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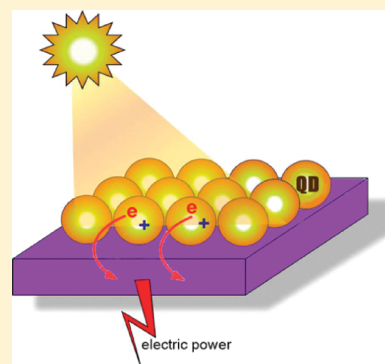
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# Semiconductor Nanocrystal Quantum Dots as Solar Cell Components and Photosensitizers: Material, Charge Transfer, and Separation Aspects of Some Device Topologies

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**ABSTRACT:** Nanocrystalline wide band gap semiconductors photosensitized with semiconductor nanocrystal quantum dots have recently attracted increasing attention as promising photovoltaic devices. This Perspective addresses several issues related to the choice of nanocrystal materials for quantum dot sensitized solar cells, the methods of quantum dot deposition on mesoporous wide band gap semiconductor layers, and combinations of quantum dots and classical ruthenium dyes as panchromatic sensitizers. It further discusses charge transfer kinetics and electron recombination in quantum dot sensitized solar cells. An alternate emerging concept, a structure combining the latter with a quantum dot based Schottky junction solar cell, is also briefly reviewed. Together these areas offer ample scope for improvements making use of the specific advantages of semiconductor nanocrystals.



The past few years have witnessed an explosive growth in research activities addressing different aspects of the use of semiconductor nanocrystals (colloidal quantum dots, QDs)<sup>1</sup> in several solar cell configurations.<sup>2–6</sup> Bulk-heterojunction hybrid solar cells based on blends of conjugated polymers and semiconductor nanorods have been investigated for almost a decade,<sup>7</sup> and certified efficiencies of 3.13% under AM 1.5 illumination have recently been reported for these types of devices utilizing semiconductor tetrapod<sup>8</sup> variants. QD-sensitized nanocrystalline wide band gap semiconductor (WBSC) solar cells (QDSSCs) have attracted particular attention as promising photovoltaic devices.<sup>6,9</sup> Compared with conventional WBSC photosensitizers widely employed in dye-sensitized (or Grätzel-type) solar cells (DSSC) such as ruthenium (Ru) dyes,<sup>10</sup> QDs are easier to prepare and are lower cost. Additionally, QDs present higher extinction coefficients than the conventional dyes,<sup>11</sup> and their band gaps and, consequently, absorption spectra can be conveniently tuned by controlling the nanoparticle size,<sup>1</sup> making them extraordinarily attractive for photovoltaic applications.<sup>12</sup> The demonstration of the phenomenon of carrier multiplication in QDs opens the possibility of obtaining quantum efficiencies higher than 100%, that is, more than one electron generated per absorbed photon at a broad wavelength range across the solar spectrum.<sup>13–15</sup> Notwithstanding other efficiency factors, the carrier multiplication process may potentially allow the innate traditional photovoltaic solar cell Shockley–Queisser efficiency limit<sup>16</sup> to be exceeded. The use of QDs as light absorbers therefore offers an undoubted potential in obtaining high-efficiency and low-cost solar cells. Even so, QDSSCs still currently present much lower efficiencies (4–5%)<sup>9</sup> than conventional DSSCs (up to 11–12%).<sup>17</sup> This Perspective addresses several issues related to the choice of QD materials for QDSSCs, the methods of QD deposition within mesoporous WBSC layers,

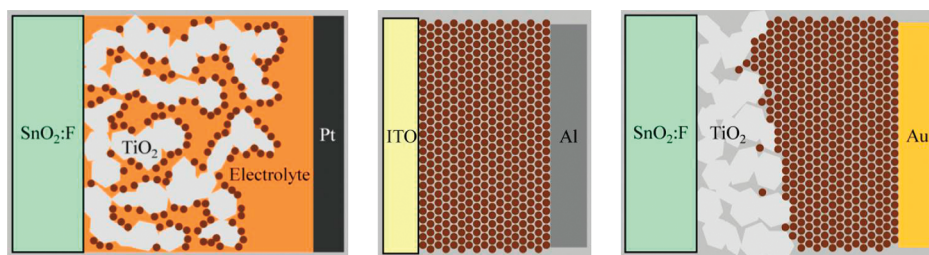
and combinations of QDs and classical Ru-dyes as panchromatic sensitizers. It further discusses charge transfer kinetics and electron recombination in QDSSCs. An alternate emerging concept, a structure combining a QDSSC with a QD-based Schottky junction solar cell, is also briefly reviewed. Schematics<sup>18</sup> of each of the three device configurations discussed are shown in Figure 1.

