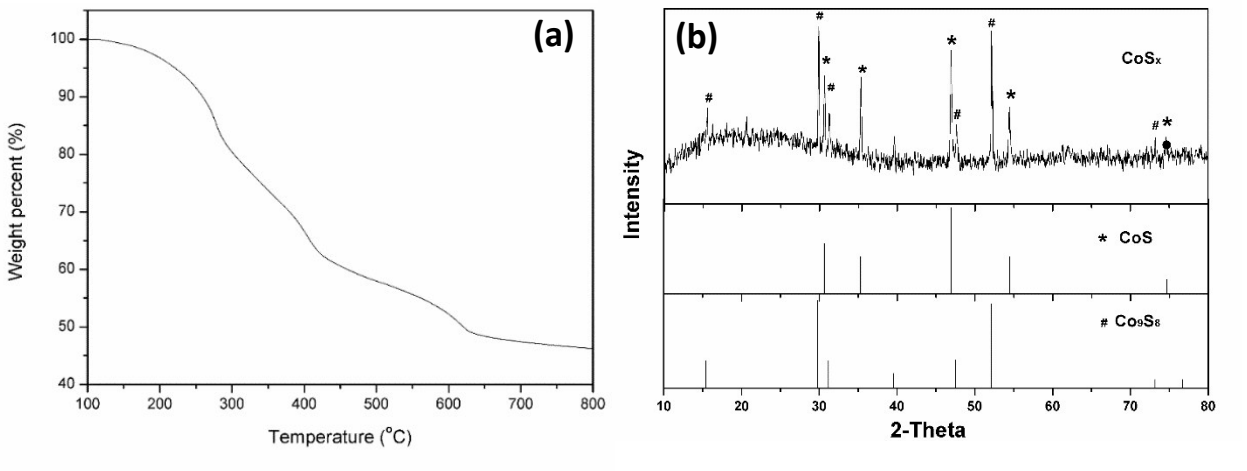

Figure S6 (a) TGA curve under Ar gas of the CoS_x composite after hydrothermal for 12 hours with the using of 200 mg sulfur and 100 mg cobalt acetate, (b) XRD curve of the CoS_x composite after the same heat treatment process with TGA.

We reheated the sample in TGA at 100 for 2 h to remove the absorbed water on the sample surface. The weight loss before 100 °C is about 4%. After that, the temperature increased to 800 °C at a rate of 5 °C/min. Figure S6a shows the weight change curve from 100-800 °C. The weight percent remained at 800 °C is about 46.5 wt.%. The weight loss of 3.5 wt.% before 200 °C is the loss of crystal water in the sample. Base on the weight loss, we can calculate that the weight percent of the residual material in the composite is 46.5 wt.% / (1-3.5 wt.%) = 48.2 wt.% and sulfur lose is 51.8 wt.%. If the product is Co_9S_8, then x is 3.8. If the product is CoS, then x is 4. The product is a mixture of Co_9S_8 and CoS, then x is estimated to be 3.9.

Ratio calculated by mass conservation

Assuming that the cobalt in $Co(ac)_2$ is completely transferred into CoS_x, because the use of sulfur in the experiment is far more than needed to precipitate cobalt. In our hydrothermal experiment, when the usage amount of $Co(ac)_2$ and sulfur are 200 mg and 400 mg individually. The weight percent of cobalt in $Co(ac)_2$ is about 23.66 wt.%, so the cobalt mass is about 47.32 mg. Then sulfur is about 88.84 mg in the final product, so the weight ration of S/Co is 1.9. (This result is based on the deducting of 7.5% of water in the system according to TGA result). Based on the molecular weight of sulfur and cobalt, the mole ratio of S/Co is 3.5. We double check the weight of another sample with twice the weight of precursors and the final product weight is about 296.1mg, which is about two times of the weight of 148mg, so the S/Co ratio is nearly the same. We repeated this experiment for at least 5 times, and every time the consistency of the result is good. However, during the operation process (wash and transfer), we still may lose some weight and there have very small amount of nitrogen and carbon in the system, so the ratio is not very accurate but just a rough result.

