

Supporting Information

Experimental Section

Synthesis of 3D Flowerlike CoS Hierarchitectures: In a typical synthesis, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.05 M) and thioacetamide (TAA, 0.1 M) were dissolved in absolute ethanol, and then the blue solution was loaded into a 50 ml Teflon-lined stainless steel autoclave. After heating at 160 °C for 24 h, the tank was cooled down to room temperature naturally. The resultant black products were centrifuged and washed repeatedly with distilled water and absolute ethanol to remove any possible residual reactant. The flowerlike CoS hierarchitectures were finally obtained after drying in a vacuum at 50 °C for 10 h.

Synthesis of CoS Microspheres: CoS microspheres with nanoblocks enclashing on the surface was synthesized at the starting concentration of 0.1 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.2 M TAA solution with other conditions unchanged.

Characterization: Powder X-ray diffraction (XRD) were performed on a Rigaku D/Max-2500 powder diffractometer (Cu K α radiation, $\lambda=0.15418$ nm). The XRD profiles were refined by the Rietveld refinement program RIETAN-2000.¹ Energy Dispersive Spectroscopy was recorded on an Oxford Instrument EDS-7421. Scanning electron microscopy (SEM) was progressed on a JEOL JSM-6700F (Field Emission) scanning electron microscope. Transmission electron microscope (TEM),

high-resolution transmission electron microscope (HRTEM) and the corresponding selected area electron diffraction (SAED) were taken on a Tecnai G2 F20 TEM.

The anodes for lithium cells were fabricated by mixing the active material, acetylene black, and polytetrafluoroethylene (PTFE) binder in a weight ratio of 80:10:10. The testing cells were assembled with the anodes as-fabricated, metallic lithium cathode, Celgard 2300 film separator and 1 M LiPF₆ in 1:1 ethylene carbonate (EC)/dimethyl carbonate (DMC) electrolyte. The assembly of the testing cells was carried out in an Ar (99.999%)-filled glovebox (Mikrouna Co., Ltd., Universal). The discharge-charge cycle tests by Land were run at a current density of 50 mA g⁻¹ between 3.00 and 0.1 V (vs. Li/Li⁺). All the tests were performed at room temperature.

Reference

1. F.Izumi, T. Ikeda, Mater. Sci. Forum, 2000, **198**, 321.

Table S1. Summary of the experimental parameters and their corresponding morphologies of CoS obtained under various conditions.

T (°C)	dwel time (h)	CoCl ₂ ·6H ₂ O (mol/L)	TAA (mol/L)	Morphology
160	4	0.05	0.1	sphere-like particles
160	8	0.05	0.1	agglomerate particles
160	16	0.05	0.1	irregular flowers
160	24	0.05	0.1	3D flowerlike hierarchitectures
120	24	0.05	0.1	flower clusters
200	24	0.05	0.1	Intersectional hexagonal
160	24	0.025	0.05	perfect flowers
160	24	0.1	0.2	microspheres

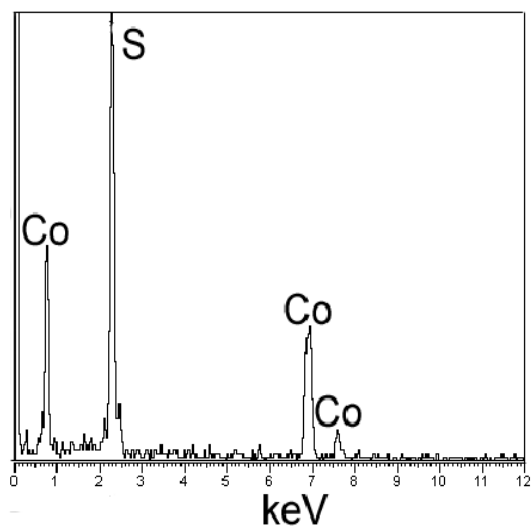


Fig. S1. EDS spectrum of the 3D flowerlike CoS hierarchitectures, confirming the chemical composition of the flowerlike CoS with Co/S ratio close to 1.01:1.

