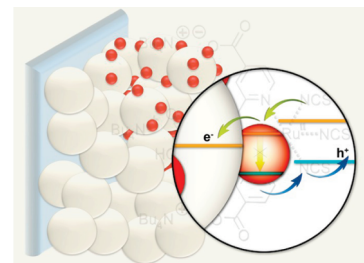


Breakthroughs in the Development of Semiconductor-Sensitized Solar Cells

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ABSTRACT Semiconductor sensitized solar cells have attracted growing interest in the past few years. Starting from quite low conversion efficiencies, these have grown very rapidly to values of around 4–5%. This Perspective analyzes the optimization of three aspects toward an increase in cell performance, (i) materials, including not only light-absorbing material but also electron and hole conductors and counter electrodes, (ii) control of recombination and band alignment by surface treatments, and (iii) development of absorbing nanocomposites with enhanced light-harvesting and -collecting properties. We argue that these key topics could promote major breakthroughs in the design and development of semiconductor-sensitized solar cells.



Nanotechnology is believed to revolutionize industry in the coming years and will have a significant economic impact allowing a considerable cost reduction of the photovoltaic energy, both by reducing the cost of the devices and by increasing efficiencies. Conventional Si solar cells rely on high-quality materials since the carriers generated in the device, after photon absorption, remain in the same material until they are extracted at the selective contacts. This involves the use of sophisticated technologies with high production cost in order to avoid carrier recombination prior to their extraction. Conversely, nanoscale absorbers can quickly separate the photogenerated carriers into two different media, which allows for a less-demanding materials quality and therefore facilitates costs reduction. The concept of an absorber material that separates the photogenerated charge carrier electrons and holes into two different media has been extensively studied for the dye-sensitized solar cells (DSCs),¹ where a molecular dye acts as an absorber on a cell formed by complementary nanostructured electron and hole transport materials.

Starting from quite low conversion efficiencies, these semiconductor sensitized solar cells have grown very rapidly to values around 4–5%.

On the other hand, semiconductor materials clearly constitute the basis of the photovoltaic devices governing the energy market (>99%). When these materials are translated to the nanoscale, new and fascinating properties appear as consequence of quantum confinement.² Additionally, some of their

bulk properties such as the high extinction coefficient are preserved at the nanoscale.³ Semiconductor quantum dots (QDs) possess a large intrinsic dipole moment, and their band gap can be easily tuned by the control of their size and shape, providing an excellent tool for nanoscale design of light-absorber materials.⁴ Importantly, the production of semiconductor QDs or thin layers is significantly cheaper compared to their bulk counterparts since their synthesis takes place at significantly lower temperatures and with solution-based approaches. In this sense, they are excellent materials for the development of sensitized solar cells.

The use of semiconductor materials as sensitizers goes back to the 1990s.^{5–8} However, it has only been in the last years when semiconductor-sensitized solar cells (SSCs; see Figure 1) have attracted more attention due to a number of factors. The development of nanotechnology has enabled the preparation and characterization of semiconductor QDs and thin layers in a relatively easy way. The experience obtained in the research with DSCs permits transfer of many of the developments in this field to SSCs. As a result, currently, an increasing number of research groups have been drawn toward studying and realizing this kind of devices.

In the past few years, a rapid increase of SSC efficiencies has been reported, reaching values of around 4–5% at 1 sun.^{9–11} The efficiency of SSCs still lags behind those of DSCs; however, a further performance improvement for SSCs can be anticipated. From our point of view, significant breakthroughs allowing this increase will come from three main fronts of advance that we discuss in this perspective, (i) materials, (ii) surface treatments, and (iii) nanocomposite absorbers.

