Colloidal quantum dots (QDs) are widely studied due to their promising optoelectronic properties. This study explores the application of specially designed and synthesized “giant” core/shell CdSe/(CdS)\(_x\) QDs with variable CdS shell thickness, while keeping the core size at 1.65 nm, as a highly efficient and stable light harvester for QD sensitized solar cells (QDSCs). The comparative study demonstrates that the photovoltaic performance of QDSCs can be significantly enhanced by optimizing the CdS shell thickness. The highest photoconversion efficiency (PCE) of 3.01% is obtained at optimum CdS shell thickness \(= 1.96 \text{ nm} \). To further improve the PCE and fully highlight the effect of core/shell QDs interface engineering, a CdSe\(_{8}\)S\(_{1}\) interfacial alloyed layer is introduced between CdSe core and CdS shell. The resulting alloyed CdSe/(CdSe\(_{8}\)S\(_{1}\)+S)/CdS\(_1\) core/shell QD-based QDSCs yield a maximum PCE of 6.86%, thanks to favorable stepwise electronic band alignment and improved electron transfer rate with the incorporation of CdSe\(_{8}\)S\(_{1}\) interfacial layer with respect to CdSe/(CdS)\(_6\) core/shell. In addition, QDSCs based on “giant” core/CdS-shell or alloyed core/shell QDs exhibit excellent long-term stability with respect to bare CdSe-based QDSCs. The giant core/shell QDs interface engineering methodology offers a new path to improve PCE and the long-term stability of liquid junction QDSCs.

1. Introduction

The efficient use of solar energy is expected to play a critical role in addressing the growing demand for power and related environmental challenges.\(^{[1–3]}\) High-efficiency, low-cost quantum dot (QD) sensitized solar cells (QDSCs) represent a promising opportunity to partially address this challenge.\(^{[4–6]}\) Colloidal QDs are considered a promising material to be used as light harvester in QDSCs due to their multiple appealing properties such as size-tunable band gap,\(^{[7]}\) high absorption coefficient over broad spectral range,\(^{[8]}\) large dipole moment,\(^{[9]}\) and solution processability.\(^{[10]}\) In addition, the possibility of multiple exciton generation by single photon absorption\(^{[11]}\) and direct hot electron extraction before thermalization\(^{[12]}\) can boost the theoretical photoconversion efficiency (PCE) of the QDSCs beyond the theoretical Queisser–Shockley limit of 32%.\(^{[13,14]}\)

In the past few years, the photovoltaic (PV) performance of QDSCs has improved significantly. The PCE for liquid junction QDSCs rapidly increased to above 11%\(^{[15]}\) and 10.7% for solid-state PV devices.\(^{[16]}\) On the other hand, the PCE of QDSCs is significantly lower than that of commercial silicon solar cells (typically in the range of 20%–40%). This is mainly attributed to undesirable carrier recombination occurring at the semiconductor metal oxide/QD/electrolyte interface and within the QDs\(^{[17]}\) (see Figure 1a, red dotted arrows). In addition, the limited long-term stability of liquid junction QDSCs, largely attributed to leakage of volatile electrolytes\(^{[18]}\) and QDs corrosion,\(^{[19]}\) is a major issue for their large scale commercial use. Multiple recent efforts have attempted to replace liquid electrolytes with solid or semi-solid hole conducting materials in QDSCs to improve long-term stability, which is still considered as a major challenge.\(^{[20,21]}\)

Due to their extremely small size (typically in the range of 2–6 nm), QDs possess a high density of surface trap states/defects, which degrade the chemical and optical stability during synthesis and further act as recombination centers during device operation.\(^{[22,23]}\) The surface passivation of QD core with shell layer of different materials/thickness has been shown to be an effective approach to address this challenge.\(^{[24,25]}\) This core/shell QD architecture offers a significantly enhanced quantum yield (QY), prolonged photoluminescence (PL) lifetime, and improved chemical, thermal, and photochemical/physical stability compared to bare QDs, due to the reduced density of surface trap states/defects and optimized electronic band alignment between core and shell.\(^{[26–28]}\)

Recent studies revealed that quasi-type-II core/shell colloidal QDs heterostructures (for example, CdTe/CdS,\(^{[29]}\)
In such QDs, electron delocalization into the shell region reduces the spatial electron–hole (e–h) overlap, which in turn accelerates exciton dissociation and enhances electron injection from the conduction band (CB) of the QD into the CB of the semiconductor metal oxide.\textsuperscript{[25,29]} These properties of quasitype-I core/shell QDs significantly suppress the overall charge carrier recombination probability in the device.\textsuperscript{[33–45]} To date, few studies reported the use of giant core/shell QDs systems for photoelectrochemical solar energy conversion.\textsuperscript{[38,46]} However, to the best of our knowledge, there is no report on the application of giant core/shell QDs as light harvesters for QDSCs. In particular, the effect of the shell thickness and chemical composition on the carrier separation/recombination dynamics is not yet understood.

Here, we synthesized CdSe/(CdS)\textsubscript{x} core/shell QDs with tunable CdS shell thickness (H = 0.66, 1.96 and 4.51 nm) with constant CdSe QDs core size (R = 1.65 nm) by the successive ionic layer adsorption and reaction (SILAR) approach (see the Experimental Section). We obtained the highest PV performance for CdSe/(CdS)\textsubscript{x} QDs (H = 1.96 nm) based QDSCs, which is PCE = 3.01\%, current density (J\textsubscript{sc}) = 9.30 mA cm\textsuperscript{-2}, open circuit voltage (V\textsubscript{oc}) = 0.539 V, and fill factor (FF) = 60\% under one-sun simulated sunlight at AM 1.5G (100 mW cm\textsuperscript{-2}). To further improve the PV performance of giant CdSe/(CdS)\textsubscript{x} core/shell QDs, we synthesized alloyed CdSe/(CdSe\textsubscript{x}−S\textsubscript{1−x})/(CdS)\textsubscript{y} (x = 0.5) and CdSe/(CdSe\textsubscript{0.5}S\textsubscript{0.5}) core/shell QDs and obtained a significantly improved PCE, as high as 5.12\% and 6.86\%, respectively. All the PV results, including both simple CdTe/CdSe\textsuperscript{[25]} and ZnSe/CdS\textsuperscript{[30]}), in which one of the carriers (electron or hole) is partly delocalized into the shell region, are a promising system as light harvesters for QDSC applications.\textsuperscript{[31]} The core/shell architecture allows to tailor the optoelectronic properties by changing either the shell thickness or the composition of the shell material.\textsuperscript{[25,32]} However, the PCE reported so far for QDSCs based on core/thin shell QDs with shell thickness less than 1 nm is around 3\%–4\%.\textsuperscript{[13,14]} Recently, the PCE of QDSCs based on PbS/CdS core/shell QDs (shell thickness less than 0.1 nm) was improved to 5.6\% by optimizing the shell thickness.\textsuperscript{[15]} Among different kinds of QDs, specially designed QDs called “giant” core/shell QDs with relatively thick shell (1.5 nm up to tens of nm) and core exhibiting quantized electronic properties were used to fabricate high efficiency and stable optoelectronic\textsuperscript{[36]} and energy conversion devices.\textsuperscript{[37,38]} In the giant core/shell QDs, the core is efficiently isolated from the surrounding chemical environment by thick shell materials, leading to superior photophysical/chemical stability, significantly suppressed nonradiative Auger recombination, improved QY, and prolonged exciton lifetime compared to both pure QDs and core/thin-shell (shell thickness ≤1.5 nm) QDs.\textsuperscript{[39–43]} Such optoelectronic properties of giant core/shell QDs are strongly associated with the core size and shell thickness.\textsuperscript{[25]} As the shell thickness increases over the core, the electronic band structure alignment of core/shell QDs changes and leads to the formation of a quasi-type-II core/shell structure (see Figure 1b).\textsuperscript{[25,28,29]}

**Figure 1.** Schematic diagrams: a) Working principle of QDSCs; and, b) electronic band gap engineering of CdSe/(CdS)\textsubscript{x} (x = 0, 2, 6, 13) core/shell QDs: CdSe core (red color) with increasing CdS shell thickness (yellow color) with or without interfacial CdSe\textsubscript{1−x} (x = 0.5) alloyed layer (orange color). R is the radius of core and H is the shell thickness.
form CdSe/(CdSe$_x$S$_{1-x}$)$_4/(CdS)_2$ QDs. The diameter of the initial CdSe core QDs is around 3.30 ± 0.29 nm with uniform size distribution (standard deviation <10%). The increased size of QDs after CdS shell growth was confirmed by transmission electron microscopy (TEM) imaging (see Figure 2). The average CdSe core size and CdS shell thickness of all synthesized QDs are reported in Table 1. In brief, after the growth of 2, 6, and 13 monolayers of CdS, the final diameters of the as-synthesized CdSe QDs in toluene before and after different CdS SILAR cycles are 4.6 ± 0.5 nm (shell thickness, $H = 0.66$ nm), 7.2 ± 0.5 nm ($H = 1.96$ nm), and 12.3 ± 1.1 nm ($H = 4.51$ nm), respectively, whereas for alloyed core/shell QDs, with the growth of four interfacial layers of CdSe$_x$S$_{1-x}$ ($x = 0.5$) and two monolayers of CdS, the diameter reaches 7.5 ± 0.8 nm ($H = 2.07$ nm). The size distribution of all synthesized core/shell QDs is shown in Figure 2g.

