

Supplementary Information

High catalytic activity and stability of the nickel sulfide and cobalt sulfide hierarchical nanospheres on the counter electrodes for dye-sensitized solar cells

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Experimental details

Fabrication and characterization of the nickel sulfide and cobalt sulfide hierarchical nanospheres

The optimized nickel sulfide and cobalt sulfide thin films were in-situ grown on the FTO conductive glass by solvothermal method without any post-treatment. The preparation processes of the nickel sulfide and cobalt sulfide thin films are as follows. For the nickel sulfide precursor solution, 0.02 M NiCl₂ · 6H₂O and 0.03 M C₂H₅NS were dispersed homogeneously in 10 ml ethanol. For the cobalt sulfide precursor solution, 0.02 M Co(NO₃)₂ · 6H₂O and 0.03 M C₂H₅NS were dispersed homogeneously in 10 ml ethanol. The nickel sulfide and cobalt sulfide precursor solution were then transferred to 30 mL Teflon-lined stainless steel autoclaves, in which two pieces of cleaned FTO glass were placed diagonally with the FTO side down respectively. The autoclaves were sealed and heated at 150 °C for 24 hours. The obtained films coated FTO glass were washed with distilled water and ethanol and dried at 60 °C in air after the autoclaves were cooled to room temperature.

The crystallinity of the as-synthesized nickel sulfide and cobalt sulfide was characterized by X-ray diffraction (XRD, ARL X'TRA, Switzerland, CuKα, λ=1.540562Å). The results of XRD were shown in Fig. S1. EDS and XPS spectrums were used to determine the composition of the prepared nickel sulfide and cobalt sulfide thin films. Fig. S2a and Fig. S2c show the XPS spectra

of the nickel sulfide and cobalt sulfide films respectively. Fig. S2b and Fig. S2d show the EDS spectra of the nickel sulfide and cobalt sulfide films respectively. From Fig. S2a and Fig. S2b, it can be seen that the prepared nickel sulfide sample is composed of Ni and S elements. The surface atomic ratio of Ni/S was determined as 18.18: 35.86 using XPS for XPS could just detect less than 10 nm depth on the surface. The Ni/S ratio of the whole sample was determined as 31.99: 68.01 using EDS for more than 100 nm depth could be detected using EDS. Fig. S2c and Fig. S2d demonstrate that the prepared cobalt sulfide sample is composed of Co and S elements. The surface atomic ratio of Co/S is 20.7: 34.66, while the atom Co/S of the whole prepared sample is 42.37:57.63

Fabrication of the dyed photoanodes

The photoanodes ($\sim 12\mu\text{m}$ in thickness) were fabricated with commercial TiO_2 paste (Dyesol) and sensitized with N719 dye (Dyesol). The cleaned FTO glass was firstly immersed in 40 mM aqueous TiCl_4 at 70°C for 30 min and washed with distilled water and ethanol, heated at 450°C in air for 30 min. Then the substrate was coated with TiO_2 paste by screen printing, which was dried at 125°C for 30 min and then annealed at 450°C in air for 30 min. After that, the sample was secondly immersed in 40 mM aqueous TiCl_4 at 70°C for 30 min as post-treatment and sintered in an oven at 500°C for 30 min. When being cooled to 80°C , the film was immersed into N719 ethanol solution overnight. The dyed electrode was then rinsed with ethanol and dried at 60°C .

Fabrication of the full cells and the symmetrical cells

The nickel sulfide and cobalt sulfide porous films synthesized with optimized concentrations were used as the counter electrodes. The platinized electrode was fabricated by sputtering Pt on the FTO glass for comparison. The electrolyte was composed of 1.0 M BMII, 50 mM LiI, 30 mM I_2 , and 0.5 M tert-butylpyridine in a mixed solvent of acetonitrile and valeronitrile. The as-prepared photoanodes and counter electrodes were integrated into full cells using Surlyn film (DuPont 1702, 60 μm thick) as the sealant. The electrolyte was injected into the cells through the hole drilled in the counter electrodes beforehand. The symmetrical cells (0.28 cm^2) were fabricated with two identical counter electrodes clipping the same electrolyte in DSSCs with the similar process.