The general scheme of a QDSSC device is very similar to the DSSC concept (Figure 1a). Light excites electron–hole pairs in the QDs; the electron is injected into a nanostructured WBSC (i.e., TiO<sub>2</sub>, ZnO) electron conductor, and it is transported in this medium to the transparent conductive oxide (ITO, SnO<sub>2</sub>:F) electrode. The hole is injected into the liquid or solid electrolyte (or the reducing species in the electrolyte injects an electron into the hole of the WBSC) that acts as a hole-transporter medium. The resulting hole is transported to the counter electrode, where the oxidized counterpart of the redox system is reduced.

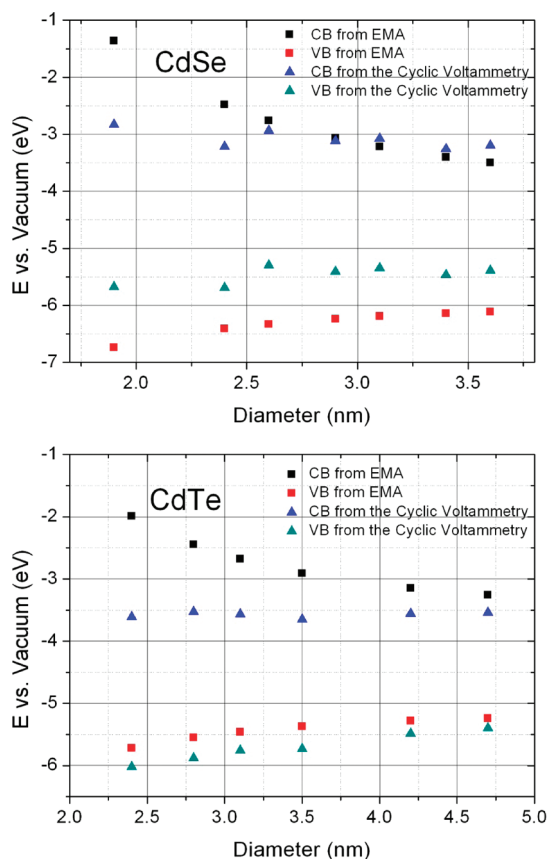
**For the comparison of different QDs and to best match them with various WBSCs, data on the absolute positions of their CB and VB are crucial.**

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**Figure 1.** Schematic arrangement of the three QD-based solar cell designs discussed in this Perspective. From left to right: QDSSC, Schottky cell, depleted heterojunction cell. Adapted with permission from ref 18. Copyright 2010 ACS.



**Figure 2.** Comparison of the absolute positions of CBs and VBs of CdSe and CdTe QDs estimated by EMA (with infinite potential well) with corresponding experimental values determined by cyclic voltammetry.<sup>30,31</sup>

#### A. Material Aspects Important for QDSSC Optimization.

**A.1. QD Materials.** Starting from earlier studies introducing CdS<sup>19</sup> and InP<sup>20</sup> nanocrystals as sensitizers of for WBSC TiO<sub>2</sub>, different semiconductor QDs such as CdS, CdSe, CdTe, CuInS<sub>2</sub>, Cu<sub>2</sub>S, PbS, PbSe, InAs, Ag<sub>2</sub>S, Bi<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>S<sub>3</sub> have been used as QDSSC components.<sup>2,5,6,9</sup> The conduction band (CB) of the QDs should be positioned higher than that of the WBSC, and the valence band (VB) of the QDs should be lower than the Fermi level of the electrolyte. The relative positions of the CBs of WBSC and QDs are fixed not only by the material properties but can also be varied by interactions between the electrolyte/dipolar molecule and the semiconductor.<sup>6</sup> Sargent et al. have considered the optimum QD bandgap to balance light harvesting efficiency against output current and voltage, recommending values in the range 1.1–1.4 eV for optimal power efficiency in single junction

cells.<sup>21</sup> In an effort to develop panchromatic absorbers, Kamat et al. have raised the concept of rainbow solar cells, with different sizes of QDs assembled into TiO<sub>2</sub> nanotubes.<sup>22</sup> This follows a previously introduced idea of creating light-harvesting, funnel-like, band gap profiles in multiple layers of QDs of different sizes.<sup>23</sup> Combinations of several types of QDs, such as CdS with CdSe<sup>24,25</sup> and CdS with PbS,<sup>26</sup> have indeed been shown to improve light harvesting in QDSSCs over a broader range of wavelengths. For the comparison of different QDs and to best match them with various WBSCs, data on the absolute positions of their CB and VB are crucial, although unfortunately are often not readily available in literature. One common approach to at least estimate these values relies on an effective mass approximation (EMA) using an infinitely high potential well, with an equation for the size-dependent band gap energy of QDs going back to the pioneering work of Brus:<sup>27</sup>

$$E_{\text{gap}}^{\text{NC}}(r) = \frac{\hbar^2 \pi^2}{2r^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{4\pi\epsilon_0\epsilon_\infty r} + E_{\text{gap}}^{\text{bulk}} \quad (1)$$

where  $r$  is the QD radius,  $m_e^*$  and  $m_h^*$  are effective masses of electrons and holes, and  $\epsilon_\infty$  is the macroscopic dielectric constant of the QD material at optical frequencies. The absolute position of the QD's CB can be calculated using the relation<sup>28</sup>