Table 1. Optoelectronic parameters of the as-synthesized core/shell QDs in toluene and QDs deposited on TiO$_2$ mesoporous film.

<table>
<thead>
<tr>
<th>QDs structure</th>
<th>$R$</th>
<th>$H$</th>
<th>Absorption peak position</th>
<th>PL peak position</th>
<th>Electron life time</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe/(CdS)$_2$</td>
<td>1.65</td>
<td>0.0</td>
<td>551</td>
<td>566</td>
<td>20 ± 2</td>
</tr>
<tr>
<td>CdSe/(CdS)$_6$</td>
<td>1.65</td>
<td>0.66</td>
<td>576</td>
<td>583</td>
<td>21 ± 1</td>
</tr>
<tr>
<td>CdSe/(CdS)$_{13}$</td>
<td>1.65</td>
<td>1.96</td>
<td>591</td>
<td>605</td>
<td>23 ± 2</td>
</tr>
<tr>
<td>CdSe/(CdSe$<em>x$S$</em>{1-x}$)$_4/(CdS)_2$</td>
<td>1.65</td>
<td>2.07</td>
<td>630</td>
<td>650</td>
<td>16 ± 2</td>
</tr>
</tbody>
</table>

$R$ is the radius of CdSe core; $H$ is CdS shell thickness for CdSe/(CdS)$_x$, whereas for CdSe/(CdSe$_x$S$_{1-x}$)$_4/(CdS)_2$ including CdS and CdSe$_x$S$_{1-x}$ ($x = 0.5$) shells.

Figure 2. TEM images of CdSe QDs: a) before CdS SILAR cycles; b) after 6 CdS SILAR cycles; c) after 13 CdS SILAR cycles; and d) after the 4 CdSe$_x$S$_{1-x}$ ($x = 0.5$) and 2 CdS SILAR cycles (alloyed QDs). e) HRTEM image of sample in (d). f) HRTEM image of CdSe/(CdS)$_6$ QDs sensitized TiO$_2$ film; dotted circles highlight the presence of QDs. g) Size distribution of CdSe QDs before and after different CdS and alloyed CdSe$_x$S$_{1-x}$ SILAR cycles (solid lines are Gaussian fits of the experimental data). Optical measurements: h) UV-vis absorption spectra of as synthesized CdSe QDs in toluene before and after different CdS SILAR cycles. The inset shows the magnified absorption spectra of QDs in toluene, where the corresponding first excitonic absorption peaks are clearly seen. i) PL spectra of corresponding QDs in toluene.
QDs, which are consistent with our previous work (Figure S1a,b, Supporting Information).[47] The homogenous dispersion of the giant core/shell (for instance, CdSe/(CdS)$_x$) QDs (dotted circle) on the surface of the TiO$_2$ photoanodes after 2 h electrophoretic deposition (EPD) without any noticeable QD aggregation is confirmed from Figure 2f and is consistent with energy-dispersive X-ray spectroscopy (EDS) measurements (Figure S4, Supporting Information).

The crystal structure of QDs was characterized by small-angle powder X-ray diffraction (XRD). Figure S3 in the Supporting Information shows XRD patterns of QDs deposited on a silicon substrate, revealing that the CdSe core has a ZB crystal structure, which is consistent with the literature.[28] After growing the CdS shells over the CdSe core via SILAR, the overall diffraction patterns of giant core/shell QDs with 6 and 13 CdS SILAR cycles are dominated by the hexagonal Wurtzite (WZ) crystal structure of CdS due to large volume of the CdS shell as compared to the CdSe core, consistent with previous work.[36,38,47,48] On the other hand, the XRD pattern of the alloyed core/shell QDs with CdSe$_{S-x}$ interfacial layer exhibits combined reflections from the WZ structure of CdS and WZ of CdSe, indicating the formation of alloyed WZ CdSe$_{S-x}$ (Figure S3, Supporting Information).

2.2. Optical Characterization of Colloidal “Giant” Core/Shell QDs

The optical properties of as synthesized giant and alloyed core/shell QDs in toluene are shown in Figure 2 h.i. The corresponding values are reported in Table 1. The absorption spectra of all QDs range from ultraviolet (UV) to visible (vis) region (see Figure 2h). The first excitonic peak is observed near 551 nm for pure CdSe QDs. It then shifts toward longer wavelengths with the sequential growth of CdS shell over the CdSe QDs. With the increase of CdS shell thickness (H = 0.66, 1.96, and 4.51 nm), the first-excitonic absorption peak systematically shifts toward longer wavelength (red shift) with respect to pure CdSe QDs: 576, 591, and 605 nm for CdSe/(CdS)$_x$ (x = 2, 6, and 13, respectively) (inset of Figure 2h), whereas the alloyed CdSe/(CdSe$_{S-x}$)$_x$/CdS$_2$ (x = 0.5) core/shell QDs system (H = 2.07 nm) shows first-excitonic absorption peak near 630 nm, with absorption spectra extended from 400 to 700 nm. A systematic comparison of the absorption spectra of alloyed core/shell QDs and all other giant core/shell QDs confirmed that the presence of four monolayers of CdSe$_{S-x}$ (x = 0.5) alloyed shell with thickness of ≈1.41 nm along with two monolayers of CdS (H = 0.66 nm) significantly broaden the absorption spectra toward longer wavelengths. This spectral broadening does not occur in other giant CdSe/(CdS)$_x$ core/shell QDs having comparable shell thickness (i.e., CdSe/(CdS)$_x$, H = 1.96 nm). This feature of the alloyed core/shell QDs may be due to higher carrier delocalization into the shell region as a consequence of reduced CB/VB interface offset potentials compared to giant core/shell QDs.[49]

The PL spectra of corresponding as synthesized core/shell QDs in toluene are shown in Figure 2i. Consistently with the increase of CdS shell thickness (H = 0.66, 1.96, and 4.51 nm) over the CdSe core QDs, the PL peaks shifted to longer wavelengths (583, 605, and 623 nm), respectively (see Figure 2i), as we observed in the absorption spectra of the corresponding QDs. This behavior of core/shell QDs is mainly due to the electron leakage into the shell region, while the hole is confined to the core.[23,50] Similarly, after the growth of (CdSe$_{S-x}$)$_x$/CdS$_2$ (H = 2.07 nm) alloyed shell over CdSe, the QDs show a significant red shift (~650 nm). This significant red shift (~51 nm) in the PL peak position of alloyed core/shell QDs as compared to giant core/shell QDs of comparable shell thickness is due to reduced band offsets between CdSe core and CdS shell, which enhances the carrier delocalization into the shell region.[49] These results are consistent with UV–visible measurements and further confirmed by PL lifetime measurements and theoretical wave function calculations.

In addition, giant CdS/(CdS)$_x$ core/shell QDs show better stability during the EPD process as compared to bare CdS QDs. This is confirmed through a systematic comparison (peak position and shape) of PL measurements of QDs in toluene and deposited onto TiO$_2$ via EPD. We found that the peak position and shape remain unchanged after giant core/shell QDs deposited on TiO$_2$ via EPD with respect to PL spectra of QDs in toluene (see Figure S2b–d, Supporting Information).