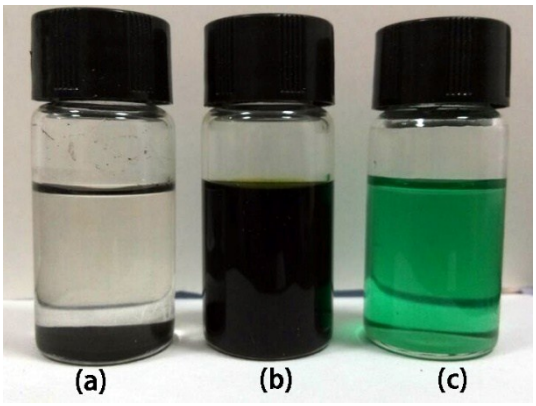

Figure S7 Photographs of (a) 75 mg silk-cocoon CoS_x composite in 7.5 ml EDA solvent, (b) 75 mg sulfur in 7.5 ml EDA solvent, and (c) 30 times dilution of (b).

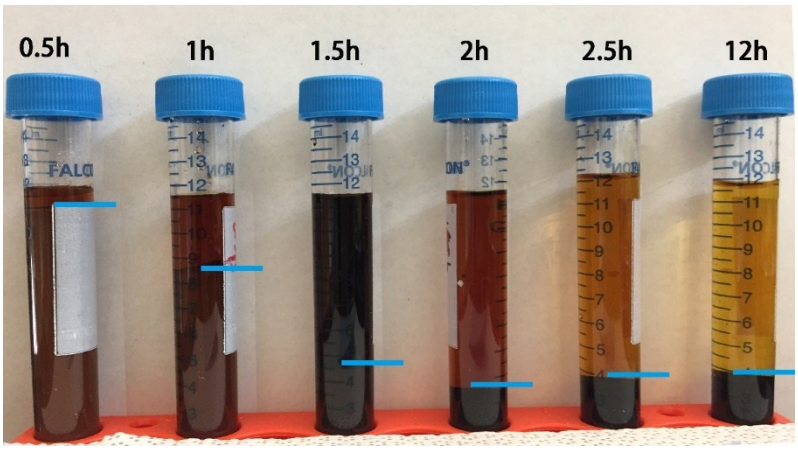

Figure S8 Photographs of the product after hydrothermal for different time.

Figure S8 shows the photographs of the solution after hydrothermal at different time (0, 1, 1.5, 2, 2.5, and 12 h). We can see that the color of the solution became more and more dark at the first 1.5 h and after that, it became more and more light with the increase of time. The 1.5 h picture shows the typical color of high concentrated polysulfides solution. After 1.5 h, the polysulfides chains became shorter and the concentration became lower as the reaction proceeded. The UV spectrum of the supernatant shows that polysulfides exist in the solution The color of the precipitation changed from dark red to black, and the volume decreased first and kept stable after 2 h.