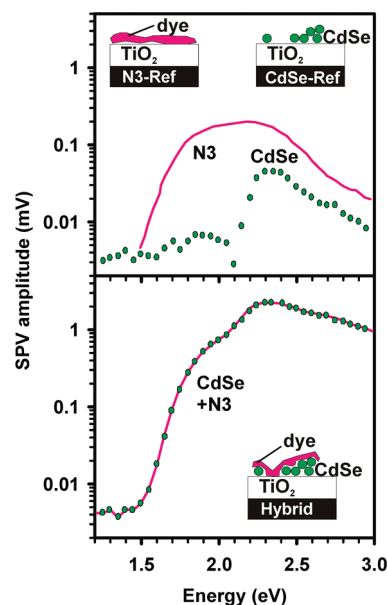
$$E_{\text{CB}}^{\text{NC}}(r) = E_{\text{CB}}^{\text{bulk}} + (E_{\text{gap}}^{\text{NC}}(r) - E_{\text{gap}}^{\text{bulk}}) \left[ \frac{m_h^*}{m_e^* + m_h^*} \right] \quad (2)$$

while the absolute position of the QD's VB can be obtained by simple addition of the value of the band gap of QDs calculated using eq 1 or the optical band gap of QDs experimentally determined from the position of their lowest energy absorption peak.<sup>11</sup> Figure 2 compares the values of absolute CB and VB positions for differently sized CdSe and CdTe QDs estimated by EMA with infinite potential wells (for parameters of CdSe and CdTe used in eqs 1 and 2, see ref 29) with experimental values for these two materials determined from cyclic voltammetry measurements.<sup>30,31</sup> The deviation is evident in particular for the CB levels of the smallest QDs, where the EMA overestimates the opening of the QD band gap as being dominated by the CB shift. This discrepancy is further exacerbated in low bandgap materials with small effective masses. The use of an EMA algorithm modified to account for the finite height of the potential well,<sup>32</sup> on the other hand, was shown to provide much better agreement with experimental values, predicting the shift of the VB and CB to be almost equal.<sup>33</sup> While the finite potential well model attempts to incorporate more realistic boundary conditions, this is still one of the main problems in deriving an accurate match to real QD systems, where the surface region

influencing the QD wave functions may comprise a mixture of (ionic) ligand material, solvents, and host materials such as electrolytes and substrates, and where the QD subsurface itself may have been modified by partial oxidation or the uptake of other elements (most notably sulfur) during or postsynthesis. Such considerations are an issue both in accurately modeling QD CB and VB positions and also in the experimental determination of the levels. Wang et al., for example, pointed out the environmental sensitivity of the experimentally determined reduction potential of identical samples of 7 nm diameter CdSe QDs with alkylthiol and with trioctylphosphine oxide ligands, citing a 0.27 eV difference ( $-1.07$  eV and  $-0.8$  eV, respectively).<sup>34</sup> This is typical of the spread of experimental data often seen with nominally the same material from different groups or in different systems. In order to accurately design well-aligned heterojunction structures, it is therefore essential to use data, whether theoretical or experimental, that take the local structural composition into account (i.e., in the latter case, are measured in the same type of host, employ the same ligand, etc.).

**A.2. Deposition of QDs on Mesoporous WBSC.** Methods of deposition of QDs on mesoporous WBSC substrates are often classified into two major categories: in situ and ex situ.<sup>6</sup> In situ growth methods of QDs within the mesoporous matrix are either chemical bath deposition (CBD)<sup>35</sup> or successive ionic layer absorption and reaction (SILAR).<sup>36,37</sup> They typically achieve high surface coverage and direct connection between QDs and the oxide matrix, but offer a poor control over QD size and their surface passivation, resulting in a broad size distribution and a high probability of internal recombination. Presynthesized colloidal QDs, on the other hand, are easily controllable in terms of size, shape, and surface passivation.<sup>1</sup> They can be deposited on WBSC using ex situ approaches such as direct absorption (DA)<sup>38,39</sup> or linker assisted absorption (LAA).<sup>40,41</sup> For the QDs synthesized in organic solvents, typical surface capping agents are long-chain organic molecules such as alkylphosphines, alkylphosphine oxides, and alkylamines,<sup>42</sup> which act as a barrier layer hindering efficient charge transfer over the WBSC/QD interface. For DA deposition, they may also lack anchoring functional groups for good coupling to the TiO<sub>2</sub> surface. To overcome these limitations, the LAA approach has been widely used, relying on surface modification of the TiO<sub>2</sub> matrix (or ligand exchange on a QD solution) with a short-chain bifunctional linker (e.g., mercaptopropionic acid, MPA) that anchors to TiO<sub>2</sub> with its carboxylic group. This is similar to the functionalization commonly used for Ru-dyes in DSSC and offers a thiol group that has high affinity to the QD surface.<sup>41,43</sup> QDs prepared in water are typically already capped with water-soluble bifunctional molecular linkers such as MPA or thioglycolic acid as-synthesized,<sup>44,45</sup> thus they may be directly coupled to the WBSC surface without the need for LAA.<sup>46</sup> Nevertheless, both DA and LAA methods applied to either organic-based or aqueous-based colloidal QDs often result in a low surface coverage of the WBSC compared to in situ deposition techniques,<sup>6</sup> reducing the light absorption ability of the QD layer and thus the short circuit current of the QDSSC. To improve surface coverage, the electric-field-driven electrophoretic deposition (EPD) of colloidal nanocrystals is a particularly promising approach as recently shown by Salant et al. using organically soluble QDs.<sup>47</sup>