In the case of bare CdSe QDs on the other hand, both the PL peak position and shape significantly changed after deposition on TiO$_2$ with respect to QDs in toluene due to the presence of surface traps/defects caused by structural modification during EPD (see Figure S2a in the Supporting Information). This finding highlights that the presence of a thick CdS shell reduces the surface traps/defects of CdSe core QDs and also leads to outstanding chemical and thermal stability during the EPD process and further in solar cell fabrication and operation with respect to bare QDs and core/thin shell QDs as confirmed in our previous work (more details are reported in the following sections).[38,46,51]

The cross-sectional scanning electron microscopic (SEM) view of TiO$_2$ mesoporous film sensitized with giant CdSe/(CdS)$_x$ core/shell QDs is shown in Figure S4a in the Supporting Information. EDS elemental mapping shows a uniform coverage of the QDs throughout the TiO$_2$ mesoporous film (see Figure S4 in the Supporting Information), and the corresponding concentration values of the elements in this area are reported in Table S1 in the Supporting Information. The dispersion of QDs along the thickness of the photoanode is visible in Figure S4i in the Supporting Information. This plot confirms the in-depth uniform distribution of the QDs throughout the TiO$_2$ mesoporous film.

2.3. Carrier Dynamic Measurements of QDs Coupled with TiO$_2$

Transient PL spectroscopy was used to study the carrier dynamic of the QDs after coupling with the semiconductor metal oxide. The electron lifetime and transfer rate of QDs deposited on TiO$_2$ or ZrO$_2$ mesoporous films were measured under an excitation wavelength $\lambda = 444$ nm.

In this measurement, the QDs/ZrO$_2$ system is considered as a benchmark, since the electronic band alignment of ZrO$_2$ ($E_g = 5$ eV) does not favor electron transfer from the QDs to ZrO$_2$.[32] A systematic comparison of PL decay of all QDs
with TiO₂ mesoporous and QDs with ZrO₂ was carried out to understand the electron transfer dynamics. All the PL decay curves were well fitted with an exponential decay. The intensity-weighted average lifetime (〈τ〉) is calculated by using the following equation:

\[
\langle \tau \rangle = \frac{a_1 \tau_1^2 + a_2 \tau_2^2 + a_3 \tau_3^2}{a_1 \tau_1 + a_2 \tau_2 + a_3 \tau_3},
\]

where \(a_i\) (i = 1, 2, 3) are the fitting coefficients of the PL decay and \(\tau_i\) (i = 1, 2, 3) are the characteristic lifetimes, respectively. For all types of QDs, the PL decay is faster in the case of QDs deposited on TiO₂ as compared to QDs on ZrO₂, which confirms that charge transfer is more efficient in the former case (Figure 3a and Figure S5, Supporting Information). This is mainly due to the difference in electronic band alignment of ZrO₂ (position of CB edge) and TiO₂, which is not suitable for electron transfer from QDs in case of ZrO₂.[32] The variation of the calculated electron lifetime versus shell thickness for all QDs anchored to TiO₂ mesoporous film is shown in Figure 3b and corresponding values are reported in Table S1 in the Supporting Information. With the growth of CdS shells over CdSe core QDs, the lifetime increases from 20 ± 2 ns (CdSe, \(H = 0.0\) nm) to 23 ± 2 ns (CdSe/(CdS)_6, \(H = 1.96\) nm), and 36 ± 1 ns (CdSe/(CdS)_{13}, \(H = 4.51\) nm). With the growth of CdS shell over CdSe core QDs, the spatial e−h overlap decreases, which is due to enhanced electron leakage from CdSe core region into CdS shell region, where the holes are confined to the core region.[27,50] However, the lifetime of the alloyed CdSe/(CdSe_{S_{1−x}})/(CdS)_2 (\(x = 0.5, H = 2.07\) nm) core/shell QDs is only 16 ± 2 ns, which is less than the lifetime of bare (20 ± 2 ns) and “giant” core/shell (36 ± 1 ns) QDs. Similar to giant core/shell QDs, electrons still leak into the shell region in alloyed core/shell QDs. At the same time, due to favorable stepwise band alignment of the CdSe core and alloyed shell, holes have a higher probability to leak into the shell region as compared to holes in giant CdSe/(CdS)_2 core/shell QDs. This combined leakage of the electron and hole in alloyed shell QDs increases the e−h spatial overlap (confirmed in the theoretical section below) and accelerates the e−h recombination,[34] which leads to a reduction in electron lifetime values in case of alloyed core/shell QDs (see Figure 3), as reported by Brovelli et al.[34] A similar lifetime trend was also observed for the QDs after deposition into the TiO₂ film (Table S1, Supporting Information) except the bare QDs, which exhibit the longer lifetime (42 ± 1 ns) than CdSe/(CdS)_6 core/shell QDs.

We also studied how the CdS shell thickness (\(H = 0.66, 1.96,\) and 4.51 nm) affects the electron transfer rate \(K_{et}\) by considering bare CdSe QDs as a benchmark. The possibility of energy transfer from QDs to metal oxide film, which can also lead to a decrease of the measured lifetime due to PL quenching, was already ruled out in a previous investigation,[38] because of the absence of spectral overlap between the PL of QDs and absorption of metal oxides.[32] Therefore, the faster PL decay of the QDs in the case of TiO₂ compared to ZrO₂ is mainly due to the possible electron transfer from the QDs to TiO₂ (Figure 3a and Figure S5, Supporting Information). The \(K_{et}\) of QDs, with different CdS shell thickness, \(H = 0.66, 1.96,\) and 4.51 nm) and alloyed CdSe/(CdSe_{S_{1−x}})/(CdS)_2 core/shell QDs (\(H = 2.07\) nm) loaded on mesoporous TiO₂ and ZrO₂ via EPD process has been calculated.

The electron lifetime values for all QDs with TiO₂ mesoporous are shorter than the QDs with the ZrO₂ mesoporous film (see Table S2 in the Supporting Information). From these differences in the lifetime values, we calculated \(K_{et}\) by using the following equation:

\[
K_{et} = \frac{1}{\langle \tau \rangle_{QDs/TiO2}} - \frac{1}{\langle \tau \rangle_{QDs/ZrO2}},
\]

where \(\langle \tau \rangle_{QDs/TiO2}\) and \(\langle \tau \rangle_{QDs/ZrO2}\) are the average electron lifetimes of the QDs with TiO₂ and QDs with ZrO₂, respectively. \(K_{et}\) decreases as the CdS shell thickness increases from 1.96 to 4.51 nm in the case of CdSe/(CdS)_2 core/shell QDs with respect to bare CdSe QDs, as shown in Figure 3d. This can be attributed to large interfacial potential at the sharp interface of CdSe core and thick CdS shell. The lattice mismatch between CdSe and CdS (4.4% mismatch)[55] leads to the formation of interfacial defects and undesirable carrier confinement,[28,56] which reduces the overall carrier transport. However, \(K_{et}\) in the case of alloyed CdSe/(CdSe_{S_{1−x}})/(CdS)_2 core/shell QDs is higher than both giant CdSe/(CdS)_2 core/shell and bare CdSe QDs (Figure 3d and corresponding value reported in Table S2 in the Supporting Information). This significantly higher value of \(K_{et}\) (>2.4 ± 0.2 10⁻⁹ s⁻¹) is due to efficient electron injection because of favorable electronic band alignment of the CdSe core QD with CdSe_{S_{1−x}} and CdS shells (see Figure 1b). Hence, we can improve the optoelectronic properties of the giant CdSe/(CdS)_2 core/shell QDs by tailoring both the CdS shell thickness and the incorporation of CdSe_{S_{1−x}} (\(x = 0.5\)) interfacial shell layer, while maintaining the other parameter constant, i.e., \(R\) of CdSe core QDs is 1.65 nm.

### 2.4. Theoretical Electron–Hole (E–H) Wave Function Calculations

The electron \(ψ_e(r)\) and hole \(ψ_h(r)\) wave function for CdSe/(CdS)_x (\(x = 2, 6, 13\)) core/shell QDs with different CdS shell thickness and alloyed CdSe/(CdSe_{S_{1−x}})/(CdS)_2 (\(x = 0.5\)) core/shell QDs are calculated by solving the stationary Schrödinger equation in spherical geometry (more details in the Experimental Section).[34] The calculated spatial probability distribution \(ρ(r)\) of \(ψ_e(r)\) and \(ψ_h(r)\) as the function of QDs radius \(R + H, nm\) is shown in Figure 3e. With the sequential increase of the CdS shell thickness (\(H = 0.66, 1.96,\) and 4.51 nm) over the CdSe core (\(R = 1.65\) nm), the \(ψ_e(r)\) shows increasing leakage into shell region, while the hole remained confined in the CdSe core (Figure 3e), indicating the formation of a quasi-type II core/shell band alignment.[25,28,29] The calculated e−h spatial overlap area (% of \(ψ_e(r)\) and \(ψ_h(r)\), plotted as a function of the shell thickness (Figure S6, Supporting Information and corresponding values reported in Table S3 in the Supporting Information). The highest e−h spatial overlap area (%) we obtained is 94% for bare CdSe QDs, which decreased to 80% for CdSe/(CdS)_6 (\(H = 0.66\) nm), 64% for CdSe/(CdS)_6 (\(H = 1.96\) nm), 57% for CdSe/(CdS)_{13} (\(H = 4.51\) nm), and 67% for CdSe/(CdSe_{S_{1−x}})/(CdS)_2 (\(x = 0.5, H = 2.07\) nm) QDs.