Further research in materials is needed to optimize the performance of these devices. First, light-absorbing semiconductors

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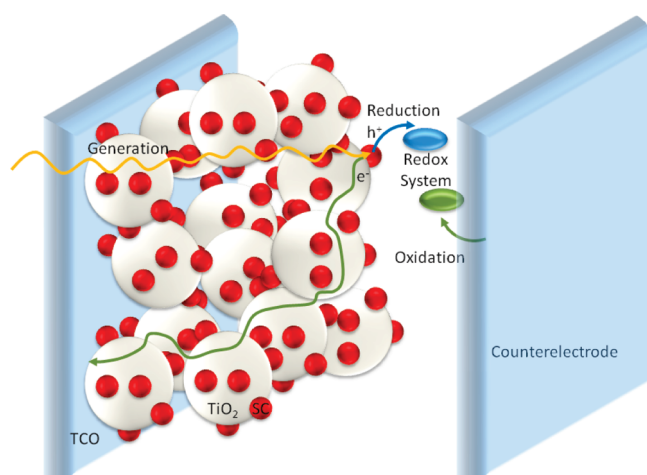


Figure 1. General scheme of a semiconductor-sensitized device. Light generates electron–hole pairs in the semiconductor absorber; the electron is injected in a nanostructured wide band gap semiconductor (i.e., TiO_2 , ZnO) employed as an electron conductor, and it is transported in this medium to the transparent conductive oxide (TCO) used as a collecting substrate and light window. The semiconductor is regenerated by reducing species in the electrolyte that acts as a hole-transporter medium. Finally, the hole is transported to the counter electrode, where the oxidized counterpart of a redox system is reduced. In a solid-state system, the liquid electrolyte is substituted by a solid hole transporter. The light-harvesting material is a semiconductor that usually takes the form of discrete particles, as represented in this scheme, or a more continuous thin layer. The former can produce quantum confinement and are usually known as quantum-dot-sensitized solar cells (QDSCs). The latter is commonly known as extremely thin absorber (eta) solar cells, but the general processes taking place on both configurations are quite analogous and can be grouped with the more generic denomination of SSCs.

have to be analyzed from two points of view, semiconductor nature and semiconductor preparation. The choice of semiconductor material gives great versatility to SSCs. For example, the use of the quantum dot confinement as a tool to tune the semiconductor band gap in PbS SSCs extends the light absorption range from NIR to UV.^{12,13} Thus, different semiconductors have been utilized for SSCs (see, for example, refs 4 and 14), but it is a field where further progress could be expected. There is proof of this in the latest reports using the Sb_2S_3 semiconductor as a sensitizer.^{15–17} This approach has given solid-state devices with the highest reported efficiency¹¹ of SSC devices, with power conversion of 5.13% under full 1 sun illumination using poly(3-hexylthiophene) both as a hole conductor and an assisting light absorption material. However, further research is needed for a complete understanding of this system, for example, to explain the effect of light soaking and gas atmosphere on the cell performance.¹⁸

One of the main advantages of using SSCs appears from the fact that the same type of semiconductor can be prepared in many different ways. This offers enormous versatility to the fabrication process of the solar cell. CdSe is probably the most extensively used semiconductor in SSCs and offers a good example to this adaptability. On the one hand, CdSe can be pre-synthesized in a colloidal form with different shapes and sizes which may be directly attached to the wide band gap semiconductor^{19,20} or through bifunctional linker molecules.^{21–23}

On the other hand, CdSe may be directly grown on the surface on a wide band gap semiconductor (the electron-transport matrix) by means of different techniques. The most common processes are chemical bath deposition (CBD),^{24–26} successive ionic layer adsorption and reaction (SILAR),²⁷ or electrodeposition.²⁸ The properties of the semiconductor material and the final performance of the solar cell will depend strongly of the preparation method, that is, colloidal CdSe SSCs present good performance but low QD loading, or alternatively, CBD confers high semiconductor loading to the SSCs but could lead to higher internal recombination in the closed-packed QDs structure.²⁹ The preparation method also affects the charge-transfer kinetics.³⁰ Semiconductors directly grown on the electron-transporter surface require thickness optimization for the wide band gap semiconductor film. Although thick layers increase the light absorption, they have other associated drawbacks. Thus, a reduced cell performance may be observed due to the presence of sensitizer crystals with no direct contact with the electron transporter leading to higher recombination.^{31,32} Likewise, thick layers may generate a reduced wetting of the semiconductor pores by the hole transporter, decreasing consequently the regeneration efficiency.⁹ In summary, both the choice of preparation method and the type of semiconductor used influence the final performance of SSCs and need to be taken into account during the device optimization process.

