Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

Hierarchical micro/nano-structured cobalt sulfide spindles as low-cost counter electrode for dye-sensitized solar cells

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Preparation of cobalt sulfide spindles

All the chemicals with analytic grade were purchased from Aladdin Chemical Ltd. (China) and used without further purification. In a typical synthesis, 50 ml of 0.1M thiourea (CH_4N_2S) solution in deionized water was added slowly to 50 ml of 0.06 M $Co(CH_3COO)_2 \cdot 4H_2O$ solution in deionized water. Then, 9 ml ammonium hydroxide and 5 ml 1-butanol were added to the above solution with vigorous stirring. The resulting mixture was transferred into a Taflon-lined autoclave, that was then sealed and kept at 195 ^oC for 24 h followed by cooling down to room temperature. The prepared products were washed with deionized water and ethanol repeatedly and dried in a vacuum oven at 60 ^oC for 12 h.

Preparation of cobalt sulfide spindles electrode

100 mg of as-prepared cobalt sulfide spindles sample was dispersed in 10 ml of isopropanol and n-butanol solution with the volume ratio of 7:3. Then 5 μl of tetrabutyl titanate was added into above dispersion and sonicated for 30 min. The obtained dispersion was sprayed onto FTO glass using an airbrush. Subsequently, as-prepared electrodes were sintered at 300 ^oC for 10 min.

Fabrication of dye-sensitized solar cells

TiO_2 electrodes with the thickness of 10 μm were prepared by depositing TiO_2

colloidal paste onto FTO glass and then sintered at 450 ^{o}C for 30 min. After cooling to 80 ^{o}C, TiO_2 electrodes were immersed into the ethanol solution of N3 dye (0.5 mM) for 12 h at room temperature. A dye-sensitized solar cell was fabricated by clamping a dye-sensitized TiO_2 electrode, a drop of electrolyte and a counter electrode with two clips. The electrolyte was prepared by dissolving 0.4 M 1-methyl-3-propylimidazolium iodide, 0.3 M LiI, 0.05M I_2 and 0.4 M 4-tert-butylpyridine in 3-methoxypropionitrile.

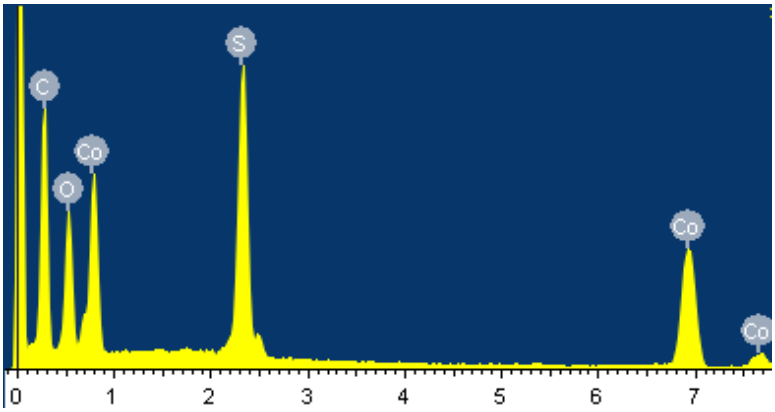

Fig. S1 EDX analysis of as-prepared cobalt sulfide

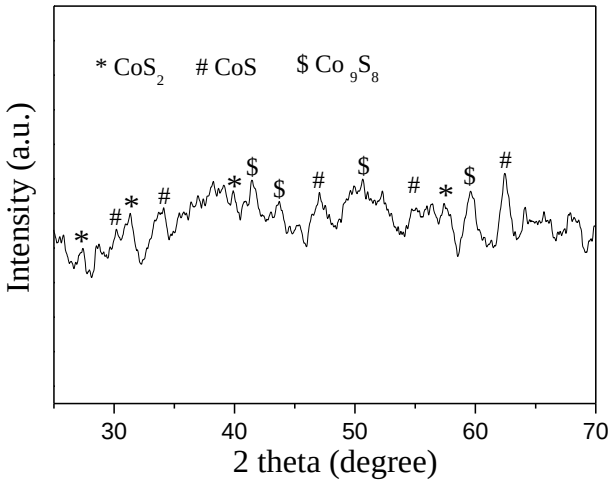

Fig. S2 X-ray diffraction pattern of as-prepared cobalt sulfide spindles

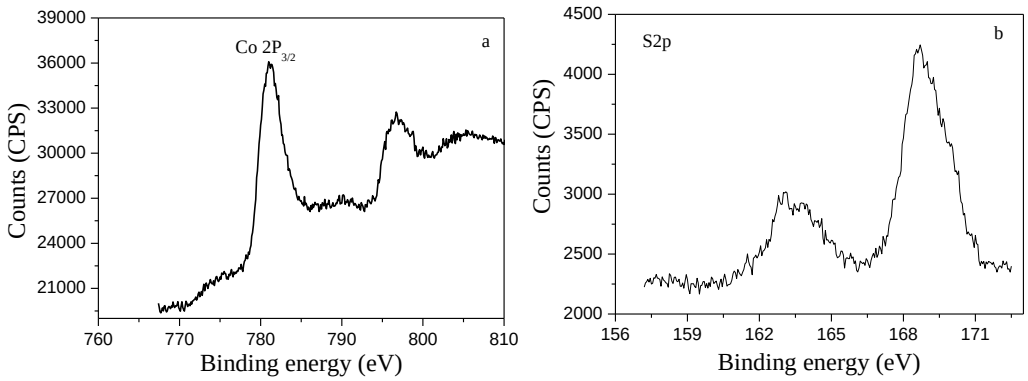

Fig. S3 Co2p (a) and S2p (b) XPS spectrum of as-prepared cobalt sulfide

Table S1 Surface area and pore structure parameters of as-prepared hierarchical micro/nano-structured cobalt sulfide