The reduced e–h spatial overlapping in the case of giant core–shell QDs with increase of CdS shell thickness \( (H) \) enhances the recombination time period between the electron and hole, speeds up the e–h separation, which significantly increases the electron lifetime of the giant core/shell QDs with respect to bare CdSe QDs.\(^{[28,49,57]}\) However, the increase in lifetime values from 20 ± 2 ns to 23 ± 2 ns is not very high as compared to the significant decrease in e–h spatial overlap area (%)
values from 94% to 64% for bare CdSe QDs and CdSe/(CdS)$_6$ core/shell QDs, respectively. This is because the measured lifetime ($\tau_{\text{measured}}$) value depends on both radiative decay rate ($K_{\text{ret}}$) and nonradiative decay rate ($K_{\text{net}}$)

$$\tau_{\text{measured}} = \frac{1}{(K_{\text{ret}} + K_{\text{net}})}$$

The e–h spatial overlap area (%) affects only the $K_{\text{ret}}$, not the $K_{\text{net}}$. This $K_{\text{net}}$ depends on the presence of surface traps/defects of QDs. The surface traps/defects are higher in the case of bare CdSe QDs than that of CdSe/(CdS)$_6$ core/shell QDs (confirmed by the lower quantum yield of 9% in CdSe QDs compared to 40% in giant core/CdS-shell QDs). Thus, $K_{\text{ret}}$ is faster for bare CdSe QDs with respect to CdSe/(CdS)$_6$ core/shell QDs, which results in $K_{\text{ret}}$ being slower in bare CdSe QDs than CdSe/(CdS)$_6$ core/shell QDs. This is consistent with the trend of e–h spatial overlap area (%) and lifetime values variation with the growth of CdS shell over CdSe core. In addition, for alloyed core/shell QDs, the e–h spatial overlap is 67%, slightly higher than giant CdSe/(CdS)$_6$ (64%) core/shell QDs of comparable CdS shell thickness ($H = 1.96$ nm), as shown in Figure 3f. As in alloyed core/shell QDs, due to favorable stepwise band alignment, holes have a higher probability to leak into the shell region, compared to holes in pure CdS-shelled QDs.[54] This combined leakage of electrons and holes in alloyed core/shell QDs leads to a comparative increase in the e–h spatial overlap area. These results are consistent with carrier dynamic studies of the respective QDs reported in the previous section.

### 2.5. Photovoltaic Measurements

The current density–voltage ($J–V$) characteristics of QDSCs based on CdSe/(CdS)$_x$ core/shell QDs with CdS shell of different thickness ($H = 0.66, 1.96,$ and $4.51$ nm) and reference bare CdSe QDs, are shown in Figure 4 and the calculated PV parameters are reported in Table 2. From the systematic comparison of QDSCs with CdSe/(CdS)$_x$ core/shell QDs having CdS shell of different thickness ($H = 0.66, 1.96,$ and $4.51$ nm), among all shell thicknesses, the device based on CdSe/(CdS)$_6$ core/shell QDs with shell thickness of 1.96 nm shows the best PV performance (PCE = 3.01%, $J_{\text{sc}} = 9.30$ mA cm$^{-2}$, $V_{\text{oc}} = 0.539$ V and FF = 60%) under one-sun simulated sunlight (AM 1.5G, 100 mW cm$^{-2}$). These values are comparable to the PV performance of devices based on regular core/shell[58–61] and core/thin shell QDs ($H \leq 0.9$ nm).[32,33] In addition, the PCE can be further improved to 6.86% by inserting a CdSe$_x$S$_{1-x}$ interfacial layer between CdSe core and CdS shell (discussed in Section 2.7). The giant core/shell QDs reported herein offer superior optoelectronic properties such as broad absorption spectrum, fast carrier separation due to reduced e–h spatial overlap, high carrier transfer rate, and better chemical stability with respect to core/thin shell QDs ($H \leq 1.5$ nm).[39] Due to these appealing properties exhibited by giant core/shell QDs, the device based on these giant core/shell QDs exhibit excellent long-term stability (detailed discussion reported in Section 2.8).

The variation of all PV parameters (PCE, $J_{\text{sc}}, V_{\text{oc}},$ and FF) of the QDSCs as a function of CdS shell thickness is shown in Figure S7 in the Supporting Information and reported in

![Figure 4](image-url)  
**Figure 4.** $I–V$ measurements: a) Current density versus voltage curve of CdSe/(CdS)$_x$ core/shell QDs-sensitized cells under one sun irradiation (AM 1.5 G, 100 mW cm$^{-2}$), showing the effect of shell thickness on photovoltaic performances.Transient photovoltage decay measurements for the devices with CdSe/(CdS)$_x$ core/shell QDs of different CdS shell thickness: b) Open circuit voltage ($V_{\text{oc}}$) decay as the function of time (s). c) Electron lifetime ($\tau$) as function of $V_{\text{oc}}$ calculated from $V_{\text{oc}}$ decay measurements. Electrochemical impedance spectroscopy measurements: d) Recombination resistance ($R_{\text{rec}}$) versus bias voltage ($V_{\text{bias}}$); e) Chemical capacitance ($C_{\mu}$) versus $V_{\text{bias}}$; f) $\tau$ versus $V_{\text{bias}}$.  


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Similarly, \( \rho \) increases from 4.81 to 9.30 mA cm\(^{-2} \) as the CdS shell thickness increases from 0.66 to 1.96 nm, the functional performance improves: \( \rho \) increases significantly from 4.81 to 9.30 mA cm\(^{-2} \) (see Figure S7a in the Supporting Information). Similarly, \( V_{oc} \) increases from 0.473 to 0.539 V (see Figure S7c in the Supporting Information) and FF increases from 54% to 60% (see Figure S7b in the Supporting Information), hence the overall PCE reaches 3.01% from 1.22% (see Figure S7d in the Supporting Information). This is consistent with the significant improvement in other opto-electronic properties of the corresponding core/shell QDs, despite the slight increase in lifetime values (as discussed in Section 2.4). By growing the CdS shell over the CdSe core QDs (\( H = 0.66–1.96 \) nm), the QD’s absorption spectra is broadened toward longer wavelength and carrier separation and transfer rate are improved as \( e^{-h} \) spatial overlapping area reduced from 94% in bare CdSe to 64% in CdSe/(CdS)\(_x\) QDs, as discussed previously (see Figure S6 in the Supporting Information).

However, with the further increase in the CdS shell thickness from 1.96 to 4.51 nm, the device’s performance decreases as shown in Figure 4a. In brief, \( j_{sc} \) decreases from 9.30 to 7.54 mA cm\(^{-2} \) (see Figure S7a in the Supporting Information), which may be ascribed to partial reduction of electron injection efficiency from the CB of CdSe/CdS core/shell QDs to CB of the TiO\(_2\) by thick CdS shell barrier layer. Other functional parameters show a similar behavior: \( V_{oc} \) and FF decreases from 0.539 to 0.513 V and 60% to 58% respectively, hence the overall PCE decreases from 3.01% to 2.25% as shown in Figure S7 in the Supporting Information. These results demonstrate that the 1.96 nm thick CdS shell can effectively suppress carrier recombination, without reducing carrier injection efficiency and is considered the optimal CdS shell thickness. In the quasi-type II CdSe/CdS QDs, the presence of the shell can minimize charge trapping, yet they still serve as physical barrier to slow down charge separation and increase charge recombination rate. These results are further confirmed through transient photovoltage decay and EIS measurements.

Table 2. PV parameters calculated from I–V measurements of QDSCs based on different types of giant CdSe/(CdS), core/shell QDs light harvesters.

