Supplementary

Experimental

1. Preparation of CdS/CdSe sensitized TiO_2 films

TiO_2 films were prepared by coating commercial P25 (Degussa) on FTO through a doctor-blade method. CdS/CdSe cosensitized TiO_2 electrode was obtained by a chemical bath deposition (CBD) technique as reported before.[1] Typically, TiO_2 film was firstly immersed in an aqueous solution containing $CdCl_2$, NH_4Cl, $NH_3.H_2O$ and thiourea at ~ 5℃ for 16 h to deposit CdS on TiO_2. After rinsed with distilled water and dried in air, the resulted film was then immersed into an aqueous solution containing sodium selenosulphate (Na_2SeSO_3) (generated by the reaction of Se and Na_2SO_3 at 80℃), trisodium salt of nitilotriacetic acid [$N(CH_2COONa)_3$] and $CdSO_4$ at ~ 10℃ for 28 h to form CdS/CdSe cosensitized TiO_2 electrode.

2. Post-treatments

Post-treatments were performed using a successive ionic layer adsorption and reaction (SILAR) method. For the CdS treatment, CdS/CdSe cosensitized TiO_2 electrodes were twice dipped in 0.1M $Cd(NO_3)_2$ for 1 min and 0.1 M Na_2S aqueous solutions for 1 min alternatively, rinsing with distill water between each dip. ZnS treatment was carried out using the same route as CdS treatment, by sequentially dipping the CdS/CdSe cosensitized TiO_2 electrodes or CdS treated electrodes in 0.1 M $Zn(CH_3COO)_2$ for 1 min and 0.1 M Na_2S aqueous solutions for 1 min. The thickness of ZnS coating was controlled by altering the numbers of SILAR cycles.

3. Solar cell fabrication

The QDSSC was assembled by sandwiching a sensitized TiO_2 electrode and a Cu_2S on brass electrode, where polysulfide electrolyte composed of 0.5 M S, 2.0 M Na_2S and 0.2 M KCl dissolved in water/ethanol (volume ratio of 7:3) was used as the electrolyte.

4. Characterizations

The crystalline structures were characterized by an X-ray powder diffractometer (XRD, Riguku

D/max 2500 with a CuKa irradiation). Film thickness of photoanode was determined by scanning electron microscopy (SEM, S-4800F, Hitachi) measurements.

Photocurrent-voltage measurements were performed with a computer-programmed Keithley 2611 Source Meter at room temperature under illumination of simulated sunlight (Oriel, 91160-1000, AM1.5, 100 mW.cm^{-2}). The active area of the cell is 0.2 cm^{2}. Intensity-Modulated Photocurrent Spectroscopy (IMPS) and Intensity-Modulated Photovoltage Spectroscopy (IMVS) were performed using a green light emitting diode (λ_{max}=520nm) driven by a solartron 1255B frequency-response analyzer. The LED provided both dc and ac components of the illumination. Electron Impedance Spectroscopy (EIS) was carried out at open-circuit voltage under illumination, using a frequency response analyzer (Solartron 1255B) coupled with an electrochemical interface system (Solartron analytical SI, 1287). The frequency range was 10^{-1} to 10^{5} Hz and the amplitude of the AC voltage was 10 mV.

1 Q. Zhang, G. Chen, Y. Yang, X. Shen, Y. Zhang, C. Li, R. Yu, Y. Luo, D. Li, Q. Meng, *Phys. Chem. Chem. Phys.*, 2012, **14**, 6479.