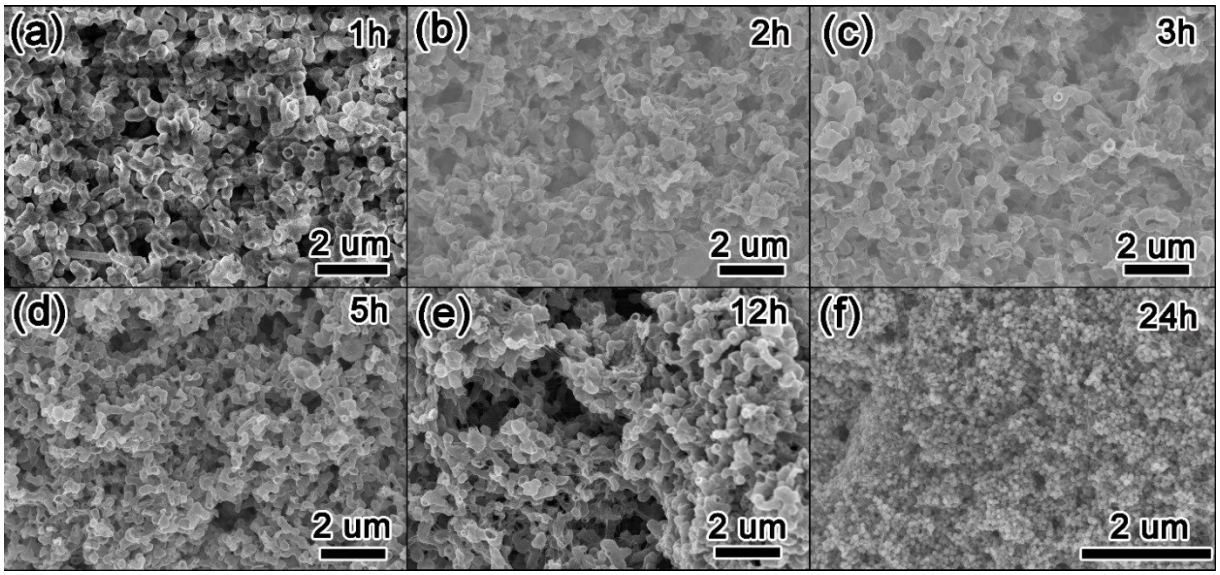

Figure S9 The SEM morphology of CoS_x at different hydrothermal time: (a) 1h, (b) 2h, (c2) 3h, (d) 5h, (e) 12h, and (f) 24h.

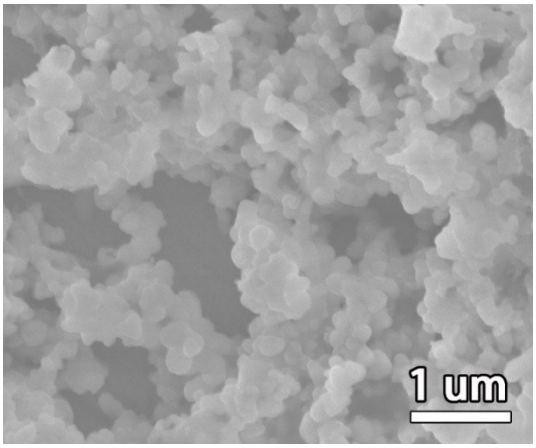

Figure S10 SEM image of precursor without hydrothermal and stirred for 12 hours.

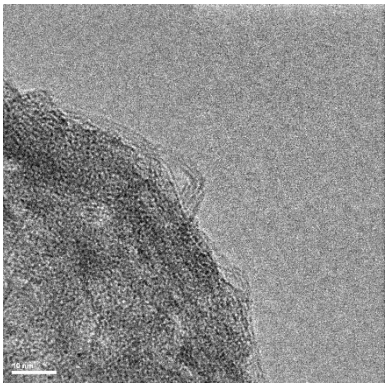

Figure S11 TEM images of the CoS_x composite at 2.5 hours hydrothermal time, scale bar 10 nm.