<table>
<thead>
<tr>
<th>QDs structure</th>
<th>( H ) [nm]</th>
<th>( J_{sc} ) [mA cm(^{-2} )]</th>
<th>( V_{oc} ) [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe/(CdS)(_0)</td>
<td>0.0</td>
<td>4.81</td>
<td>0.473</td>
<td>54</td>
<td>1.22</td>
</tr>
<tr>
<td>CdSe/(CdS)(_2)</td>
<td>0.66</td>
<td>5.45</td>
<td>0.504</td>
<td>57</td>
<td>1.58</td>
</tr>
<tr>
<td>CdSe/(CdS)(_3)</td>
<td>1.96</td>
<td>9.30</td>
<td>0.539</td>
<td>60</td>
<td>3.01</td>
</tr>
<tr>
<td>CdSe/(CdS)(_13)</td>
<td>4.51</td>
<td>7.54</td>
<td>0.513</td>
<td>58</td>
<td>2.25</td>
</tr>
</tbody>
</table>

Table 2. The devices based on bare QDs exhibit the worse PV performance due to the high density of QD surface trap states, which act as sites for nonradiative carrier recombination during device operation as compared to all other CdSe/(CdS), core/shell QDs. With the increase of the CdS shell thickness from 0.66 to 1.96 nm, the functional performance improves: \( j_{sc} \) increases significantly from 4.81 to 9.30 mA cm\(^{-2} \) (see Figure S7a in the Supporting Information). Similarly, \( V_{oc} \) increases from 0.473 to 0.539 V (see Figure S7c in the Supporting Information) and FF increases from 54% to 60% (see Figure S7b in the Supporting Information), hence the overall PCE reaches 3.01% from 1.22% (see Figure S7d in the Supporting Information). This is consistent with the significant improvement in other opto-electronic properties of the corresponding core/shell QDs, despite the slight increase in lifetime values (as discussed in Section 2.4). By growing the CdS shell over the CdSe core QDs (\( H = 0.66–1.96 \) nm), the QD’s absorption spectra is broadened toward longer wavelength and carrier separation and transfer rate are improved as \( e^{-h} \) spatial overlapping area reduced from 94% in bare CdSe to 64% in CdSe/(CdS)\(_x\) QDs, as discussed previously (see Figure S6 in the Supporting Information).

However, with the further increase in the CdS shell thickness from 1.96 to 4.51 nm, the device’s performance decreases as shown in Figure 4a. In brief, \( j_{sc} \) decreases from 9.30 to 7.54 mA cm\(^{-2} \) (see Figure S7a in the Supporting Information), which may be ascribed to partial reduction of electron injection efficiency from the CB of CdSe/CdS core/shell QDs to CB of the TiO\(_2\) by thick CdS shell barrier layer. Other functional parameters show a similar behavior: \( V_{oc} \) and FF decreases from 0.539 to 0.513 V and 60% to 58% respectively, hence the overall PCE decreases from 3.01% to 2.25% as shown in Figure S7 in the Supporting Information. These results demonstrate that the 1.96 nm thick CdS shell can effectively suppress carrier recombination, without reducing carrier injection efficiency and is considered the optimal CdS shell thickness. In the quasi-type II CdSe/CdS QDs, the presence of the shell can minimize charge trapping, yet they still serve as physical barrier to slow down charge separation and increase charge recombination rate. These results are further confirmed through transient photovoltage decay and EIS measurements.

The transient photovoltage decay of the QDSCs provides the dynamic information about how the photogenerated carrier recombination occurs at the TiO\(_2\)/QDs/electrolyte interface. In this work, transient photovoltage decay was applied to study the effect of CdS shell thickness on the functional performance of QDSCs. In this measurement, all QDSCs were illuminated with solar simulator under one sun simulated sunlight (AM 1.5G, 100 mW cm\(^{-2} \)) until a steady voltage was attained, which is the \( V_{oc} \) of the device. Then the simulator shutter was closed and the voltage decay versus time was recorded for all devices under dark conditions. The \( V_{oc} \) decay for all devices made of QDs with different CdS shell thickness is shown in Figure 4b. The rate of \( V_{oc} \) decay is faster in the device with bare CdSe QDs than the device with QDs having a CdS shell. As the CdS shell thickness increases (from 0.66 to 1.96 nm), the \( V_{oc} \) decay rate decreases with respect to bare CdSe QDs and CdSe/(CdS)\(_2\) QDs with thin CdS shell (\( H = 0.66 \) nm). Beyond the optimum CdS shell thickness (\( H = 1.96 \) nm), a further increase in CdS shell thickness from 1.96 to 4.51 nm accelerates the \( V_{oc} \) decay rate than the device with the CdS shell thickness of 1.96 nm as shown in Figure 4b. The electron lifetime (\( \tau \)) was calculated from the \( V_{oc} \) decay measurements by using the following equation\(^{[62,63]}\)

\[
\tau = \frac{k_b T}{e} \left( \frac{dV_{oc}}{dt} \right)^{-1}
\]

where \( k_b \) is Boltzmann’s constant, \( T \) is the absolute temperature, and \( e \) is the electronic charge.

This calculated \( \tau \) is directly related to the carrier recombination occurring at the TiO\(_2\)/QDs/electrolyte interface. As expected, the \( \tau \) of QDSCs based on CdSe/(CdS)\(_x\) \((x = 2, 6, \) and 13) core/shell QDs is higher than the bare CdSe QDs (see Figure 4c). This prolonged \( \tau \) confirms that nonradiative carrier recombination at the TiO\(_2\)/QDs/electrolyte interface is suppressed, which is mainly due to the reduction of density of surface trap states of CdSe QDs by the CdS shell. At a particular value of \( V_{oc} (=0.350 \text{ V}) \), the \( \tau \) first increases with the increase in CdS shell thickness from 0.66 to 1.96 nm, then decreases with further increase in shell thickness (from 1.96 to 4.51 nm). This reduction in \( \tau \) may be due to a large interfacial potential at the CdSe/CdS core/shell interface caused by the lattice mismatch between CdSe and CdS.\(^{[54]}\) This large interfacial potential acts as potential barrier for electron injection from the CB of CdSe/ CdS core/shell QDs to CB of the TiO\(_2\), which enhances the recombination probability and reduces the \( \tau \).

2.6. Electrochemical Impedance Spectroscopy

To further investigate the effect of different CdS shell thicknesses of the QDs on the electronic proprieties of the solar cells, we used EIS on representative samples without CdS shell (CdSe/(CdS)\(_0\)), 6 layers (CdSe/(CdS)\(_6\)) and 13 layers (CdSe/(CdS)\(_{13}\)) under dark conditions.\(^{[64]}\) Figure 4d reports the trend of recombination resist ance (\( R_{rec} \)) for the different samples at various applied voltage biases (\( V_{bias} \)). The overall trend of \( R_{rec} \) clearly shows that the cell with CdSe/(CdS)\(_6\) has the highest \( R_{rec} \) values across the whole bias range as compared to the other cells. \( R_{rec} \) is inversely proportional to the charge recombination rate, so a higher value of \( R_{rec} \) in the CdSe/(CdS)\(_{13}\) QDs based cell leads to a significant suppression of the recombination rate.\(^{[64,65]}\) The main consequence of a lower recombination rate is an increased injection of electrons from the CB of CdSe/ CdS core/shell QDs to CB of the TiO\(_2\), boosting the \( j_{sc} \) (as seen in the \( J-V \) analysis, Figure 4a). On the contrary, chemical capacitance (\( C_{dl} \)) has a similar behavior for all the different samples.
(see Figure 4e). This trend is also found in the literature and indicates that the different QDs do not affect the CB position of TiO₂.[64,66]

Figure 4f displays the \( \tau \) calculated from the impedance as the product between \( R_{\text{rec}} \) and \( C_\mu \): \( \tau = R_{\text{rec}} * C_\mu \).[64,67] Also in this case, the \( \tau \) of the solar cell based on CdSe/(CdS)₆ QDs is notably higher as compared to the other samples, confirming the results obtained from the \( V_{\text{oc}} \) decay measurement. This shows that the recombination phenomena are reduced for the optimal CdS shell thickness, thereby enhancing the PCE of the cell.

2.7. “Giant” Alloyed Core/Shell QDs with CdSe\(_{x}\)S\(_{1-x}\) Interfacial Layer

After the optimization of CdS shell thickness of the giant CdSe/(CdS)\(_x\) core/shell QDs, we chose the CdSe/(CdS)₆ core/shell QDs for further improvement. We engineered the sharp interface between CdSe core and CdS shell by introducing the (CdSe\(_{x}\)S\(_{1-x}\))\(_4\) \((x = 0.5, H = 2.07 \text{ nm})\) interfacial layers, without altering the CdSe core structure \((R = 1.65 \text{ nm})\). The presence of CdSe\(_{x}\)S\(_{1-x}\) \((x = 0.5)\) interfacial layer between the CdS shell and the CdSe core could improve the hole transfer to the electrolyte and electron transfer to the metal oxide due to energetically favorable electronic band structure of core/alloyed shell QDs.

