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Graded bandgap structure for PbS/CdS/ZnS quantum-dot-sensitized solar cells with a PbₓCd₁₋ₓS interlayer

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To suppress the electron-hole recombination in the multishell sensitizer for quantum-dot-sensitized solar cells (QDSCs), the PbₓCd₁₋ₓS interlayer is incorporated between the PbS core and CdS shell. The PbS/PbₓCd₁₋ₓS/CdS structure enhances the cell efficiency by ~60% compared to PbS/CdS QDSCs, and consequently shows a power-conversion efficiency of 1.37% with ZnS coating. Open-circuit voltage decay confirmed that the PbₓCd₁₋ₓS interlayer effectively reduces the recombination at the PbS/CdS interface. Furthermore, with respect to the peak shift of incident photon-to-current conversion efficiency, the interlayer also increases the light-harvesting efficiency in the higher-wavelength region by reducing the exciton confinement within the PbS sensitizer.

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Recently, quantum-dot-sensitized solar cells (QDSCs) have received much attention for the alternative of dye-sensitized solar cells (DSSCs) owing to their bandgap tunability, higher absorption coefficient of quantum dots compared to dye molecules, and the ability of multiple-carrier generation.¹–⁴ Because the main difference between QDSCs and DSSCs is the quantum dots as the sensitizer material, manipulating and understanding the band structure of the quantum dots itself are key issues for enhancing the efficiency of QDSCs.⁵

PbS is a fascinating sensitizer for quantum-dot solar cells. The bulk bandgap of PbS (0.41 eV) can be easily manipulated by changing the particle size due to its large exciton radius of 18 nm.⁶ Because the poor stability of PbS quantum dots is a major drawback for QDSC applications, in order to solve these problems, CdS and ZnS shells are coated on the PbS sensitizer to prevent the corrosion by the polysulfide electrolyte and suppress the recombination at the semiconductor/electrolyte interface.⁷–⁹ However, abrupt changes of phase and lattice can reduce the crystal quality of quantum dots.¹⁰,¹¹ Different from the dye molecules, quantum-dot sensitizers may have defects or dislocations. Therefore, enhancing the quality of the quantum dots is an important issue for optimizing QDSCs.¹²

In the research field of luminescent nanoparticles, there have been studies of multishell structures by gradually changing the shell composition in order to enhance the crystallinity and reduce the lattice mismatch.¹³–¹⁵ For example, Mews’ group synthesized CdSe/CdS/Zn0.5Cd0.5S/ZnS nanocrystals, and showed quantum-efficiency enhancement compared to the single-shell (CdSe/ZnS) structure.¹⁵ However, investigations on graded bandgap structures by incorporating alloyed interlayers for quantum-dot sensitizers have been rare. In this study, the effects of graded bandgap structure on the photovoltaic and optical properties of QDSCs were investigated by changing the thickness of the PbₓCd₁₋ₓS interlayer in the multishell structures.

The commercial TiO₂ nanopaste (Ti-Nanoxide D; Solaronix) was spread using a doctor blade method on the 40 mM TiCl₄ pre-treated fluorine-doped tin oxide electrode (FTO, TEC 8; Pilkington), and the paste-coated electrodes were annealed at 450 °C for 30 min in ambient air. The sintered electrodes were treated with TiCl₄ again at 70 °C for 30 min. The thickness of the TiO₂-nanoparticle electrode was ~5 μm, and the active area was 0.126 cm². The successive ionic-layer adsorption and reaction (SILAR) method was used to form the multilayered quantum dots onto the TiO₂-nanoparticle electrode. The TiO₂ electrodes were immersed in 0.03 M lead nitrate (Pb(NO₃)₂; Aldrich) dissolved in methanol for 30 s, and then dipped for another 30 s into 0.04 M sodium sulfide (Na₂S; Aldrich) in methanol. The PbS-sensitized electrode was immersed into 0.04 M cadmium nitrate (Cd(NO₃)₂; Aldrich) dissolved in methanol for 1 min, and then dipped for another 1 min into 0.04 M sodium sulfide in methanol. Finally, the electrode was treated with 0.1 M zinc acetate solution and 0.04 M sodium sulfide solution to form a ZnS shell layer. For the PbₓCd₁₋ₓS interlayer deposition, considering the solid-solution region in nanoscale systems and the deposition rate of each ion, a mixed solution of 0.04 M Pb/Cd (5/95 by molar ratio) was used.¹⁶,¹⁷ A polysulfide solution of 0.5 M Na₂S, 1 M S, and 0.02 M KCl in methanol/water (7/3 by volume ratio) was used as the electrolyte. The CuS counter electrode was prepared by depositing Cu on FTO substrate and immersing the Cu film in the polysulfide solution for 10 s. A thermoplastic foil (25 μm; DuPont) was used as a spacer for the solar cells.

