Band Gap Engineering of Multinary Metal Sulfides for Quantum-Dot Sensitized Solar Cells (QDSSCs); $Pb_xCd_{1-x}S$ and $Pb_xCd_{1-x}S_{1-y}Se_y$

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Abstract

Binary metal sulfide quantum dot-sensitized solar cells (QDSSCs) have been widely studied as efficient solar absorbers. One of the most extensively studied materials is cadmium sulfide (CdS). It produces a relatively large open-circuit voltage (V_{oc}) of about 0.6 V. In contrast, it produces a low short-circuit current density (J_{sc}) due to its wide band gap E_g and narrow optical absorption. Theories predicted that E_g could be tuned to a lower value by changing the material composition through the incorporation of larger cationic and anionic ions. This work aims to develop metal sulfide's structure to increase the short-circuit density J_{sc} and produce a broader absorption range by the incorporation of a larger cationic and anionic radius than that of Cd and S, respectively.

Firstly, solid-state $Pb_xCd_{1-x}S$ QDSSCs were successfully demonstrated by the incorporation of Pb, cationic radius = 119 pm, into the CdS host (Cd^{2+} 95 pm) using a facile two-stage successive ionic adsorption and reaction (SILAR) method with Spiro-OMeTAD as the hole transporting material. The Pb content x increases with the number of PbS SILAR n cycles with x = 0, 0.02, 0.05, 0.10 and 0.17 corresponding to n = 0, 1, 2, 3 and 4, respectively. The optical energy gap E_g decreased with increasing Pb content x with E_g = 2.40, 2.17, 2.04, 1.88 and 1.78 eV corresponding to x = 0, 0.02, 0.05, 0.10 and 0.17, respectively. The best cell $Pb_{0.05}Cd_{0.95}S$ yields a J_{sc} of 8.34 mA/cm^2, a V_{oc} of 0.70 V, a fill factor (FF) of 62.8% and a power conversion efficiency (PCE) of 3.67% under 100% full sun illumination. The efficiency further increases to 5.93% and 8.48% under 10% and 1% sun illumination, respectively.

Secondly, quaternary solid-state $Pb_xCd_{1-x}S_{1-y}Se_y$ QDSSCs were demonstrated by replacing a fraction of anionic atoms S (S^{2-} radius 184 pm) with larger anionic Se atoms (Se^{2-} 198 pm). The Spiro-OMeTAD was served as a hole transport material. The Se content *y* was varied by controlling the Se ion-exchange reaction time of 0,15, 20, 25 and 30 seconds. The Se content *y* increases with increasing Se reaction times, producing five different samples: (1) $y = 0$ ($Pb_{0.14}$ $Cd_{0.86}S_{0.88}$, Se 0 second), (2) $y = 0.15$ ($Pb_{0.13}Cd_{0.77}S_{0.85}Se_{0.15}$, Se 15 seconds), (3) $y = 0.18$ ($Pb_{0.15}Cd_{0.85}S_{0.75}Se_{0.18}$, Se 20 seconds), (4) $y = 0.20$ ($Pb_{0.14}Cd_{0.86}S_{0.80}Se_{0.20}$, Se 25 seconds) and (5) $y = 0.22$ ($Pb_{0.11}Cd_{0.72}S_{0.78}Se_{0.22}$). The E_g decreases with increasing Se content *y* with 1.91 eV ($y = 0$), 1.74 eV ($y = 0.15$), 1.65 eV ($y = 0.18$), 1.59 eV ($y = 0.20$) and 1.55 eV ($y = 0.22$), resulting in broader optical absorption. The best cell $Pb_{0.15}Cd_{0.85}S_{0.75}Se_{0.18}$ yields a J_{sc} of 13.71 mA/cm^2, a V_{oc} of 0.59 V, a FF of 54.81% and a PCE of 4.43% under 100% sun. The efficiency further increases to 7.18% and 9.24% under 10% and 1% sun, respectively. The high photovoltaic performance of over 8% suggests that both $Pb_xCd_{1-x}S$ and $Pb_xCd_{1-x}S_{1-y}Se_y$ QDSSCs are candidate materials for efficient solar cells.

Keywords**:** quantum-dots sensitized solar cells (QDSSCs), band gap E_g, metal sulfide and power conversion efficiency (PCE)