Research in this field over the past few years has highlighted a very important fact; the semiconductor light-absorber properties dictate the requirements that the other components of the device need to satisfy. For DSCs using liquid electrolyte as a hole conductor, a standard configuration exists. This is composed of a nanostructured wide band gap semiconductor, a dye, the $\text{I}^- - \text{I}_3^-$ redox electrolyte, and a platinized counter electrode. SSCs are formally analogous to DSCs (see Figure 1), but a more careful analysis indicates that currently, there is no consensus on a standard configuration for SSCs. For stability reasons, the $\text{I}^- - \text{I}_3^-$ redox couple is not a good choice for many semiconductors.³² Corrosion of the semiconductor normally takes place, unless the semiconductor light absorber is protected with a coating material such as TiO_2 .³³ To overcome this problem, alternative redox couples have been employed, such as Co-redox^{23,27} and polysulfide.^{10,20–22,24–26,34} However, the former shows diffusion limitations that restrict the photocurrent at high illumination. Although polysulfide shows high photocurrents, this redox system presents high charge-transfer resistance, with the standard platinized electrode generating a new issue to solve.²² In order to increase the fill factor (FF), alternative counter electrodes have been used.^{10,20,35} As a consequence of this, the choice of electrolyte will depend on the specific absorbing semiconductor used. The fact that higher conversion efficiencies have been obtained for cells using a solid hole conductor¹¹ than those for cells using a liquid electrolyte^{9,10,36} is a clear indication that no optimized electrolyte system has been obtained for SSCs. In the most general case, the optimized electrolyte will depend on the specific absorbing semiconductor used. The situation with DSCs is just opposite, showing the best performances with liquid hole carriers. In this latter case, the reverse situation is observed due to the better diffusion and screening of the liquid electrolyte and a direct contact along the whole effective surface of the device.

Regarding the wide band gap semiconductor used as an electron transporter, its structure was originally designed to tailor organometallic dyes properties. The sizes of these dyes are generally below 1 nm. However, the size of a semiconductor thin layer or a QD with the addition of the capping molecules is in the range of 3–4 nm, or even higher. Therefore, a limitation arises from the size of the nanostructured electrode. In the case of colloidal QDs, it has been shown that practically 100 % covering of flat TiO₂ surface can be attained, but the covering area decreases dramatically to 14 % when Degusa P25 TiO₂ nanostructured electrodes are employed.¹⁹ The observed performance variation of different particle size TiO₂ pastes also confirms this observation.²⁰ A different approach enables the use of open structures with lower surface area than nanoporous TiO₂ for a wide band gap semiconductor. In this strategy, the high extinction coefficients of the semiconductor are exploited, preserving an efficient light-harvesting ability.⁵ Examples of this kind of structure are nanowires,^{28,31} nanotubes,^{13,37} or inverse opals²⁶ that have shown very promising results.

Breakthroughs will come from (i) materials, (ii) surface treatments, and (iii) nanocomposite absorbers.

Surface treatment is another area from which progress is expected in the development of SSCs. These treatments can be employed to protect QDs, enhancing their stability and allowing the use of the I⁻/I₃⁻ redox electrolyte as in the case of the previously commented TiO₂ coating of CdS QDs.³³ In addition, surface treatments allow the control of recombination processes and band alignment, and therefore electron injection, in this kind of cell.^{20,24,25,29,32,34} Surface treatments can strongly influence the charge-transfer, -recombination, and -transport processes for photogenerated electrons and holes in SSCs, represented in Figure 2. Recombination mechanism R4 (see Figure 2) from thermalized electrons in the TiO₂ to the hole-transport material is the main recombination process present in DSCs. In the case of SSCs, R4 depends strongly on the preparation method of the light-absorbing semiconductor.³⁰ For colloidal QDs used as sensitizers, a large fraction of the wide band gap semiconductor surface is in direct contact with the hole conductor. Therefore, the recombination probability of the separated electrons and holes is high. A different scenario is found for processes that allow an increased coverage of the wide band gap semiconductor surface. Processes that enable a low wide band gap semiconductor surface exposure are directly grown QDs and a compact thin layer deposited as a light-sensitizing material. For these systems, the recombination resistance increases due to the presence of an additional coating, indicating that QDs themselves act as a blocking layer between electron and hole conductors (R5 in Figure 2).²⁹ Additionally, recombination from the QDs to the thermalized holes in the hole transporter