Figure 5a shows that the PV performance of CdSe/(CdSe\(_{x}\)S\(_{1-x}\))\(_4/(CdS)\)_2 \((x = 0.5)\) alloyed core/shell QDs based QDSC is better than the CdSe/(CdS)\(_6\) core/shell QDs based QDSC, which is the best performing system among all the giant core/shell QDs investigated. The corresponding PV parameters are reported in Table 3. Briefly, \( J_{\text{sc}} \) increases from 9.30 to 16.07 mA cm\(^{-2}\) and \( V_{\text{oc}} \) from 0.539 to 0.580 V, leading to a PCE of 5.12%. As all the other components of the cells (photoanode, electrolyte and counter electrode) are the same, this difference in the solar cell’s PV performance could be mainly due to the properties of the QDs such as: (i) light harvesting efficiency, (ii) charge separation, (iii) charge injection efficiency, etc. The optical measurements demonstrated that the alloyed CdSe/(CdSe\(_{x}\)S\(_{1-x}\))\(_4/(CdS)\)_2 \((x = 0.5)\) core/shell QDs show broader absorption spectra from 400 to 700 nm (see Figure 2h) with respect to CdSe/(CdS)\(_6\) core/shell QDs, which confirms the better light harvesting efficiency of alloyed core/shell QDs as compared to CdSe/(CdS)\(_6\) core/shell QDs. This improved efficiency is further supported by external quantum efficiency (EQE) measurements (Figure 5b, discussed below). The second factor, the charge carrier separation ability, mainly depends on the electronic band alignment of the QDs. The large red shift in PL peak in the case of alloyed core/shell QDs (PL peak at 650 nm) as compared to CdSe/(CdS)\(_6\) (PL peak at 605 nm) core/shell QDs (see Figure 2i), which is attributed to
Table 3. Comparison of the photovoltaic parameters calculated from I-V measurements of QDSCs based on giant CdSe/(CdS)\(_x\) alloyed CdSe/(CdSe\(_{1-x}\))/CdS\(_2\) (x = 0.5), and alloyed CdSe/(CdSe\(_{1-x}\))/CdS\(_3\) (x = 0.9–0.1) core/shell QDs as light harvesters.

<table>
<thead>
<tr>
<th>QDs structure</th>
<th>H</th>
<th>(J_{oc})</th>
<th>(V_{oc})</th>
<th>FF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CdSe}/(\text{CdS})_6)</td>
<td>1.96</td>
<td>9.30</td>
<td>0.539</td>
<td>60</td>
<td>3.01</td>
</tr>
<tr>
<td>((\text{CdSe}/(\text{CdSe}_{1-x})_0)/\text{CdS}_2)</td>
<td>2.07</td>
<td>16.07</td>
<td>0.580</td>
<td>55</td>
<td>5.12</td>
</tr>
<tr>
<td>((\text{CdSe}/(\text{CdSe}_{1-x})_0)/\text{CdS}_3)</td>
<td>2.00</td>
<td>20.95</td>
<td>0.566</td>
<td>58</td>
<td>6.86</td>
</tr>
</tbody>
</table>

\(x = 0.5\) in all monolayers of shell; \(^{(3)}\)The alloyed shell contains 6 monolayers. With the layer of 1–5, \(x\) varies from 0.9, 0.7, 0.5, 0.3 and 0.1, respectively.

enhanced delocalization of electrons into the shell, is due to reduced offsets of the CB and VB in the case of alloyed core/shell QDs, hence a faster e–h separation with respect to CdSe/(CdS)\(_6\).


to CdSe/(CdSe\(_{1-x}\))/CdS\(_3\) (x = 0.9–0.1) core/shell QDs confirming a lower carrier recombination rate than in the device with CdS/(CdS)\(_6\) core/shell QDs, hence the better PV performance.

To further enhance the PCE of QDSCs based on alloyed core/shell QDs, we engineered interfacial layers by tailoring the selenium (Se) and sulfur (S) molar ratios during in situ growth of each interfacial layer. The resulting graded alloyed CdSe/(CdSe\(_{1-x}\))/CdS\(_1\) (x = 0.9–0.1) core/shell QDs shows broader absorption response toward longer wavelength with respect to alloyed CdSe/(CdSe\(_{1-x}\))/CdS\(_2\) (x = 0.5) as shown in Figure S8 in the Supporting Information. QDSC based on alloyed CdSe/(CdSe\(_{1-x}\))/CdS\(_1\) (x = 0.9–0.1) core/shell QDs, yielding the PCE of 6.86%, which is 33% higher than PCE of QDSC based on CdSe/(CdSe\(_{1-x}\))/CdS\(_2\) (x = 0.5) core/shell QDs (see Figure S9a in the Supporting Information). This enhanced PV performances is mainly due to the increase of \(J_{oc}\) (mA cm\(^{-2}\)). By engineering the CdSe\(_{1-x}\) interfacial layers, we broadened the absorption response toward longer wavelength and better \(K_{oc}\) (Table S2, Supporting Information) due to favorable stepwise electronic band alignment with respect to alloyed CdSe/(CdSe\(_{1-x}\))/CdS\(_3\) (x = 0.5).

These results are further supported by the systematic comparison of transmittance photovoltaic decay measurements of devices with CdSe/(CdSe\(_{1-x}\))/CdS\(_1\) (x = 0.9–0.1) and CdSe/(CdSe\(_{1-x}\))/CdS\(_2\) (x = 0.5) alloyed core/shell QDs, as performed previously. Figure S9b in the Supporting Information shows that the \(V_{oc}\) decay rate is slower for the device based on CdSe/(CdSe\(_{1-x}\))/CdS\(_1\) (x = 0.9–0.1) alloyed core/shell QDs than the device based on CdSe/(CdSe\(_{1-x}\))/CdS\(_2\) (x = 0.5) alloyed core/shell QDs. Similarly at a particular \(V_{oc}\) the calculated \(\tau\) from this decay rate is higher for CdSe/(CdSe\(_{1-x}\))/CdS\(_1\) (x = 0.9–0.1) than the CdSe/(CdSe\(_{1-x}\))/CdS\(_2\) (x = 0.5) alloyed core/shell QDs as shown in Figure S9c in the Supporting Information. Such higher lifetime values in the case of device with CdSe/(CdSe\(_{1-x}\))/CdS\(_1\) (x = 0.9–0.1) alloyed core/shell QDs confirming the lower carrier recombination than in the device with CdSe/(CdSe\(_{1-x}\))/CdS\(_3\) (x = 0.5) alloyed core/shell QDs, hence the improved PV performance. As shown in Table 3, all these measurements point to an outstanding PV performance of the device based on alloyed CdSe/(CdSe\(_{1-x}\))/CdS\(_3\) (x = 0.9–0.1) core/shell QDs as compared to CdSe/(CdSe\(_{1-x}\))/CdS\(_2\) (x = 0.5) alloyed core/shell QDs alloyedCdSe/(CdS)\(_6\) core/shell QDs based devices.