The photocurrent-voltage (J-V) curves were measured using a solar cell measurement system (K3000; McScience, Korea) under a solar simulator (Xenon lamp, air mass (AM) 1.5, 100 mW cm⁻²). High-resolution transmission electron
microscopy (HRTEM, JEM-3000F: JEOL, Japan) was used to identify the morphology of sensitizer. The elemental distributions were examined using energy-dispersive x-ray spectroscopy (EDX, ISIS-300: Oxford Instruments). The external quantum efficiency was characterized by an incident photon-to-current conversion efficiency (IPCE) measurement system (K3100: McScience, Korea). X-ray diffraction (XRD, M18XHF-SRA: MAC Science, Japan) was used to characterize the quantum-dot multilayers, and open-circuit voltage decay curves were measured by a potentiostat (CHI 608C: CH Instrumental Inc., Austin, USA). The compositions of interlayers were determined using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Optima-4300 DV: Perkin-Elmer, MA, USA).

The current density-voltage (J-V) curves of PbS/CdS/ZnS QDSCs with different SILAR cycles of Pb_xCd_{1-x}S interlayers are shown in Fig. 1. Incorporation of the interlayer between the PbS and the CdS layer enhances both $J_{sc}$ and $V_{oc}$, and thereby enhancement of power-conversion efficiency by 60% is achieved (Table I). However, further increase of the interlayer-deposition cycle decreases the efficiency of the solar cell.

The calculated thicknesses of each layer for the graded PbS/Pb_xCd_{1-x}S/CdS sensitizer are 3.0/0.9/1.1 nm, respectively. While TEM image of the interface with EDX mapping is ideal for clarifying the morphology of quantum-dot sensitizer (Fig. 2), each multilayer could not be resolved due to the approximately 1-nm-thin interlayer thickness.

While the similar crystal structures of PbS and CdS can induce epitaxial growth of CdS on PbS, the Pb_xCd_{1-x}S interlayer can reduce the lattice mismatch and trap states between the PbS and the CdS layers. The intensity of each peak (especially (220)) increases with the addition of the interlayer.

The thickness of each sublayer was estimated from the ICP results with some approximations. The actual Pb/(Pb+Cd) ratio of the interlayer is ~0.2, as confirmed by ICP-AES analysis. In nanoscale systems, mixed Pb_{0.2}Cd_{0.8}S can exist as a stable solid-solution phase despite the phase-separating bulk diagram. The crystal structures of the multilayer quantum dots were measured by x-ray diffraction. The bare PbS/CdS multilayer constitutes of cubic rock-salt (PbS) and cubic zinc-blende (CdS) phases.