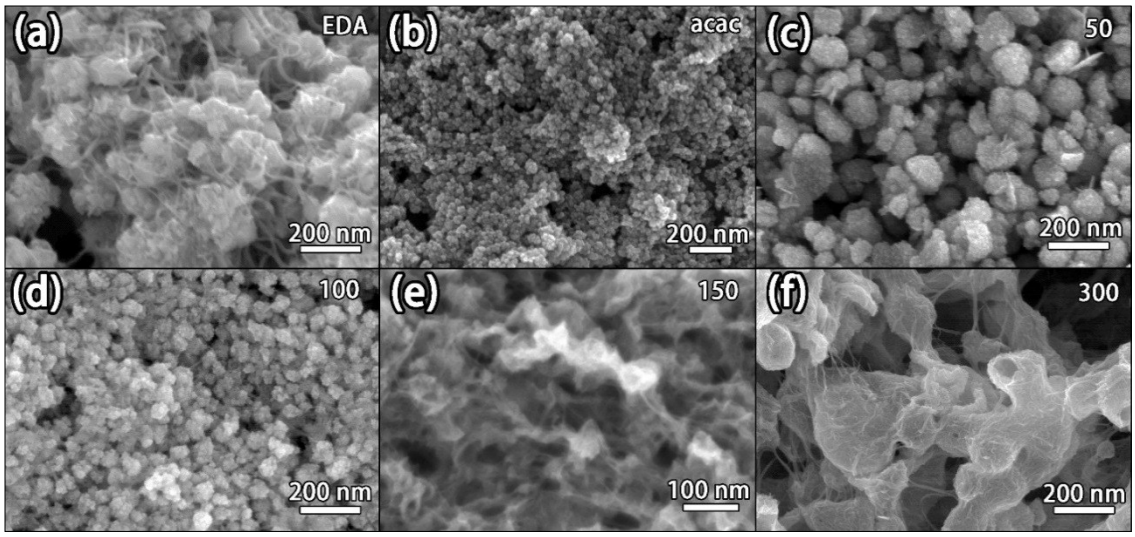

Figure S12 SEM images of CoS_x at different synthesis conditions (a) using only EDA as the solvent for solvothermal, (b) using cobalt acetylacetonate as the cobalt source for the hydrothermal, using different sulfur amounts for the hydrothermal: (c) 50 mg, (d) 100 mg, (e) 150 mg, and (f) 300 mg.

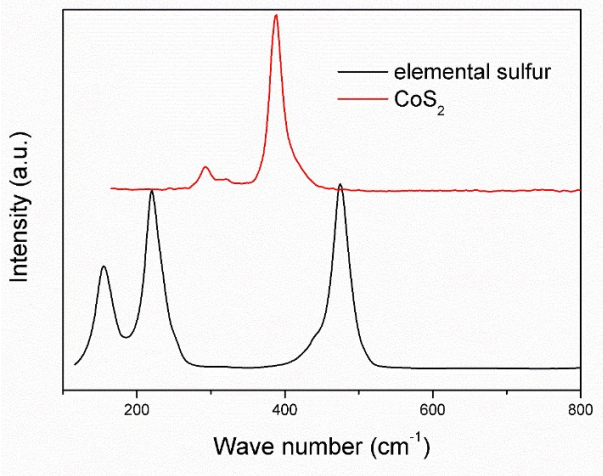

Figure S13 Raman spectra of CoS_2 and elemental sulfur.

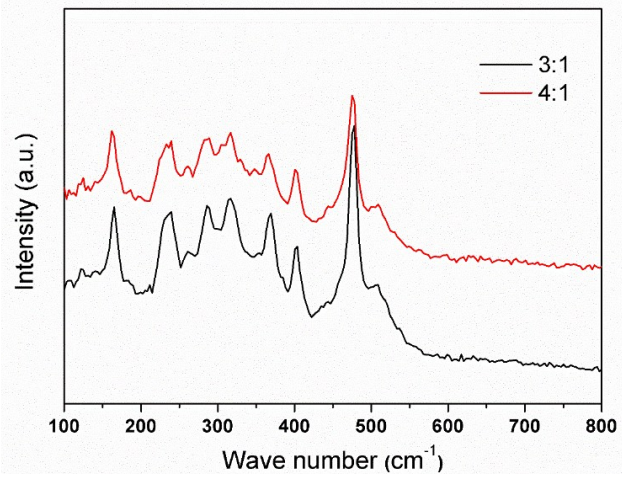

Figure S14 Raman spectra of CoS_x that were synthesized with a S to $Co(ac)_2 \cdot 4H_2O$ to S mass ratio of 3:1 and 4:1.