2.8. Stability and Reproducibility Measurements

The long-term stability is one of the most important and critical issues for QDSCs. To evaluate how the pure shell and alloyed shell affects the long term stability, the QDSCs based on giant CdSe/(CdS)\(_6\) core/shell QDs and alloyed core/shell QDs with CdSe\(_{1-x}\) interfacial layers were subjected to a long-term stability test over 10 d and compared with QDSCs based on bare CdSe QDs. After fabrication, current–voltage (I–V) measurements of all QDSCs were carried out under one sun simulated sunlight (AM 1.5G, 100 mW cm\(^{-2}\)) every day (24 h delay between two successive measurements). The systematic comparison of the functional parameter trends over time of these respective QDSCs are reported in Figure 6.
The QDSCs based on giant CdSe/(CdS)₆ core/shell QDs and alloyed core/shell QDs with CdSeₓS₁₋ₓ interfacial layers, show overall excellent stability for 240 h, whereas the QDSC based on bare CdSe QDs is very poor in stability and stops working after 96 h of intermittent operation. Briefly, for the QDSC with “giant” CdSe/(CdS)₆ core/shell QDs, the $V_{oc}$ slightly decreased from 0.492 to 0.480 V after 72 h since fabrication, then improved to 0.501 V, after 168 h since fabrication due to better penetration of the electrolyte in the mesoporous TiO₂ film and after 240 h, this decreased to 0.450 V (see Figure 6d). The trend of $J_{sc}$ is similar to that of $V_{oc}$: after 240 h, $J_{sc}$ decreased only by 9% with respect to $J_{sc}$ obtained after 24 h since fabrication (see Figure 6e). The PCE decreased from 1.77% (after 24 h since fabrication) to 1.31% (after 240 h since fabrication), i.e., 26% with respect to the performance measured after 24 h since fabrication (see Figure 6f). Similarly, QDSC based on giant alloyed core/shell QDs with CdSeₓS₁₋ₓ interfacial layers also exhibits significant long-term stability (see Figure 6). The rate of decrease in functional parameters ($V_{oc}$ (V), $J_{sc}$ (mA cm⁻²), and PCE (%)) of QDSCs is slightly higher in the case of alloyed core/shell QDs with respect to CdSe/(CdS)₆ core/shell QDs. This is attributed to the difference in their respective structural composition. CdSe/(CdS)₆ core/shell QD has CdS shell thickness up to 1.96 nm, whereas that in core/alloyed shell QD is only 0.33 nm. In general, CdS is more stable in the polysulfide electrolyte solution ($pH = 13$) with respect to CdSe or CdSeS.⁶⁸,⁶⁹ Moreover, in core/shell QDs, holes are confined within the core region, while in core/alloyed shell QDs holes leak into the shell region due to favorable stepwise band alignment, which also enhances the sensitivity of core/alloyed QDs in polysulfide electrolyte solution. In the long-term stability testing, the alloyed QDs may interact with the electrolyte due to the limited protection from the ZnS and silica layer, leading to a decrease in functional parameters of QDSCs as compared to devices based on core/shell QDs. In particular, the $V_{oc}$ decreased from 0.584 to 0.556 V after 72 h since fabrication, then slightly improved to 0.563 V, after 168 h since fabrication due to improved electron penetration in the mesoporous TiO₂ film and then decreased to 0.521 V after 240 h (Figure 6d), similarly to what was observed for giant CdSe/(CdS)₆ core/shell QDs based QDSC. The $J_{sc}$ decreased from 10.61 to 9.19 mA cm⁻² after 96 h since fabrication, and then further reduced to 7.32 mA cm⁻² after 240 h (Figure 6e). The trend of PCE is similar to that of $J_{sc}$ after 240 h since cell fabrication, it decreased from 3.52% to 1.84% (Figure 6f).

In large contrast, the corresponding functional performance of the QDSC with bare CdSe QDs reduced by 55%, 73%, and 93%, respectively, which is mainly due to the instability of the bare CdSe QDs in the polysulfide electrolyte environment. This huge difference in long-term stability of the device with giant CdSe/(CdS)₆ core/shell QDs and alloyed core/shell QDs as compared to the device based on bare CdSe QDs is attributed to the improved thermal, photophysical and chemical stability of giant core/shell and alloyed core/shell QDs provided by thick CdS pure shell and alloyed shell with CdSeₓS₁₋ₓ interfacial layers because all other components in the tested QDSCs were...
identical, except the structure of QDs. This thicker CdS pure shell \((H = 1.96 \text{ nm})\) and alloyed shell with CdSe\(_x\)S\(_{1-x}\) interfacial layers over the CdSe core can protect efficiently the core and insulate it from the surrounding environment.\(^{[25,26]}\) This finding highlights the new possibility to improve the long time stability of liquid junction QDSCs by using giant core/shell QDs and alloyed core/shell as light harvester, instead of replacing the liquid electrolytes with solid or quasi-solid electrolytes.\(^{[20,21]}\)

To assess the reproducibility of device fabrication and functional performance based on different types of QDs, three devices of each type of QDs were fabricated and their \(I−V\) curves were measured under one-sun simulated sunlight (AM 1.5G, 100 mW cm\(^{-2}\)). Figure S10 in the Supporting Information shows the statistic comparison of all functional parameters \((J_{sc} \text{ (mA cm}^{-2}), V_{oc} \text{ (V)}, PCE \text{ (%) and FF (%)})\) for each cell’s batch, with corresponding values reported in Table S4 in the Supporting Information. Each batch of cell series exhibits reproducible functional performance indicating remarkable reproducibility of device fabrication procedure.

3. Conclusions and Perspectives

We synthesized “giant” core/shell CdSe/(CdS)\(_x\) QDs with tunable CdS shell thickness \((H = 0.66, 1.96 \text{ and } 4.51 \text{ nm})\) while maintaining the same core size \((1.65 \text{ nm})\) to fabricate highly efficient and stable QDSCs. The thick CdS shell enhanced the photophysical and chemical stability of QDs and simultaneously broadened the light absorption spectrum toward the visible region, lifetime and carrier separations with respect to bare CdSe and core/thin shell \((H \leq 1.5 \text{ nm})\). The optimization of the CdS shell thickness \((H = 1.96 \text{ nm})\) leads to a PCE of 3.01% for giant CdSe/(CdS)\(_x\) QDs due to efficient charge separation, injection, and transport as compared to bare and core/thin shell CdSe/(CdS) QDs. By exploring advanced interface engineering on the best performing giant CdSe/(CdS)\(_x\) core/shell QDs, newly synthesized CdSe/(CdSe\(_x\),S\(_{1-x}\))\(_{1/2}\)/(CdS)\(_{1/2}\) \((x = 0.5, H = 2.07 \text{ nm})\) alloyed core/shell QDs based QDSC showed a significantly enhanced PCE of 5.12%, which is mainly due to broadening of the absorption spectrum from UV region to the visible region (400–700 nm range), higher \(K_{oc}\) and slower rate of \(V_{oc}\) decay (longer \(\tau\)) as compared to giant CdSe/(CdS)\(_x\) core/shell QDs. By further engineering the structure of giant CdSe/(CdSe\(_x\),S\(_{1-x}\))\(_{1/2}\)/(CdS)\(_{1/2}\) QDs, we obtained QDSCs with a maximum PCE of 6.86%. The giant core/CdS-shell or core/alloylshed QDs based QDSCs were subjected to a stability test for 240 h and exhibited excellent long term stability with respect to bare CdSe based QDSC. This is a crucial point, since stability plays a decisive role in driving opportunities for commercialization of QDSCs. The combined results of this work highlight how engineering the core/shell interface of QDs offers a new tool to improve the optoelectronic properties of QDs for the development of cost effective, high efficiency, and stable QDSCs. Future work will focus on improving the PCE and the long-term stability of the QDSCs by exploring different core sizes, shell thicknesses, and composition.

4. Experimental Section

**Materials:** Sulfur \((100\%),\) oleylamine (OLA) \((\text{technical grade, } 70\%),\) cadmium oxide \((99\%),\) cadmium nitrate tetra hydrate \((\geq 99\%),\) oleic acid \((\text{OA}),\) Rhodamine 6G, octadecene \((\text{ODE}),\) selenium pellet \((\geq 99.999\%),\) trioctyl phosphine oxide \((\text{TOPO}),\) trioctyl phosphine \((\text{TOP})\) \((97\%),\) hexane, zinc acetate dihydrate \((98\%),\) cetyl-trimethyl ammonium bromide \((\text{CTAB}),\) tetraethyorthosilicate, sodium hydroxide, sodium sulfide nonahydrate \((\geq 99\%),\) hydrochloric acid, toluene, methanol, acetone, ethanol, isopropanol and ZrO\(_2\) nanoparticles powder \((<100 \text{ nm sized})\) were obtained from Sigma-Aldrich Inc.

Ti-Nanoxide BL/SC was bought from Solaronix. TiO\(_2\) pastes composed of 20 nm sized anatase nanoparticles (Transparent, Code 18 NR-T) and larger 150–250 nm sized anatase scattering particles (Opaque, code WER2-O) were supplied by Dyexol. Transparent fluorine doped tin oxide (FTO) coated conducting glass substrates with sheet resistance 10 \(\Omega\) square\(^{-1}\) were bought from Pilkington glasses. All chemicals were used as purchased without any purification.