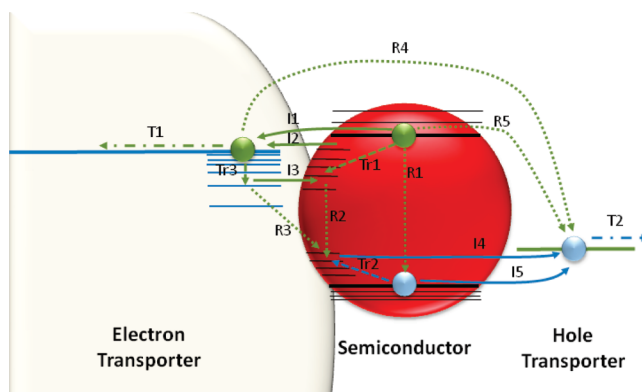


Figure 2. Charge-transfer and -transport processes for photogenerated electrons (green arrows) and holes (blue arrow) in SSCs, following ref 32. A semiconductor QD with discrete energy levels is taken as an example. For clarity requirements, each arrow could denote more than one process. Injection (solid arrow), trapping (dashed arrow), recombination (dotted arrow), and transport (dash-dot arrow) are indicated. Photogenerated electrons can be injected from the QD conduction “band” (CB) to the wide band gap semiconductor CB, I1. It can also be trapped, Tr1, and injected into the wide band gap semiconductor CB or into its traps, I2, depending on the band alignment. The injected electron is transported in the electron conductor media, T1, and can be trapped in this material, Tr3. Trapped electrons in the wide band gap semiconductor can be released to the CB or back injected in the semiconductor, I3. On the other hand, holes generally are fast trapped in band gap states, Tr2, and can be injected into the hole-transporting media from trap states, I4, or before being trapped, I5. Processes I1, I4, I5, T1, and T2 are strictly required for solar cell operation, and the other ones are not necessarily harmful for cell performance. All of the processes mentioned so far compete with recombination processes. For efficient cell operation, charge-transfer and -transport processes have to be faster than recombination. There are different recombination pathways in SSCs. Inside of the semiconductor, direct recombination of photogenerated electron–hole pairs, R1, or recombination through trap states, R2, can occur. On the other hand, electrons in the CB of the wide band gap semiconductor or in its traps states can recombine with trapped holes in the semiconductor or holes in the semiconductor valence band (VB), R3, or with holes in the hole-transporter material, R4. Another recombination pathway that can have importance if I1 is not fast enough is the recombination of trapped electrons in the semiconductor or electrons in the semiconductor CB with holes in the hole-transporter media, R5.

is reduced (R4).³² In this way, the use of ZnS^{20,25} and SiO₂³⁸ increases enormously the IPCE obtained for QDSCs. Using these blocking layers, a two-fold photocurrent increase is obtained by increasing the recombination resistance.²⁹

The band alignment has been modified in DSCs by the use of different additives in the electrolyte solution.^{39,40} Likewise, similar additives may be utilized in QDSCs either with liquid electrolyte or solid hole conductor, that is, LiSCN¹⁸ or KSCN¹⁵ have been used in combination with Sb₂S₃ SSCs; however, their actual effect of the additive is not fully understood. Other variants have been studied such as benzenethiol, which acts as a molecular dipole to produce a more favorable band alignment between QDs and TiO₂. This alignment causes an increase of the photocurrent, as shown for CdS⁴¹ and CdSe³⁴ QDs grown by CBD; see Figure 3a. The use of a molecular dipole causes a downward displacement of the TiO₂ CB, as can be observed by a shift in the capacitance versus voltage plot; see Figure 3b. Besides, molecular dipole treatment produces an additional beneficial effect increasing the recombination resistance;