While this review mainly concerns the role of the QD element of solar cells, it is pertinent to mention developments in the fabrication of WBSCs at this point. Deposition of typically 3–8 nm diameter QDs into electrodes with pores that are often

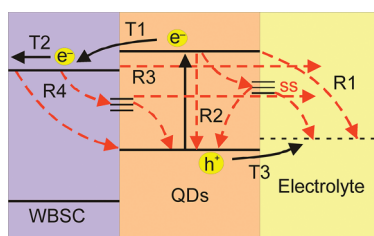


**Figure 3.** Top: SPV amplitude spectra of individual N3 dye and individual CdSe QDs deposited on compact TiO<sub>2</sub> layers. Bottom: hybrid structure of CdSe QDs coated with N3 dye deposited on a compact TiO<sub>2</sub> layer. The hybrid TiO<sub>2</sub>–CdSe–N3 structure contributes to the SPV signal over the broad spectral range determined by superposition of the SPV spectra of the constituent single absorbers. Remarkably, the SPV signal for the TiO<sub>2</sub>–CdSe–N3 structure is enhanced by more than an order of magnitude, indicating that CdSe QDs in combination with Ru dye enhance the charge separation efficiency. Adapted with permission from ref 29. Copyright 2010 Wiley-VCH.

not that much wider is a major problem in fabricating QDSSCs with high QD loading and therefore strong absorption. This is often a limiting factor for overall efficiencies, especially when comparing with dye-sensitized cells where dye penetration into the pores is far easier. Zhang et al.<sup>48</sup> recently demonstrated how this problem could be offset to a degree by forming WBSCs from mixtures of 20 and 300 nm TiO<sub>2</sub> particles to widen the distribution of pore sizes to give a range from just a few nanometers up to 50 nm. This allowed greater QD uptake and better permeation of the polysulfide electrolyte, and extended the light path length due to increased optical scattering. The net result was an outstanding light-to-power efficiency of 4.92%.

**A.3. Combinations of QDs and Ru-dyes as panchromatic sensitizers.** Yet another promising strategy to improve the performance of QDSSCs is the simultaneous use of colloidal QDs and Ru dyes as “supracollectors of light”<sup>9</sup> in what can be denoted as hybrid (QD and dye) sensitized solar cells (HSSCs). Hybrid structures of QDs and dyes can, in an ideal case, simultaneously satisfy several important requirements for light harvesting materials: (i) they extend the spectral absorption range by combining the absorption ranges of both components;<sup>49</sup> (ii) they reduce the internal charge recombination by fast hole scavenging from QDs and efficient spatial separation of electrons and holes via a multistep charge separation cascade;<sup>50,51</sup> and (iii) they may improve charge extraction by reduction of recombination losses in QDs.<sup>52</sup> Our recent surface photovoltage (SPV) study demonstrated a remarkable enhancement in electron injection from QDs into TiO<sub>2</sub> for the combination of CdSe QDs and N3 dye (Figure 3).<sup>29</sup> Type II alignment of energy levels between CdSe





**Figure 4.** A scheme illustrating charge transfer, transport, and recombination processes in QDSSCs. T1: photon excited electron transfer from the CB of QDs to the CB of the WBSC; T2: electron transport via WBSC; T3: hole transfer from the VB of QDs to the electrolyte; R1: electron back injection from QDs to the electrolyte; R2: electron recombination in QDs; R3: electron back injection from WBSC to the electrolyte; R4: electron recombination at the WBSC/QDs interface. SS denotes surface states.