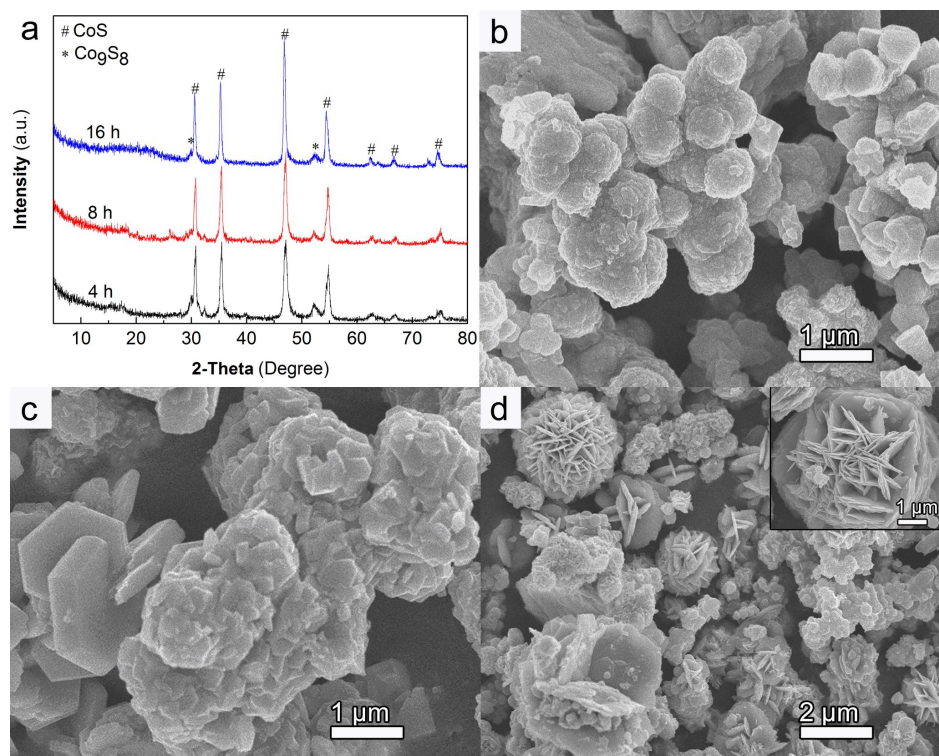


Fig. S2. (a) XRD patterns and (b, c, d) SEM images of the samples synthesized at 160 °C for various dwell time: (b) 4 h, aggregate spheres, (c) 8 h, aggregates with angular protuberances, (d) 16 h, defective flowerlike hierarchitectures.

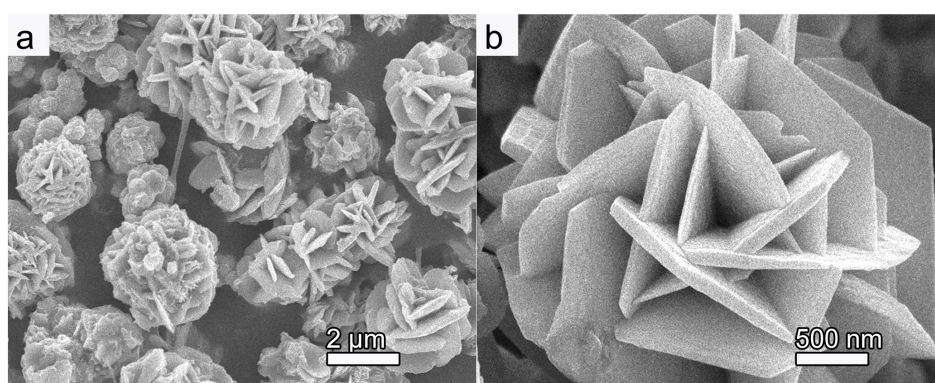


Fig. S3. SEM images of the sample obtained at 160 °C for 24 h with 0.025 M CoCl₂·6H₂O and 0.05 M TAA, perfect flowers.

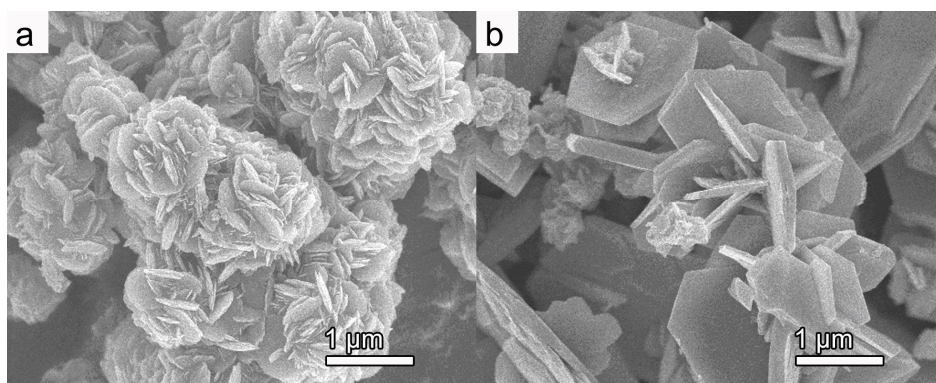


Fig. S4. SEM images of the samples obtained with 0.05 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.1 M TAA at different temperature for 24 h: (a) 120 °C, flower clusters, (b) 200 °C, intersectional hexagonal nanoplates.