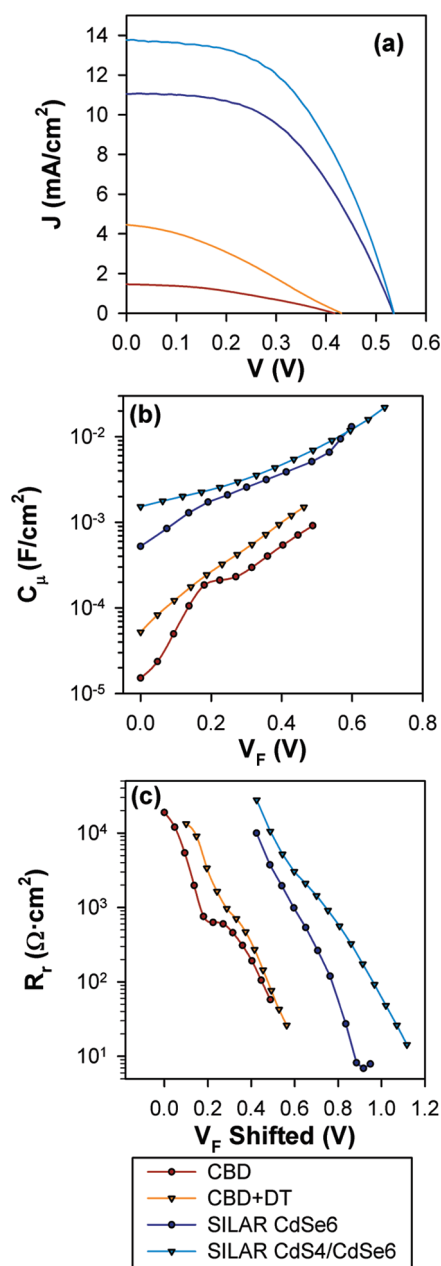


Figure 3. Two different set of samples are compared in order to analyze the effects of surface treatments and a combination of different kinds of QDs. CdSe QDSCs prepared by CBD show the effect of the molecular dipole in solar cell performance,³⁴ while CdSe QDSCs prepared by six SILAR cycles show the effect of a previous deposit of four SILAR cycles of CdS. The conversion efficiency of this last cell is 3.74%,⁹ and both samples are coated with a ZnS layer to reduce recombination. (a) J - V curves under 1 sun illumination (AM 1.5 G). (b) Chemical capacitance, C_{μ} , obtained by impedance spectroscopy plotted versus voltage drop at the sensitized electrode, V_F . V_F can be obtained from impedance spectroscopy data as $V_F = V_{\text{appl}} - V_s$, where V_{appl} is the applied voltage and V_s is the sum of the voltage drops in the series resistance, electrolyte, and counter electrode.³⁴ (c) Recombination resistance, R_r , obtained by impedance spectroscopy. The shift of the TiO_2 CB produced by the different treatments has been removed, and R_r plotted against V_F is shifted in order to compare the cells under the same conditions of the number of electrons in the TiO_2 .³⁴

see Figure 3c. As a consequence of the higher recombination resistance, no reduction of the open circuit voltage, V_{oc} , is observed. Indeed, a slight increase is obtained for the dipole treated sample; see Figure 3a. Thus, the increase of recombination resistance introduced by the dipole molecule dominates over the downward movement of the TiO_2 CB; see ref 34 for details. One of the major advantages of surface treatments is that different processes may be screened on the same sample. Hence, we have observed that a dipole treatment followed by a ZnS coating enhances around 600% of the efficiency of CdSe QDs grown by CBD.³⁴