S_{BET}[a] (m^2 g^{-1})	V_T[b] (cm^3 g^{-1})	$d_{average}$[c] (nm)
144.7	0.29	8.02

[a] BET(Brunauer-Emmett-Teller) surface area

[b] total pore volume, measured at P/P^0=0.995

[c] average pore size, calculated by $4V_T/S_{BET}$

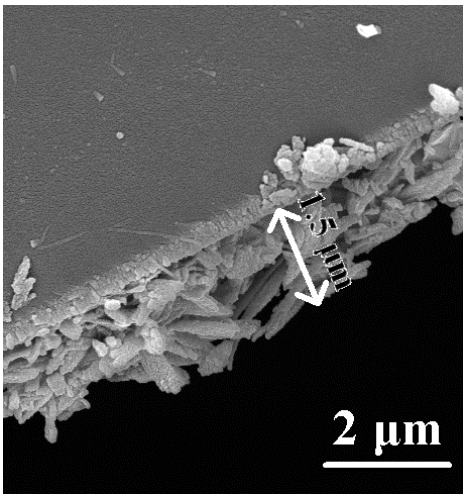

Fig. S4 Cross-section SEM image of cobalt sulfide spindles electrode

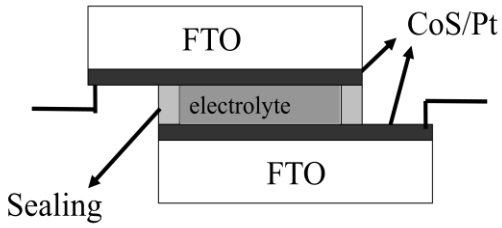

Fig. S5 Electrochemical cell used for EIS measurements

Comparison of cobalt sulfide spindles electrodes with other cobalt sulfide electrodes prepared by cathodic electrodeposition.

The cathodic deposited cobalt sulfide electrodes were prepared by depositing porous cobalt sulfide film onto FTO glass from a deposition bath containing 0.05 mM $Co(CH_3COO)_2 \cdot 4H_2O$ and 0.15 M CH_4N_2S in a three-electrode system. A Pt wire and saturated calonel electrode (SCE) were used as a counter electrode and reference electrode, respectively. The deposition was set between -0.2V and -1.3V vs. SCE at a scan rate of 10 mV S^{-1}. Fig. S6 shows the SEM image of cathodically deposited cobalt sulfide film, which displays a porous structure.

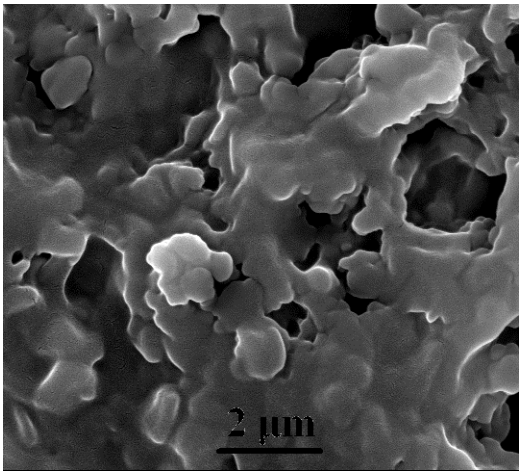

Fig. S6 SEM image of cobalt sulfide electrode prepared by cathodic electrodeposition

Photocurrent density-voltage curve of the dye-sensitized solar cell with porous cobalt sulfide electrode was measured under illumination of 100 mW cm^{-2}. The obtained photocurrent density-voltage curve is shown in Fig. S7.

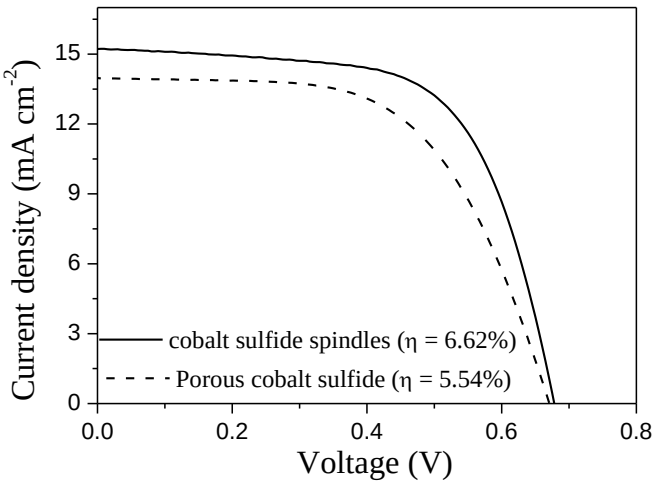

Fig. S7 Photocurrent density-voltage curves of dye-sensitized solar cells with cobalt sulfide spindles electrode and porous cobalt sulfide electrode