**QD Synthesis:** CdSe QDs of diameters \((3.3 \text{ nm})\) were synthesized by using the hot injection approach,\(^{[24]}\) In brief, TOPO \((1 \text{ g})\) and Cd–oleate \((0.38 \text{ mmol, 1 mL})\) in 8 mL of ODE were purged by \(N_2\) at room temperature for 30 min. The reaction system was evacuated for 30 min at 100 °C, then the temperature was raised to 300 °C. The multilayer of TOP-Se \((4 \text{ mmol, 4 mL})\), 3 mL of OLA, and 1 mL at room temperature was quickly injected into the Cd-oleate suspension under vigorous stirring. The reaction cell was quenched with cold water after injection. Ethanol was added, then the suspension was centrifuged. The supernatant was removed and finally, the QDs were dispersed in toluene and kept at \(−10^\circ\text{C}\) in the refrigerator.

**Deposition of CdSe layers on CdSe QDs was performed by SILAR, similar to the procedure described in Ghosh et al.**\(^{[21]}\) “Giant” CdSe/Cds QDs were synthesized by growing CdS monolayers over the CdSe core. Typically, in a 100 mL round-bottom flask, OLA \((5 \text{ mL}),\) ODE \((5 \text{ mL}),\) and CdSe QDs \((\geq 10^{-7} \text{ mol in hexane})\) were degassed at 110 °C for 30 min. The reaction flask was re-stored with \(N_2\) and the temperature was further raised to 240 °C with stirring. The Cd(OA)\(_2\) dispersed in ODE \((0.25 \text{ mL}, 0.2 \text{ mg})\) was added dropwise and the mixture allowed to react for 2.5 h, followed by dropwise addition of 0.2 \(\mu\)l sulfur in ODE with same volume. The shell was further annealed for 10 min. All subsequent shells were annealed at 240 °C for \(\approx 10\text{ min following the injection of sulfur and }2.5\text{ h}\) following dropwise addition of the Cd(OA)\(_2\) \((\text{in ODE, Sulfur/Cd(OA)2 addition volumes for shell addition cycles 1–13 are as follows: 0.25, 0.36, 0.49, 0.63, 0.8, 0.98, 1.18, 1.41, 1.66, 1.92, 2.2, 2.51, and 2.8 \text{ mL}, respectively.})\) The reaction was cooled to room temperature using cold water. Ethanol was added, then the suspension was centrifuged and the supernatant was removed. The QDs were subsequently dispersed in toluene for further characterization and labeled hereafter as “Giant” for CdSe with 2, 6, and 13 cycle of CdS shells QDs, respectively (details of the core/shell size/shell thickness are reported in Table 1).

**Anode Fabrication:** A thin and compact TiO\(_2\) blocking layer was deposited on ultrasonically cleaned FTO glass substrates by spin coating the Ti-Nanoxide BL/SC (Solaronix) solution at a speed of 6000 r.p.m. for 30 s. It was then annealed at 500 °C for 30 min under ambient atmosphere and left to cool down to room temperature. Double layer mesoporous films were prepared by tape casting a transparent layer of multilayer carbon nanotubes (MWNT-TiO\(_2\)) hybrid paste containing 0.002 \((\text{w/w})\) MWCNT \((20 \text{ nm, 18 NR-T})\) onto ultrasonically cleaned FTO glass substrates (sheet resistance 10 \(\text{Omega} \) cm\(^{-2}\)). A drying process was followed for 15 min at ambient conditions and then placed on a hot plate for 6 min at 120 °C. After this a scattering layer of anatase TiO\(_2\) nanoparticles \((150–250 \text{ nm sized, WER2-O})\) was applied on the prepared transparent layer under the same conditions as described above. All the photoanodes were then annealed at 500 °C for 30 min under ambient conditions. Photoanode thickness was measured by profilometer and an average value of 12–13 \(\mu\)m was found. Similarly, ZrO\(_2\) photoanodes
were prepared under the same conditions mentioned above by using commercial ZrO$_2$ nanopowder (>100 nm sized) paste.

**EPD of QDs on the TiO$_2$ Mesoporous Film and Further ZnS/SiO$_2$ Coating:** The double layer mesoporous TiO$_2$ photoanode were vertically immersed in QDs solution and the distance between them was adjusted at 1 cm. A direct current bias of 200 V was applied for 120 min. Subsequently the EPD photoanodes were washed with toluene to remove the unbounded QDs and finally dried with N$_2$ at room temperature. Prior to ZnS capping, a methanolic solution of CTAB was used to exchange the surface native ligands. Briefly, the anode was dipped in CTAB solution for 1 min and then washed with corresponding solvent to remove the chemical residuals from the surface and dried with N$_2$. To complete one SILAR cycle, the anode was dipped in toluene for 1 min and dried with N$_2$. This procedure was repeated three times to remove most of the ligands. Then the ZnS capping layer was formed by 4 SILAR cycles as done previously for ligand exchange. For ZnS deposition, Zn$^{2+}$ ions were deposited from 0.1 M methanolic solution of Zn(CH$_3$COO)$_2$, whereas the S$^{2-}$ ions were deposited from 0.1 M mixed solution (1:1 methane- water) of Na$_2$S. After ZnS capping, the SiO$_2$ coating was carried out by soaking in 0.01 M ethanolic solution of tetraethoxysilane for 2 h at 35 °C and then rinsed with ethanol and dried in N$_2$ gas flow.

**Device Fabrication:** QDSCs were constructed by sandwiching the QD sensitized TiO$_2$ photoanode and the Cu$_2$S counter electrode using a 25 μm thick plastic spacer. Polysulfide in H$_2$O/methanol (1:1, v/v) (1 M Na$_2$S, 1 M S, and 0.1 M NaOH) was used as electrolyte. The Cu$_2$S counter electrode was fabricated by immersing the brass in HCl (30%) at 70–75 °C for 10 min. These HCl treated brass samples were subsequently immersed in polysulfide electrolyte (2 M Na$_2$S, 2 M S, and 0.2 M NaOH) solution for 10 min to generate Cu$_2$S.

**Characterization:** TEM and HRTEM images of QDs and QD-sensitized TiO$_2$ films were collected by using a JEOL 1200F TEM. Small angle XRD of newly purified QD films deposited on a silicon substrate (suitable for measuring XRD patterns in the 2θ range) was carried out using a Bruker D8 Advance diffractometer using a Cu Kα radiation source (λ = 1.5418 Å). A JEOL JSM7401F field emission scanning electron microscope equipped with an EDS allowed to obtain the elemental composition within the QD-sensitized TiO$_2$ film. The UV–vis absorption spectra were recorded with a Cary 5000 UV–vis–near infrared spectrophotometer (Varian) with a scan speed of 600 nm min$^{-1}$. Fluorescence spectra were acquired with a Fluorolog-3 system (Horiba Jobin Yvon). The PL lifetime of the QDs deposited into TiO$_2$ and ZrO$_2$ mesoporous films was measured in the time-correlated single-photon counting mode with a 444 nm laser by considering QDs/ZrO$_2$ system as a benchmark.

Theoretical wave functions of the electron and hole were calculated by solving the stationary Schrödinger equation in spherical geometry, in a benchmark. For CDSe, the potentials for electrons and holes as a function of position were approximated as the lowest unoccupied molecular orbital and highest occupied molecular orbital levels, respectively, for the bulk materials. For CdS, these levels are −3.71 and −5.81 eV, respectively, while for CdS they are −3.3 and −5.8 eV, respectively. For the alloy CDSe$_x$Si$_{1-x}$, weighted averages (x = 0.5) of the above quantities were used. Outside the QD, the potentials were set as 0 and −9.8 eV for electrons and holes, respectively. The interaction between electrons and holes was neglected in the calculations.

The I–V and transient photovoltage decay measurements were carried out using a compact solar simulator class AAA (Scientech SLB-300A) under one sun simulated sunlight (1 sun = AM 1.5G, 100 mW cm$^{-2}$), calibrated with a silicon reference cell. The EQE of the devices was carried out by using a Xenon arc lamp passing through a monochromator. The photocurrent at each wavelength was measured with a lock in amplifier (Ametek 1256) at zero bias, whereas the light power was measured at the corresponding wavelength through the same circular aperture of 1 mm diameter, with a calibrated photodiode (Newport 918D) placed at the same position. The EIS was carried out under dark conditions using a SOLARTRON 1260 A Impedance/Gain-Phase Analyzer, with an AC signal 10 mV in amplitude, in the frequency range between 10 mHz and 300 kHz. An external bias between 0 V and 100 mV above the Voc of the solar cell was applied.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

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interface engineering, long-term stability, photovoltaics, quantum dots, solar cells

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