Test conditions

Electrochemical impedance spectroscopy (EIS) analysis and cyclic voltammograms (CVs) were conducted with an electrochemical teststation ((PAR2273, Princeton Applied Research, USA). EIS test was scanned from 0.1 Hz to 100 kHz at 0 V bias without illumination with symmetrical cells. The simulated parameters of the impedance spectra were obtained using Zsimpwin software. CVs were carried out in a three-electrode system in acetonitrile solution containing 10.0 mM LiI, 1.0 mM I_2 , and 0.1 M LiClO_4 , at a scan rate of 50 mV/s, with saturated calomel electrode (SCE) as reference electrode and Pt sheet as counter electrode. The working electrode is the synthesized nickel sulfide, cobalt sulfide and the sputtering Pt respectively. The potential range for CV comparison among the nickel sulfide, cobalt sulfide and sputtering Pt was from -0.4 V to 1 V. The potential range for CV variations in 50 cycles was from -0.2 V to 0.5 V. Polarization curves of the symmetrical cells were test with a digital sourcemeter (Keithley 236, USA). DSSCs were test with a Keithley 236 sourcemeter under AM 1.5 illumination from an Oriel 92251A-1000 sunlight simulator with a mask to define the active area as 0.132 cm^2 .

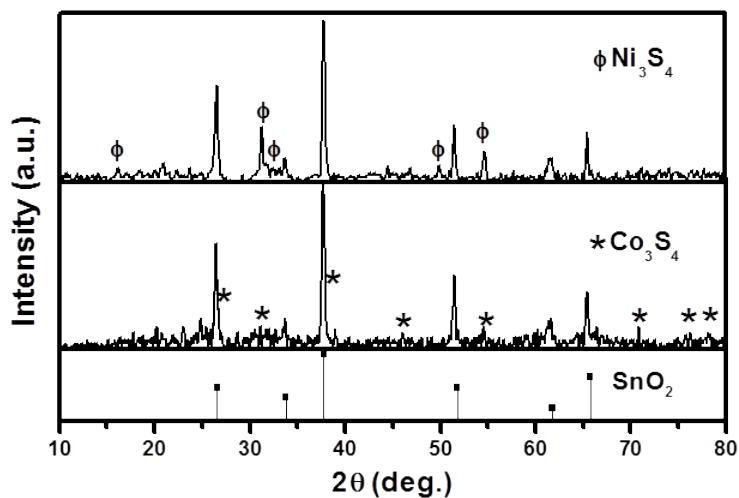


Fig. S1 XRD patterns of the synthesized nickel sulfide (JCPDS 47-1739) and cobalt sulfide (JCPDS 11-0121) thin films.

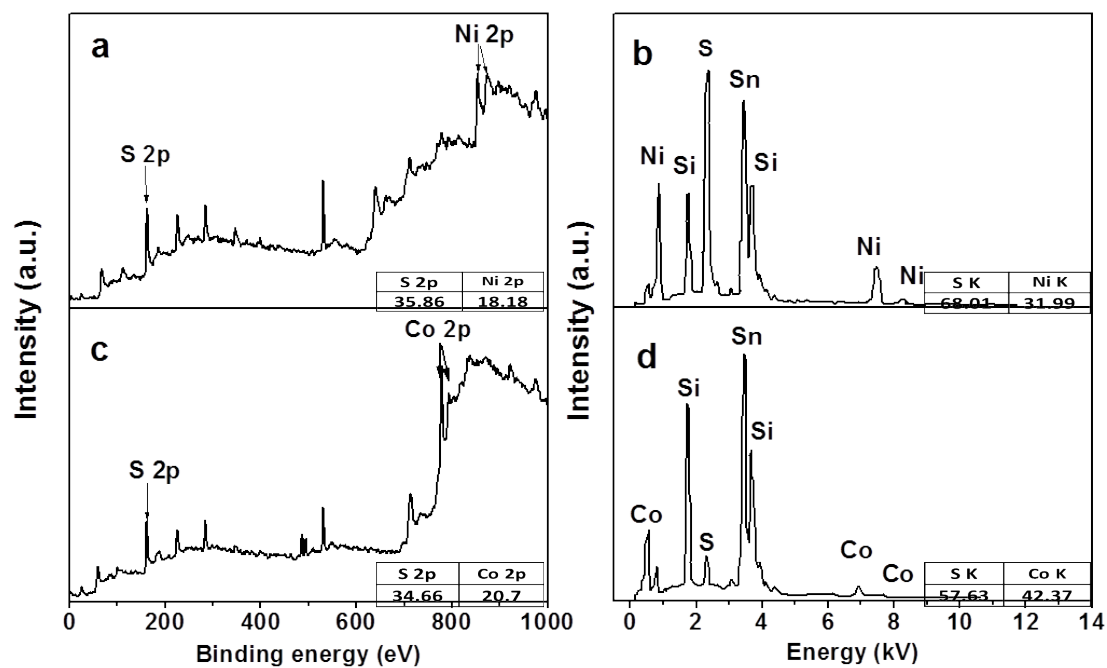


Fig. S2 The XPS spectra of the prepared nickel sulfide and cobalt sulfide electrodes respectively (a, c) and EDS analysis of the nickel sulfide and cobalt sulfide counter electrodes respectively (b, d).