QDs and several types of Ru dyes used in that study promoted electron injection from dyes into  $\text{TiO}_2$ , facilitated by the efficient extraction of holes from the VB of QDs to the ground state of the dye. By contrast, when CdTe QDs were combined with the same Ru dyes instead of CdSe QDs, the type I alignment there resulted in nonradiative energy transfer between the QDs and the dye.<sup>29</sup> The energy transfer competing with charge transfer should not necessarily be considered as detrimental for the performance of HSSCs; it can be explored in a configuration where QDs are used as antennas nonradiatively funneling<sup>23</sup> absorbed light to the charge separating dye molecules.<sup>53</sup> In recent reports demonstrating the beneficial effect of cosensitization of QDs and dyes in full solar cell device architectures, enhanced performances of the hybrid CdS QD/N3 dye on ZnO (3.04% efficiency)<sup>54</sup> compared to only N3 (0.11% efficiency) as well as of PbS QD/N719 dye structure on  $\text{TiO}_2$  (6.35% efficiency)<sup>55</sup> compared to only N719 (5.95% efficiency) was demonstrated.

**A promising strategy to improve the performance of QDSSCs is the simultaneous use of colloidal QDs and Ru dyes as “supracollectors of light”.**

**B. Charge Transfer Kinetics and Electron Recombination in QDSSCs.** With photon-electrical conversion efficiencies ( $\eta$ ) still around 4–5%, the open circuit voltage  $V_{oc}$ , the short circuit current  $J_{sc}$ , and the fill factor FF of QDSSCs are relatively low ( $\eta = J_{sc} \times V_{oc} \times \text{FF} / P \times 100\%$ , where  $P$  is the incident power), and several functional problems remain to be resolved.<sup>56</sup> Instability of II–VI semiconductor QDs (such as CdSe or CdTe) in triiodide/iodide electrolytes, and lower energy difference between the CB edge of the WBSC and the Fermi level of the commonly used polysulfide electrolytes ( $\text{S}^{2-}/\text{S}_x^{2-}$ ) often result in low  $V_{oc}$  values. Additionally, high electron transfer resistance at the polysulfide electrolyte/Pt counter electrode interface results in low fill factors (about 30–50%).<sup>38</sup> In order to improve the  $V_{oc}$  and FF of QDSSCs, it is necessary to optimize the electrolyte and counter electrode system.  $J_{sc}$  is determined by the incident

photon-to-current efficiency (IPCE) of the solar cells, which is proportional to the light harvesting efficiency,  $\eta_{\text{LH}}(\lambda)$ , photoelectron injection efficiency,  $\eta_{\text{inj}}(\lambda)$ , and photoelectron collection efficiency,  $\eta_{\text{col}}(\lambda)$ :  $\text{IPCE}(\lambda) = \eta_{\text{LH}}(\lambda)\eta_{\text{inj}}(\lambda)\eta_{\text{col}}(\lambda)$ .  $\eta_{\text{LH}}(\lambda)$  is related to the absorption properties of the QDs and the coverage of QDs at the WBSC surfaces. The adsorption edge of present QDSSCs (which are often based on CdS and CdSe nanocrystals) has not made full use of infrared solar light. This can be addressed by suitable choices of the size and composition of the QDs, with narrower bandgap materials giving a wider tuning range of the band edge into the infrared.  $\eta_{\text{inj}}(\lambda)$  and  $\eta_{\text{col}}(\lambda)$  depend on the charge separation efficiency, which is related to the photoelectron relaxation kinetics and the electron recombination. In this sense, it is necessary to probe the charge carrier dynamics, and also the electron recombination mechanism of the QDSSCs, which is fundamental to the improvement of the QDSSCs performance. Possible charge transfer routes in QDSSCs are shown in Figure 4. Electron injection, hole transfer, and carrier transport are forward processes, and beneficial for charge separation and electron collection. Conversely, electron–hole recombination is a backward process. The charge transfer time ratio between forward and backward processes determines the electron injection efficiency  $\eta_{\text{inj}}$  and electron collection efficiency  $\eta_{\text{col}}$  (effective diffusion length).<sup>56</sup>

**B.1. Electron Injection.** Concerning  $\eta_{\text{inj}}$ , the electron injection process competes directly with the electron–hole recombination rate in QDs, and also with the electron recombination at QD/electrolyte interfaces. Injection rates in  $\text{TiO}_2/\text{CdS}$ , and  $\text{TiO}_2/\text{CdSe}$  QD systems have been extensively investigated and found to be on the picoseconds or tens of picoseconds time scale.<sup>57</sup> Electron injection has been observed to occur with a wide range of rate constants between  $7.3 \times 10^9$  and  $1.95 \times 10^{11} \text{ s}^{-1}$  for 3 nm CdSe QDs molecularly linked to  $\text{TiO}_2$ . Average rates for the same system depended strongly on the CdSe nanocrystal size, ranging from  $1.2 \times 10^{10} \text{ s}^{-1}$  for 2.4 nm particles to  $10^7 \text{ s}^{-1}$  for 7.5 nm QDs.<sup>58</sup> Not only size but also surface states significantly influence the electron injection process.<sup>59</sup>