### Table I

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
</tr>
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<tbody>
<tr>
<td>Bare</td>
<td>8.39</td>
<td>0.315</td>
<td>31.8</td>
<td>0.84</td>
</tr>
<tr>
<td>1 cycle</td>
<td>9.64</td>
<td>0.343</td>
<td>31.4</td>
<td>1.04</td>
</tr>
<tr>
<td>2 cycles</td>
<td>10.25</td>
<td>0.415</td>
<td>32.3</td>
<td>1.37</td>
</tr>
<tr>
<td>3 cycles</td>
<td>9.81</td>
<td>0.363</td>
<td>32.9</td>
<td>1.17</td>
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</tbody>
</table>

### Table II

<table>
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<th></th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
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</tr>
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</table>

The red shift of PbS/Pb_xCd_{1-x}S/CdS sensitizers is also shown in the absorption spectra of the QDSCs (Fig. 4(a)). To
estimate the bandgap energy of each layer, PbS (2 cycles), Pb$_x$Cd$_{1-x}$S (2 cycles), or CdS (4 cycles) was deposited separately on the TiO$_2$ electrode, and the optical bandgap of each layer is obtained from the linear fitting of $\alpha^2$ vs. $h\nu$ and linear fits for $E_g$ of the single-layered quantum dots.

The photovoltage-decay measurement is effective for observing the recombination behavior at the TiO$_2$/quantum-dot/electrolyte interfaces (Fig. 5). The decay curves for interlayer-incorporated cells exhibit much slower decay than that of the bare PbS/CdS/ZnS cell, which demonstrates the reduced recombination in the multilayered QDSC. The corresponding electron lifetime was also calculated from

$$\tau = \frac{k_B T}{e} \left( \frac{dV_{oc}}{dt} \right)^{-1},$$

where the voltage-independent prefactors, $R_0$ and $C_0$, are the recombination resistance and chemical capacitance, respectively. Using the relation ($\beta = \gamma_n + T/T_b$), $\beta$ was obtained with the assumption that $T_b$ (bulk-trap distribution parameter) $\approx$ 1000 K (inset of Fig. 5(b)). While the $\beta$ values commonly lie between 0.5 and 0.7 in DSSCs, the $\beta$ value for the bare QDSC is lower than the interlayer-incorporated samples, and also lower than the minimum value for DSSCs. The recombination order ($\beta$) confirms that Pb$_x$Cd$_{1-x}$S interlayered QDSCs exhibit comparable carrier recombination with DSSC.

In multilayered QDSCs, some pores are indispensable for the hole transport from the inner sensitizer to the electrolyte, as shown in the schematic diagram of Fig. 6. However, unwanted defects (interfacial defects or trap states) must be reduced for enhancing the cell efficiency. Incorporation of the Pb$_x$Cd$_{1-x}$S interlayer reduces defect states and interphase strain between the PbS and the CdS layers, and also increases the absorption in the higher wavelength region by reducing the exciton confinement of the PbS layer. Therefore, more electrons are accumulated in the TiO$_2$ electrode, resulting in higher photovoltage and photocurrent concurrently.

$$\tau = R_0 C_0 \exp \left( -\gamma_n \frac{qV}{k_B T} \right).$$

FIG. 4. (a) Absorbance spectra of PbS/CdS/ZnS (bare) quantum-dot sensitizers with various graded-interlayer-deposition cycles (1, 2, or 3 cycles) on the porous TiO$_2$ electrode. (b) Absorbance spectra of individual single-layered quantum dots (PbS, Pb$_x$Cd$_{1-x}$S, or CdS). The inset shows $\alpha^2$ vs. $h\nu$ and linear fits for the single-layered quantum dots.

FIG. 5. (a) Experimental decay curves of open-circuit voltage for the PbS/ CdS/ZnS-sensitized (bare) solar cells with different interlayer-deposition cycles (1, 2, or 3 cycles). (b) Corresponding electron lifetimes as a function of voltage. The inset shows the recombination order $\beta$. The electron lifetime of the 2-cycle-interlayered QDSC shows more than one order of magnitude enhancement compared to that of the bare sample in all voltage ranges, as shown in Fig. 5(b) ($T \approx$ 295 K). To obtain the recombination order ($\beta$), $\gamma_n$ was obtained by fitting the slope of lifetime curves.