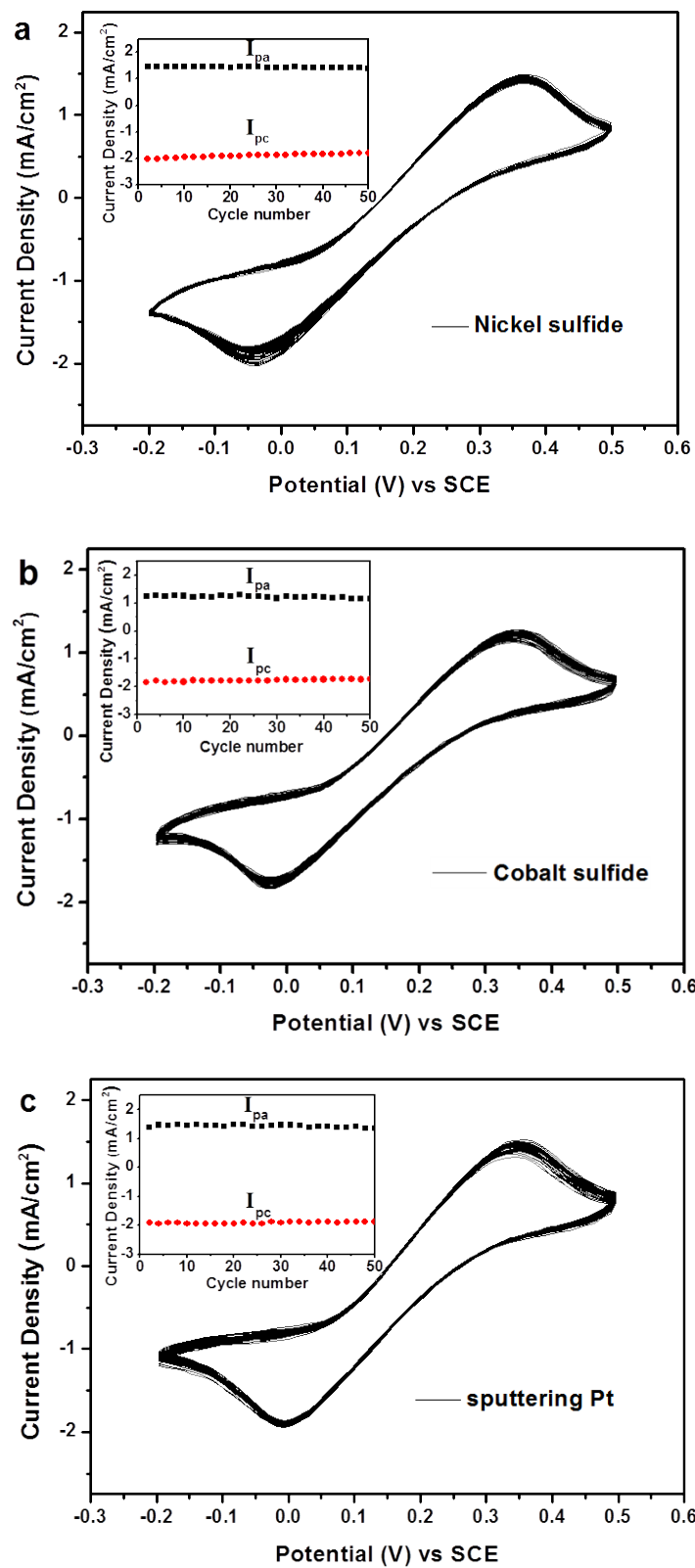


Fig. S3 CV curves of the nickel sulfide (a) , cobalt sulfide (b) and sputtering Pt (c) CEs obtained for 50 cycles in acetonitrile solution containing 10.0 mM LiI, 1.0 mM I₂, and 0.1 M LiClO₄, at a scan rate of 50 mV/s.