**B.2. Hole Injection.** Fast hole transfer from excited QDs is another important charge transfer process. Holes are involved in several processes: electron–hole recombination in the QDs, and back injection of electrons from the WBSC to the holes of the QDs (Figure 4). For redox species that are strongly adsorbed at the QDs surface (such as metal chalcogenides in polysulfide solution), the hole transfer time can be expected to be very fast; e.g., for CdS/polysulfide, times of tens of picoseconds have been reported.<sup>60</sup> Rates for hole injection from the QDs to the hole acceptors depend on the nature of both and can vary considerably from one system to another, ranging from picoseconds to nanoseconds.<sup>61</sup> Many of the hole injection processes include a follow-up chemical or diffusion step for the redox species and the overall injection rate is likely to be much lower than for a simple single-step hole injection rate. Chakrapani et al.<sup>62</sup> have studied in great detail the interplay of the pathways involved in the hole oxidation of sulfide electrolyte ions and back electron transfer in CdSe/ $\text{TiO}_2$  cells with sulfide/polysulfide electrolytes. They highlight the role of the  $\text{S}^{2-}/\text{S}_n^{2-}$  redox couples in efficiently scavenging holes from CdSe, while holes that escape this process are implicated in liberating  $\text{Cd}^{2+}$  and  $\text{Se}^0$  species at the QD surface. The metal ions may then go on to react with  $\text{S}^{2-}$  ions to reform a beneficial protective layer of CdS on the nanoparticle surface. This may account for the better stability with the sulfide electrolyte system, whereas  $\text{I}_3^-/\text{I}^-$  systems generally suffer from rapid QD corrosion.

**B.3. Electron Recombination at WBSC/Electrolyte and WBSC/QD Interfaces.** Regarding electron collection efficiency,  $\eta_{\text{col}}$  recombinations that compete with the electron transport process are the back electron transfer from the WBSC to the electrolytes and electron recombination from the WBSC to the hole of QDs either directly band-to-band or via surface states (Figure 4). Electron recombination at  $\text{TiO}_2$ /polyiodide interfaces has been widely investigated in DSSCs using a variety of techniques and typically occurs in milliseconds.<sup>63</sup>

**B.4. Surface States and Surface Passivation.** Electron traps and transfer processes at the interfaces have profound influence on the carrier transfer and recombination rates.<sup>59</sup> To prevent electron injection from WBSCs to QDs, from WBSCs to electrolytes, and also from QDs to electrolytes via surface states (Figure 4), various passivation procedures have been suggested, including coating the WBSC and QDs with a semiconductor shell having a higher CB edge, thereby forming a potential barrier for removal of an electron from the semiconductor.<sup>6</sup> A ZnS shell on CdSe has been found to improve the performance of  $\text{TiO}_2$ /CdSe-based QDSSCs, the effect being attributed to passivation of the CdSe leading to increased electron injection into the  $\text{TiO}_2$  and/or reduced electron recombination at CdSe/electrolyte interfaces due to the potential barrier at the latter.<sup>35</sup> The mechanisms responsible for the improvement in performance of CdSe/ $\text{TiO}_2$  cells overcoated with ZnS has been studied by Guijarro et al.<sup>64</sup> While both the QDs and upper parts of the host WBSC are coated, they show that the improved efficiency arises from the surface passivation of the QDs and also an increase in electron transfer rates rather than simply the blocking of the  $\text{TiO}_2$  surface.

**B.5. Multiple Carrier Generation and Collection.** Nozik suggested that QDSCs may potentially increase the maximum attainable thermodynamic photoelectrical conversion efficiency to about 66% by utilizing hot photogenerated carriers to produce higher photovoltages or higher photocurrents.<sup>13</sup> The former relies on miniband transport and collection of hot carriers in QD array photoelectrodes before they relax to the band edges through phonon emission. The latter is based on utilizing hot carriers in QD solar cells to generate and collect additional electron–hole pairs via impact ionization processes. In order to utilize hot carriers, the rate of carrier cooling must be slower or the rate of impact ionization must be faster than other relaxation processes. Slowed hot electron cooling in  $\text{InP}$ <sup>65</sup> and CdSe<sup>14</sup> QDs has been observed, as was carrier multiplication in  $\text{InP}$ ,<sup>66</sup> PbSe, and PbS QDs.<sup>4,14,67</sup> Recently, Parkinson et al. have demonstrated the collection of photocurrent with quantum efficiency greater than one electron per photon using a photoelectrochemical system composed of PbS QDs bound to  $\text{TiO}_2$  single crystals.<sup>15</sup>