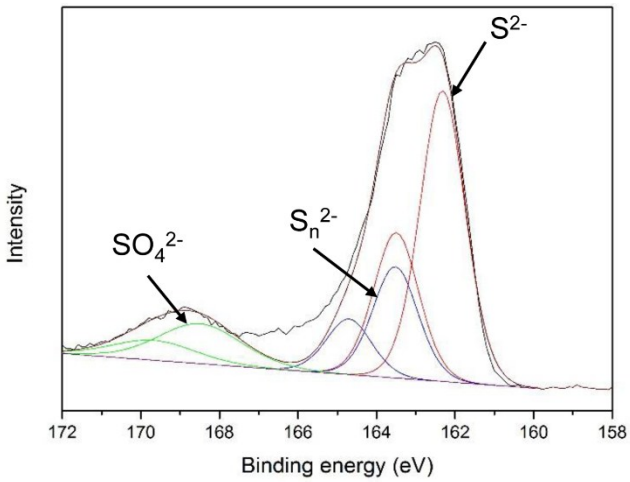

Figure S15 XPS spectra of S 2p region for CoS_x compound that obtained by reacting S to $Co(ac)_2 \cdot 4H_2O$ in a mass ratio of 4:1 for 12 h.

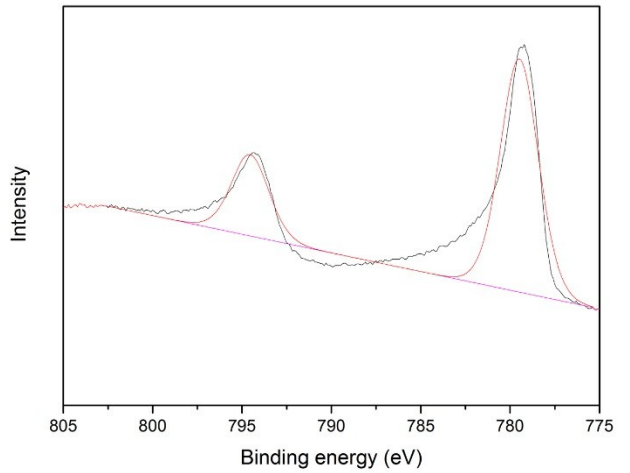

Figure S16 XPS spectra of Co 2p region for CoS_x compound that obtained by reacting S to $Co(ac)_2 \cdot 4H_2O$ in a mass ratio of 2:1 for 24 h.

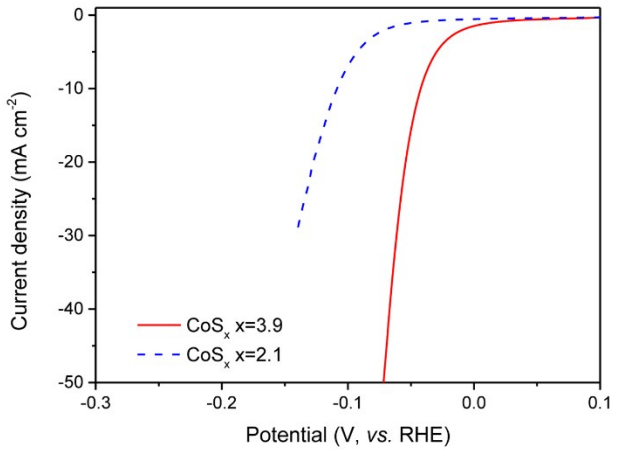

Figure S17. Polarization curves of CoS_x that were synthesized with a S to $Co(ac)_2 \bullet 4H_2O$ mass ratios of 1:2 (x=2.1) and 2:1 (x=3.9) respectively in 0.5 M H_2SO_4 at a scan rate of 2 mV s^{-1}.

