Preparation of hollow Co_9S_8 nanoneedle arrays as effective counter electrodes for quantum dot-sensitized solar cells

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Experimental Section

Preparation of Co_9S_8 hollow nanoneedle array films

First, the cleaned FTO substrates were treated with 0.18 M $TiCl_4$ aqueous solution at 70 °C for 30 min, washed with deionized water (DIW), dried under air stream, and then annealed under 550 °C for 60 min. $Co(CO_3)_{0.35}Cl_{0.20}(OH)_{1.10}\cdot 1.74H_2O$ nanoneedle arrays were grown on the pretreated FTO substrates by the following chemical bath deposition:[7] the pretreated FTO substrates were immersed in an aqueous solution containing 6.25 wt% urea and 0.15 M cobalt chloride with the conductive side facing down under 90 °C for 3 h. After chemical bath deposition, the pink $Co(CO_3)_{0.35}Cl_{0.20}(OH)_{1.10}\cdot 1.74H_2O$ films grown on FTO substrates were transferred to a sealed Teflon reactor containing 0.01 M Na_2S aqueous solution and reacted under 180 °C for 0.5-10 h. Thereafter, the pink films were turned to black and Co_9S_8 hollow nanoneedle arrays were obtained. $TiCl_4$ pretreatment is very important because the Co_9S_8 nanoneedle arrays are easy to shed from the FTO substrates without this treatment.

Preparation of the TiO_2/CdS/CdSe photoanodes

We have prepared TiO_2 nanorod array films as photoanodes for the DSCs and QDSCs in our previous works.[4, 25] TiO_2 nanorod arrays around 9 μm grown on FTO substrates were prepared as follows: (1) Cleaned FTO substrates were immersed in 0.18 M $TiCl_4$ aqueous solution in drying oven at 70 °C for 30 min, washed with deionized water (DIW), dried under air stream, and then annealed under 550 °C for 60 min; (2) The TiO_2 nanorod arrays (TNARs) were grown on the above treated FTO substrates by a hydrothermal method. 30 mL DIW was mixed with 30 mL concentrated hydrochloric acid, 3 mL $TiCl_4$ was added to the mixture slowly and stirred for around 2 h. The mixed solution was transferred into a 100 mL sealed Teflon reactor after the treated FTO substrates were placed with the conducting side facing down within the reactor under 150 ◦C for 4 h, then the Teflon reactor was cooled to room temperature and the FTO substrates that attached with TNARs on the conducting side out were taken out and rinsed with DIW; (3) The TNARs were placed in the Teflon reactor again, and the mixture of 25 mL DIW and 35 mL concentrated hydrochloric acid (36.0%-38.0% wt %) was transferred into the Teflon reactor followed by the etched treatment at 150 °C for 7 h, and then the obtained etched TNARs were taken out and rinsed with DIW thoroughly after cooling to room temperature; (4) The etched TNARs were dried in air and annealed at 450 °C for 2 h.

CdS and CdSe quantum dots (QDs) were grown on the etched TNARs following the reference:[26, 27] (1) The CdS quantum dots were deposited on the etched TNARs by soaking in the mixture of 20 mM $CdSO_4$, 66 mM NH_4Cl, 144 mM thiourea and 260 mM ammonia under 5 °C for 75 min (TNARs/CdS); (2) CdSe QDs was deposited on TNARs/CdS electrodes by soaking in a mixture of sodium selenosulphate (Na_2SeSO_3) solution and $Cd(NO_3)_2$ solution with a volume ratio of 1:1 under 5 °C for 30 h (TNARs/CdS/CdSe). Na_2SeSO_3 aqueous was used as Se source, which was prepared by dissolving Se (0.1 M) in an aqueous solution of Na_2SO_3 (0.18 M) at 70 °C for about 7 h when the black Se powder was almost reacted. After cooling to room temperature, the obtained Na_2SeSO_3 aqueous solution was filtered to remove unreacted Se. $Cd(NO_3)_2$ aqueous solution was prepared as Cd source which contained 0.08 M $Cd(NO_3)_2$ and 0.16 M $N(CH_2COONa)_3$.

Assembly and characterization of the solar cells

The TNARs/CdS/CdSe electrodes were coupled with Co_9S_8 counter electrodes to fabricate the QDSCs. The two electrodes were separated by a 60-μm thick hot-melt glue and sealed by heating at 100 ◦C for 3 min in dry oven, which were then injected with polysulfide electrolytes containing 0.5 M Na_2S, 0.2 M S, and 0.2 M KCl in a mixture of methanol and DIW (3:7 v/v). As comparison, Pt coated FTO substrate was also fabricated as counter electrode, which was prepared by thermal decomposition of 2 drops of 2 mg/mL chloroplatinic acid hexahydrate ethanol solution on 1 cm × 1.5 cm FTO substrates at 400 ◦C for 10 min.

The morphologies of cobalt sulphide films were observed by field-emission scanning electron microscope (FESEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL JEM-2100) operating at 200 kV. The crystal structure was measured by X-ray diffraction (XRD, Panalytical X'pert PRO) at a scanning speed of 20° per min. The XRD patterns were recorded from 10° to 80° using Cu Kα radiation ($\lambda = 0.15406$ nm). J-V curves of assembled QDSCs were measured under AM 1.5G simulated solar light (100 mW cm^{-2}, Oriel 300 W Xe lamp and Newport AM 1.5G filter) and the cell active area was 0.21 cm^2. Electrochemical impedance spectra (EIS) and Tafel polarization curves were measured on an electrochemical workstation (Autolab, PGSTAT30, Metrohm) using symmetric electrode. EIS measurements were carried out at open circuit conditions and frequency range was set from 0.1 to 10^5 Hz. Tafel polarization curves were measured at a scan rate of 5 mV s^{-1}. The sandwich-like symmetric electrodes were sealed with 60 μm thick hot-melt films with an active area of 0.21 cm^2 and the electrolyte used for the symmetrical cells was the same as that used for the QDSCs. Circuits of the QDSCs were fitted by ZSimpWin software and the simulated circuit.