**C. Combination of a QDSSC with a QD-Based Schottky Junction Solar Cell.** A Schottky junction solar cell is likely to be the simplest way to fabricate a solar cell with colloidal QDs as the light harvester.<sup>68</sup> The structure consists of a *p*-type semiconducting QD film on ITO with a layer of evaporated metal (Figure 1b).<sup>69</sup> Band bending occurs at the interface between the QDs and the evaporated metal, creating a depletion region that lies mainly on the semiconducting side of the Schottky junction. The Schottky barrier favors the extraction of electrons from the QD film to the metal but blocks hole withdrawal. The Schottky-type QD solar cell has several advantages and disadvantages. Among the advantages, since only a thin layer of QDs is used (ca. 100 nm), the deposition of different types of QDs (organic-based, aqueous-based) is pretty straightforward from solution.<sup>5</sup> Second, the short-circuit current can reach high values

if infrared absorbing QDs are used covering a large part of the solar spectrum. Among the disadvantages, since absorption of light mainly takes place on the ohmic ITO side, charge carriers have to diffuse and drift a long way before they reach the junction.<sup>70</sup> For efficient charge carrier extraction, the QD film needs to possess long recombination-limited lifetime and a wide depletion zone.<sup>70</sup> This is achieved in lead chalcogenides and some other NIR absorbing QDs.<sup>5</sup> Yet, with these low band gap materials, the open circuit voltage  $V_{\text{oc}}$  is typically low. The  $V_{\text{oc}}$  is further limited in a Schottky junction solar cell by Fermi-level pinning because of defect states at the metal-semiconductor interface.<sup>21</sup> Another disadvantage is that holes can be injected from the QD film to the metal, reducing the  $V_{\text{oc}}$  and FF. Zhao et al. showed that by introducing a fullerene ([6,6]-phenyl-C61-butyric acid methyl ester, PCBM) as an electron-transporting/hole-blocking layer, both high  $V_{\text{oc}}$  (0.47 V) and high FF (62%) can be achieved in PbS QD-based solar cells.<sup>71</sup> Efficient charge separation at the interface of fullerenes and CdSe, CdTe and InP QDs has been previously demonstrated.<sup>72</sup>

Sargent et al. recently proposed a novel structure combining the Schottky junction solar cell and the QDSSC with a high 5.1% AM 1.5 power conversion efficiency, described as a depleted heterojunction (DH) colloidal QD solar cell (Figure 1c).<sup>18</sup> The structure was made of a mesoporous  $\text{TiO}_2$  film covered with a QD film on which a gold film is evaporated. A depletion region was built up between the electron accepting  $\text{TiO}_2$  and the *p*-type PbS QDs. In contrast to the purely Schottky junction solar cell, the depletion region reached into the  $\text{TiO}_2$  layer, so that charge separation took place on the illuminated side. With surface passivation of the  $\text{TiO}_2$ /QD interface, the number of defect states and the related Fermi-level pinning could be reduced, allowing for higher  $V_{\text{oc}}$ . Also, the injection of holes in the electron-accepting  $\text{TiO}_2$  was reduced in comparison with the Schottky design by a large discontinuity in the VB and by minimizing the electron density in the electron acceptor near the junction. In this structure, both FF and  $V_{\text{oc}}$  as well as  $J_{\text{sc}}$  can reach high values. In addition, a large CB offset is not a requirement for efficient electron transfer from QDs into the  $\text{TiO}_2$ -electrode. The energy and charge transport within the QD film in a DH solar cell remains under discussion. Sargent et al. suggested that diffusion of excitons through Förster transfer and consequent separation at a heterojunction does not take place in their device.<sup>18</sup> Instead, a built-in field separates excitons and then charge carriers are transported through diffusion and drift. Two other groups claimed an excitonic solar cell mechanism in DH solar cells with PbSe QDs, but with ZnO instead of  $\text{TiO}_2$  as an electron accepting layer.<sup>73,74</sup> Regardless of the nature of charge generation and transfer in the DH solar cell, the step from purely Schottky or purely QDSSC to DH solar cells, improving the power conversion efficiency to a value of 5.1%, is impressive.