Regarding the surface treatment, it is important to remark about a significant difference between molecular dyes and semiconductors used as sensitizers. As suggested by Hodes,³² the probable existence of surface states in the sensitizing semiconductor is a major difference between DSCs and SSCs. These surface states have been widely studied in colloidal QDs⁴² and can be detected by different techniques such as photoluminescence or scanning tunnelling microscopy. The observed behavior strongly depends on the surface treatment, the use of a semiconductor shell,⁴² or the type of capping ligand.⁴³ The effect of semiconductor surface states on the performance of SSCs is not understood, and there are very few reports on this topic.⁹ It has been suggested that trapping in these states of photogenerated charges could produce alternative recombination pathways, processes R2 and R3 in Figure 2.³² Considering the β -recombination model,⁴⁴ we have recently shown that the β obtained for CdSe QDSCs decreases with the number of SILAR cycles, where β comes from the slope of $\text{Log}(R_r)$ versus V_F .⁴⁴ This β is the effective order of recombination with respect to free electron density. Values of around 0.5 are obtained for three SILAR cycles decreasing to values around 0.3 for seven and eight cycles.⁹ For comparison, values of 0.5–0.7 are commonly reported for β in DSCs. The decrease of the β value with the number of SILAR cycles occurs in parallel with the increase of TiO_2 surface coverage. This fact indicates a change in the main recombination pathway of photoinjected electrons in TiO_2 into electron-acceptor species. For low QD coverage, the main recombination pathway is R4; see Figure 2. On the other hand, for high QD coverage, the main recombination takes place with electron-acceptor states in the QDs, R3 in Figure 2. It is expected that this type of recombination will be reduced either by passivation of surface states in the semiconductor absorber or by the presence of a blocking layer between the electron transporter and semiconductor.¹⁸

Finally, the use of nanocomposite absorbers is regarded as the third factor from which we could expect important breakthroughs in SSCs. Semiconductor QDs are excellent building blocks for more sophisticated nanocomposite absorbers. QDs can be combined with other QDs of different size or type. The combination of CdS and CdSe is a well-known example^{9,24,45} that provides enhanced performance compared to the use of each individual semiconductor; see Figure 3a. The use of CdS increases the incident photon to current efficiency (IPCE) in the blue region of the spectra⁹ and shifts downward the TiO_2 CB; see Figure 3b. This produces a photocurrent increase with no reduction of the V_{oc} as the recombination resistance increases as well,³⁴ see Figure 3c. This clearly shows that