The electron lifetime of the 2-cycle-interlayered QDSC shows more than one order of magnitude enhancement compared to that of the bare sample in all voltage ranges, as shown in Fig. 5(b) ($T \approx$ 295 K). To obtain the recombination order ($\beta$), $\gamma_n$ was obtained by fitting the slope of lifetime curves.
FIG. 6. Schematic diagram of the effect of the PbxCd1−xS interlayer on the performance of the multilayered quantum-dot-sensitized solar cells.

effect, resulting in an interrupted electron injection from PbS to the TiO₂ electrode. Furthermore, the increase of the PbxCd1−xS layer thickness can induce phase separation within the interlayer, which raises recombination within the interlayer, and finally decreases $V_{oc}$ and $J_{sc}$.

In summary, to reduce defects and interphase strain in the multilayered quantum-dot solar cell, the PbxCd1−xS alloy layer is incorporated between the PbS core and the CdS shell. The PbS/PbxCd1−xS/CdS/ZnS structure clearly enhances the cell efficiency compared to the PbS/CdS/ZnS structure. The enhanced efficiency is attributed to the reduced recombination in the quantum-dot sensitizer and increased light absorption with the incorporation of the PbxCd1−xS interlayer.

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19See supplementary material at http://dx.doi.org/10.1063/1.4804149 for Fig. S1 and Table SI.
Supporting Information

Graded Bandgap Structure for PbS/CdS/ZnS Quantum-Dot-Sensitized Solar Cells with a Pb\textsubscript{x}Cd\textsubscript{1\textendash}xS Interlayer

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\textsuperscript{1}WCU Hybrid Materials Program, Department of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, Seoul, Korea

\textsuperscript{2}School of Engineering and Applied Sciences, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts, USA

Fig. S1. X-ray diffraction patterns of the PbS/CdS quantum dots on the porous TiO\textsubscript{2} film with and without the Pb\textsubscript{x}Cd\textsubscript{1\textendash}xS interlayer deposition (2 cycles).

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Table SI. Atomic ratios calculated from the ICP results of \( \text{PbS} \), \( \text{PbS/Pb}_x\text{Cd}_{1-x}\text{S} \), and \( \text{PbS/Pb}_x\text{Cd}_{1-x}\text{S}/\text{CdS} \) sensitizers.

<table>
<thead>
<tr>
<th></th>
<th>Pb/Ti</th>
<th>Cd/Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{PbS} )</td>
<td>0.044</td>
<td>-</td>
</tr>
<tr>
<td>( \text{PbS/Pb}<em>x\text{Cd}</em>{1-x}\text{S} )</td>
<td>0.055</td>
<td>0.040</td>
</tr>
<tr>
<td>( \text{PbS/Pb}<em>x\text{Cd}</em>{1-x}\text{S}/\text{CdS} )</td>
<td>0.052</td>
<td>0.146</td>
</tr>
</tbody>
</table>

The thickness of each sublayer was calculated using the molar ratio from the ICP data and with the assumption that the \( \text{PbS/Pb}_x\text{Cd}_{1-x}\text{S}/\text{CdS} \) sensitizer has a hemispherical shape with \(~5\) nm in radius. The calculated volume ratios are 1.0:1.1:2.3. (The molar ratio and volume ratio are almost same because of the similar molar volume for each structure (30.0 cm\(^3\)/mol for CdS and 31.5 cm\(^3\)/mol for PbS.) Approximated thicknesses of the each layer are 3.0 nm (PbS), 0.9 nm (\( \text{Pb}_x\text{Cd}_{1-x}\text{S} \)), and 1.1 nm (CdS), respectively. Other reports also show similar thickness of PbS sensitizer [1-2] and PbS/CdS sensitizer [3]. The actual thickness surely deviates from this simple calculation, due to the broad size distribution (approximately 2 - 7 nm) of sensitizer by SILAR deposition.
References