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In all of these Schottky, hybrid, and blocking layer thin film devices, it is important to achieve good carrier transport within the QD film. While having no ligand present on the surface of the nanocrystals might seem preferred in this respect, it is usually the case that some ligand passivation of the surface is more beneficial in terms of balancing surface traps against transport. Zhao et al., for example, grew PbS QDs in octadecene/oleic acid before exchanging the long ligand for much shorter and very volatile butylamine prior to deposition of their QD films.<sup>71</sup> This was probably mostly removed during a post deposition annealing stage applied to some of the structures they studied (including one Schottky device for comparison). While annealing addressed the formation of an oxide shell to improve performance, they also found that the reintroduction of some short chain ligand, in the form of a short soak in ethanedithiol (EDT)/acetonitrile solution, though it led to a reduction in conductivity, yielded higher photocurrent devices. Thus improved surface passivation with short chain EDT at the expense of slightly poorer transport offered the best compromise in terms of performance. A similar ligand exchange scheme where again the oleate ligand is exchanged for EDT in the deposited film (though without an annealing step) in QD Schottky cells was also reported by Luther et al.<sup>68</sup>

Although multiple exciton generation (MEG) has been observed in InP,<sup>66</sup> PbSe, and PbS QDs in solution<sup>4,14</sup> and in PbSe QD films,<sup>67</sup> its action has yet to be confirmed in a QD Schottky device. Luther et al.<sup>68</sup> cite a number of complicating factors that may obscure the signature of MEG in such devices: low external quantum efficiencies to date prevent a simple unambiguous demonstration; increasing ITO absorption at short wavelengths, where the onset of multiplication might be expected, distorts any observable multiplication threshold; and thin film optical interference effect in measurements also make this difficult to see. However, the most significant problem ironically appears to be associated with the ligand exchange to EDT: although it improves the photovoltaic performance, it is also observed to quench MEG in PbSe films. Therefore much further work is needed on Schottky devices to decouple in particular the material science around QD surface passivation (removal of trap sites); carrier transport within the QD layer; structural features at the QD level to support or enhance MEG; and above all to improve the long-term stability of such devices.

**D. Summary and Outlook.** Despite the surge of interest leading to a huge boost of research activities around QDSSC, there are several problem areas inherent in the current lower performance of QDSSCs compared with that of DSSCs that have to be fully addressed and resolved. These are, in particular, (i) the low light harvesting efficiency of current QDSSCs due to modest coverage of TiO<sub>2</sub> surfaces by ex situ deposited colloidal QDs, and the less than optimal absorption spectrum range of QDs used to date; (ii) the occurrence of surface defect (trap) states in QDs that lower electron injection and collection efficiencies; (iii) poor QD chemical stability for some combinations of electrolyte and QD surface modification layers, which rapidly degrades solar cell performance; (iv) low open circuit photovoltages and fill factors due to nonoptimal energy level alignment at TiO<sub>2</sub>/electrolyte and electrolyte/counter electrode interfaces. It is desirable not only to optimize operation in each of these areas on a phenomenological basis, but to also develop a full understanding of the underlying charge generation, transport and interface transfer mechanisms and their relationships with the material design and cell structure in order to get the best performance by design. If these problems,

jointly or severally, are successfully resolved, this will lead to a better, cheaper and commercially attractive solar-energy-generating technology employing colloidal QDs as solar cell components.

As well as generating a rigorous understanding of the various mechanisms, on both fast and slow time scales, it is also necessary to develop material combinations with more commercially robust stabilities. Established silicon photovoltaics have 25–30 year warranties, without which it is hard to justify the technology on a purely financial basis. New and perhaps lower cost technologies may be justifiable on shorter warranty periods (at least initially), or may serve application niches where power generation payback is less important than say weight, or aesthetics, etc. Nonetheless, it is hard to see how such technologies will gain commercial acceptance with less than 5 year service lifetimes. Again to achieve this, a full mechanistic understanding of how the component materials (especially QD/electrolyte combinations) interact is required.

**It is also necessary to develop material combinations with more commercially robust stabilities.**

Current developments are starting to show areas where the solar cell structure may be improved and where some of the existing problems may be reduced or side-stepped completely. More sophisticated solar cell structures have already shown strong improvements in performance. In QDSSCs,  $V_{oc}$  may be improved through the design and use of *pn*-type tandem QDSSCs, as recently suggested for DSSCs<sup>75</sup> and may be an attractive option.<sup>76</sup> New emerging concepts combining heterojunction (Schottky) and excitonic (Grätzel type) solar cells<sup>18</sup> offer ample perspectives for improvements making use of the specific advantages of semiconductor nanocrystal QDs. In the former case, one obvious attraction is the option to dispense with an electrolyte, and thus avoid the need to address the electrochemical stability issue. However there may still be other long-term stability problems to address (e.g., photooxidation, etc) and there is the need to understand and improve charge transport in the QD film in place of the redox chemistry. Further enhancement in charge generation efficiencies via, e.g., MEG in QDs, should enhance any of the QD solar cell variants described in this Perspective, but again a full understanding is needed to convert this into a significant performance advantage in a commercial product.

While bringing together solar cell structures comprising several different nanomaterial technologies that themselves are still undergoing development is very much a challenge, the reward for putting our understanding on a systematic basis is very clear. The materials and particularly the QDs have already been shown to have very desirable potential, which, if they are properly integrated into devices, may yield performance levels that match if not exceed current commercial photovoltaic cell specifications.

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