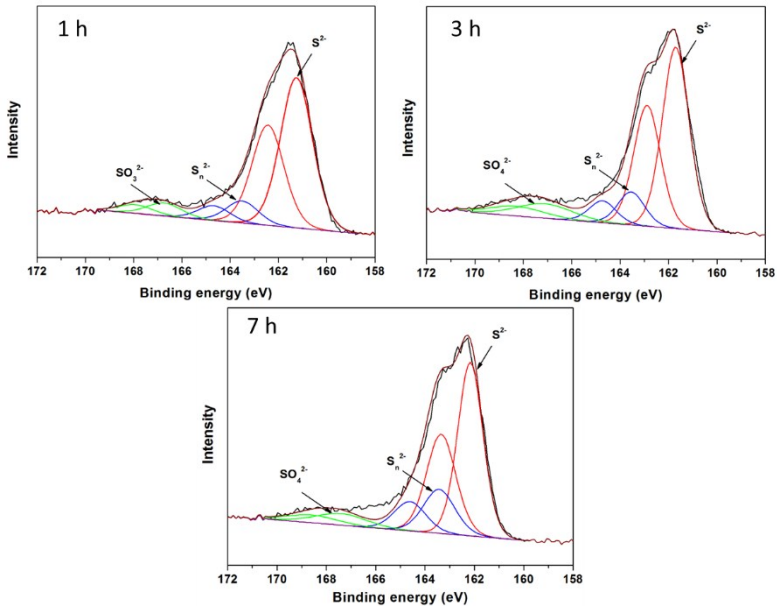

Figure S18 XPS S 2p of the silk-cocoon synthesized at different hydrothermal time: 1, 3, 7 h.

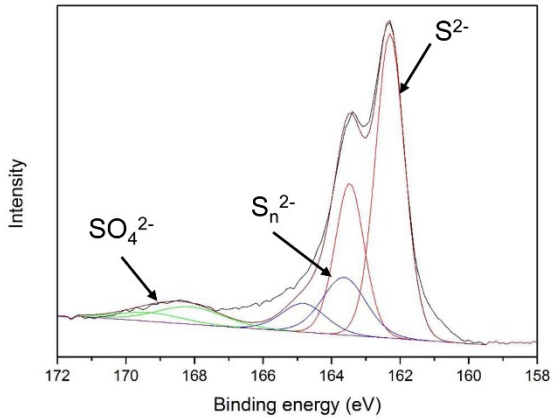

Figure S19 XPS spectra of S 2p region for CoS_x nanoparticles.

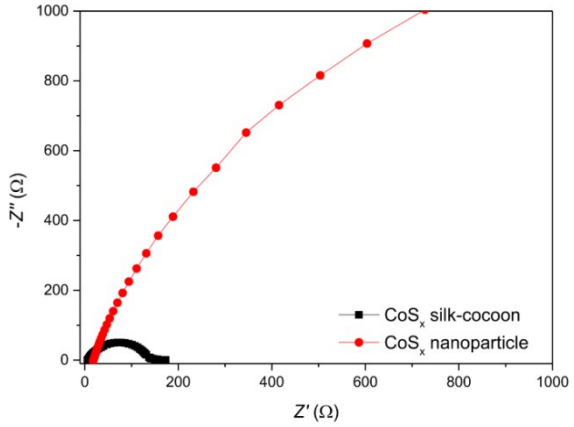

Figure S20 Nyquist plots for the impedance response of CoS_x silk-cocoons and CoS_x nanoparticles at η= 50 mV.

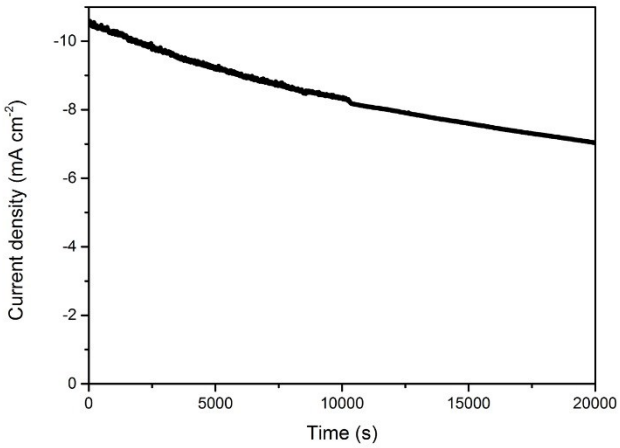

Figure S21 Chronoamperometric response of the CoS_x silk-cocoons at a constant potential of -0.045 V *vs.* RHE in 0.5 M H_2SO_4.