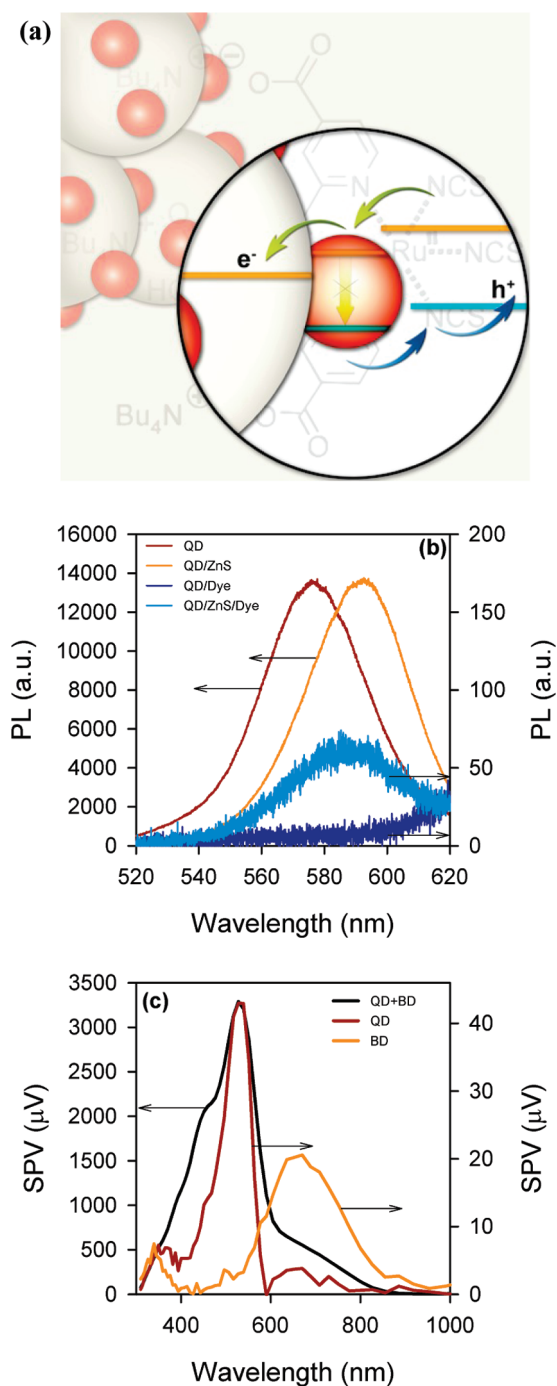


Figure 4. (a) Schematics of the proposed supracollector structure for an enhancement of the light harvesting of a composite attached to an electron collector; when the QD (in green) absorbs light, the excitons generated have to be quickly separated in order to avoid internal quenching. A key aspect for the efficiency of charge separation is the fast extraction of the hole from the QD, which will improve both exciton quenching and recombination with electrons already injected into the electron-conducting media due to an increase of separation between the electron and hole. (b) Photoluminescence quenching of colloidal CdSe QDs, adsorbed on nanostructured TiO_2 electrodes,⁴⁸ by the interaction with N719 dye, with and without ZnS coating. (c) Surface photovoltage (SPV) measurements of CdSe QDs, black dye (BD), and QD plus BD.⁴⁶

nanocomposite absorbers can improve these systems through two different beneficial effects. On the one hand, the spectral absorption range can be broadened. On the other, interactions between different absorbing parts can reduce the overall recombination.

It is also possible to obtain this effect by combining materials with different nature such as QDs and molecular dyes. The picture in Figure 4a schematically represents how the photophysics of QDs and organic dyes can favorably be tuned. In the ideal case, both absorbers can inject electrons into the electron transporter.^{46,47} The fast regeneration of the QD by the dye⁴⁸ reduces the internal recombination in the QD, increasing the charge separation between photoinjected electrons and holes.^{46,49} Figure 4b plots CdSe QD photoluminescence (PL) quenching with the addition of N719 dye. Surprisingly, PL quenching remains strong with the use of an intermediate layer of ZnS sandwiched between the QD and dye. This clearly indicates that a great interaction between the two sensitizers⁴⁸ exists. This system may potentially be employed in the development of a supracollector nanocomposite with improved properties where the whole is greater than the sum of the parts. These nanocomposites can increase the number of the photoinjected electrons from CdSe QDs into TiO_2 up to a factor of 70, as revealed by surface photovoltage measurements,⁴⁶ see Figure 4c.

Application of these ideas in a photovoltaic device with a hole transporter compatible with both QDs and dye is required. A prominent example is the use of the solid hole conductor OMeTAD.^{47,50} The compatibility with liquid electrolytes for both systems is more complicated to obtain. Two of the current redox couples used with liquid electrolytes fail to achieve this objective. Thus, many QDs are not stable in the $\text{I}^- - \text{I}_3^-$ redox electrolyte, or the high pH of polysulfide desorbs the dyes. As mentioned previously, a layer of TiO_2 coating the QDs confers protection to the QDs and allows further deposition of a second absorbing layer based on dyes. This enables an increased absorption to that imposed by the low absorbance obtained for dye monolayers.⁵¹ This configuration can also be employed in the development of panchromatic absorbing quantum dot antennas with an appropriate combination of QDs and dye. In these systems, QDs absorb light from the blue region of the solar spectrum, transferring the energy by Förster resonance energy transfer (FRET) to a dye that absorbs in the red region of the solar spectra.⁵² Electrons arising from the absorption of photons in the blue and red regions are finally injected into the TiO_2 .

The semiconductor light-absorber properties dictate the requirements that the other components of the device need to satisfy.

In summary, semiconductor-sensitized solar cells have experienced a fast increase of performance over the past few years. Breakthroughs in the area are foreseen by gaining

understanding in three topics of research that have proved successful recently. First, the development of new materials including semiconductor absorber, counterelectrodes, and electron–hole transporters should offer a range of new opportunities and challenges. Second, surface treatments have proved to be a powerful tool to provide a reduction in the recombination and to control the band alignment. Continuous research in this area may offer a new process to further enhance these desired properties. Finally, nanocomposite absorbers have shown the ability to broaden the absorption spectral region and reduce the recombination. We firmly believe that a new judicious combination of materials should present a further technology improvement in this field of research.

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