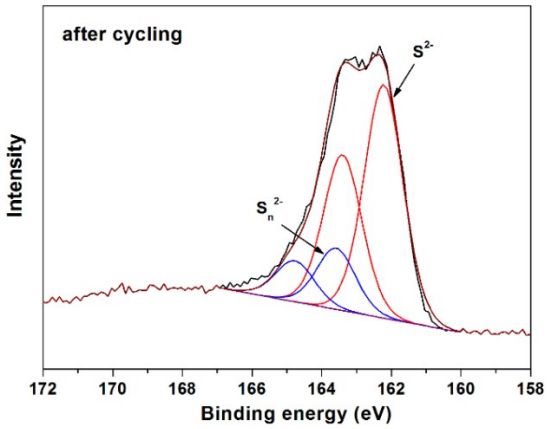

Figure S22 XPS S 2p of the silk-cocoon CoS_x after 2000 cycles

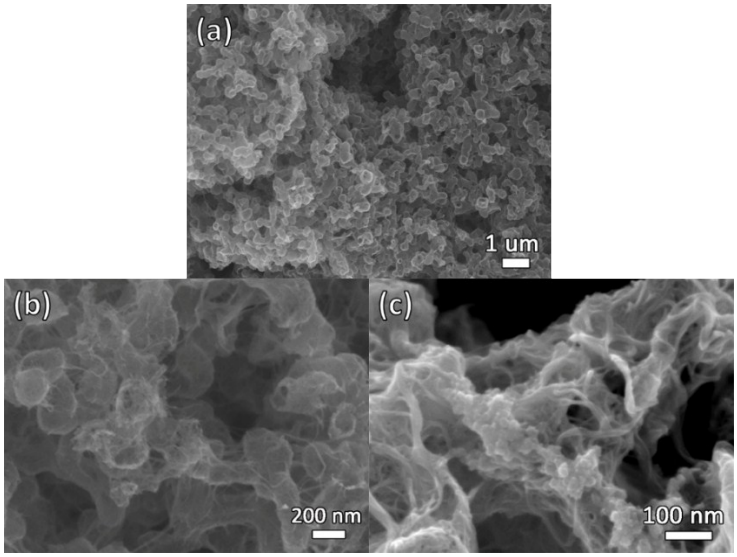

Figure S23 SEM images of the silk-cocoon CoS_x after 2000 cycles (a),(b),(c).

Table S1. Comparison of HER performance of the state-of-art transition metal sulfide electrocatalysts with our silk-cocoon S-rich cobalt polysulfide at room temperature.

Catalyst	Substrate	Electrolyte	Loading (mg cm^{-2})	Onset potential (mV)	Overpotential at 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Reference
Amorphous CoS_x	FTO	0.5 M H_3PO_4	0.0796	N/A	83 (2 mA cm^{-2})	93	1
Electrodeposited Ni-Co-S	FTO	1 M H_3PO_4	N/A	-150	280	93	2
CoS_2 wire	graphite	0.5 M H_2SO_4	25±2	-75	145	51.6	3
CoPS nanoplates	carbon paper	0.5 M H_2SO_4	N/A	N/A	48	56	4
Co-doped FeS_2	glassy carbon	0.5 M H_2SO_4	0.15	N/A	166	51	5
$CoSe_2$ nanoparticles	carbon fiber paper	0.5 M H_2SO_4	N/A	N/A	137	48	6
Cobalt sulfide hollow nanospheres	Carbon paper	1 M KOH	1.5	N/A	193	100	7
Amorphous MoS_3	glassy carbon	0.5 M H_2SO_4	N/A	N/A	200 (15 mA cm^{-2})	40	8
$[Mo_2S_{12}]^{2-}$ Cluster	FTO	0.5 M H_2SO_4	0.0864	N/A	161	40	9
CoS|P/CNT	Carbon fiber paper	0.5 M H_2SO_4	0.4	0	48	55	10
Silk-cocoon cobalt polysulfide	**glassy carbon**	**0.5 M H_2SO_4**	**0.2**	**0**	**42**	**41**	**This work**

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