ACCOUNTS
of chemical research

All-Solid-State, Semiconductor-Sensitized Nanoporous Solar Cells

GARY HODES* AND DAVID CAHEN
Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

RECEIVED ON AUGUST 24, 2011

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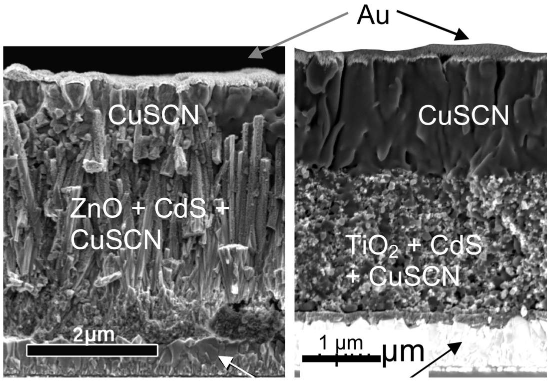

Despite the rapid increase in solar cell manufacturing capacity (~50 GW_p in 2011), maintaining this continued expansion will require resolving some major fabrication issues. Crystalline Si, the most common type of cell, requires a large energy input in the manufacturing process, which results in an energy payback time of years. CdTe/CdS thin film cells, which have captured around 10% of the global market, may not be sustainable for very large-scale use because of limited Te availability. Thus, research in this field is emphasizing cells that are energy efficient and inexpensive and use readily available materials. The extremely thin absorber (ETA) cell, the subject of this Account, is one of these new generation cells. Since the active light absorber in an ETA cell is no more than tens of nanometers thick, the direct recombination of photogenerated electrons and holes in the absorber should not compete as much with charge removal in the form of photocurrent as in thicker absorber materials. As a result, researchers expect that poorer quality semiconductors can be used in an ETA cell, which would expand the choice of semiconductors over those currently in use.

We first describe the ETA cell, comparing and contrasting it to the dye-sensitized cell (DSC) from which it developed and describing its potential advantages and disadvantages. We then explain the mechanism(s) of operation of the ETA cell, which remain controversial: different ETA cells most likely operate by different mechanisms, particularly in their photovoltage generation. We then present a general description of how we prepare ETA cells in our laboratory, emphasizing solution methods to form the various layers and solution treatments of these layers to minimize manufacturing costs. This is followed by a more specific discussion of the various layers and treatments used to make and complete a cell with emphasis on solution treatments that are important in optimizing cell performance and explaining the possible modes of action of each of these treatments. Finally, we show how ETA cells have improved over the years, their present efficiencies, our expectations for the future, and the challenges that we foresee to fulfill these expectations.

Introduction

Dye-sensitized solar cells (DSSCs), introduced some 20 years ago as a new type of photovoltaic (PV) cell,[1,2] have become a major research and development topic with best certified cell efficiencies of 11.0% and best certified submodule efficiencies of 9.9%.[3] In a DSSC, light is absorbed in a dye, adsorbed on an electron conductor, and the photogenerated electrons and holes are injected into separate electron and hole conductors. A high surface area, due to the nano(meso)porous structure of the electron conductor, allows near-total light absorption via dye monolayers. Thicker dye layers lead to quenching and poor charge separation. Thus, as in photosynthesis and in contrast to conventional photovoltaic cells, generation and spatial separation of charges occur in different phases of the device. The hole conductor in the DSSC is usually a polyiodide electrolyte that easily penetrates into the porous oxide/dye structure. Solid-state hole

Published on the Web 03/02/2012 www.pubs.acs.org/accounts
10.1021/ar200219h

TABLE 1. Timeline of Good Efficiencies Obtained from ETA Cells[a]

year	cell	efficiency (%)	comments	ref
1998	TiO_2/Se/CuSCN	0.13 (0.8)[b]	at 0.8 sun	39
2002	TiO_2/PbS/Spiro-OMeTAD	0.49	at 0.1 sun	40
2005	ZnO/CdSe/CuSCN	2.3	at 0.3 sun	25
2006	TiO_2/CdS/CuSCN[c]	1.3		23
2007	TiO_2/Sb_2S_3/CuSCN	3.4		34
2008	ZnO/In_2S_3/CuSCN[d]	3.4	at (0.1 sun)	41
2009	TiO_2/Sb_2S_3/CuSCN	3.4		22
2010	TiO_2/Sb_2S_3/CuSCN	3.7		35
	TiO_2/Sb_2S_3/Spiro-OMeTAD	3.1 (4.0, 5.2)	at (0.5, 0.1 sun)	26
	TiO_2/Sb_2S_3/P3HT[e]	5.1	visible absorbing hole conductor	42

[a] "Good efficiency" means good for that period. Only three-phase ETA cells, with both electron and hole conductors, are included. Illumination at 1 sun unless given otherwise. [b] Efficiency given as 0.13% but appears to be 0.8% from *I*−*V* curve. The cell's structure is uncertain but appears to be nanoporous TiO_2 with the pores filled with Se and CuSCN deposited on top. We present it here as it appears to be the first cell of the 3-phase type. [c] Included because this was a high efficiency for the CdS bandgap. [d] The actual absorber has a much lower bandgap than In_2S_3 due to reaction with CuSCN (→ Cu−In−S phase). [e] Since the hole conductor also absorbs light, this is not strictly an ETA cell as we have defined it. However, while there are clearly some differences in charge transport paths compared with cells using a non-light-absorbing hole conductor, it is close enough to our concept of an ETA cell that we include it here, particularly in view of its high efficiency.

conductors have also been used,[4,5] to simplify cell sealing, an important commercial consideration, but those cells perform poorer than liquid electrolyte ones.

Instead of using a molecular dye, a semiconductor absorber can be used as light absorber. Such semiconductor-sensitized solar cells (SSSC) are much less studied than the DSSC but are attracting increasing interest.[6−8] While there are potential advantages in using a semiconductor instead of a dye (see ref 6), these cells are, at present, much less efficient than DSSCs. Thus, liquid junction SSSCs reach ∼4% maximum solar efficiencies at present. Solid-state SSSCs, also known as ETA (extremely thin absorber) cells, are, however, not far behind the best solid-state DSSCs, and their >5% best efficiencies (see Table 1) are comparable to those of solid-state DSSCs.

In this Account, we define as ETA cells those with a very thin (mostly <50 nm) semiconductor absorber, deposited on a nonabsorbing porous electron conductor, which is infiltrated with a nonabsorbing solid hole conductor. According to this definition, generation and transport of both charges are not completely separated into different phases, as in the DSSC, because typical absorber widths from several nanometers to several tens of nanometers imply some transport in the absorber. Further modifications of this structure, in particular two-phase cells where the absorber is also the hole conductor and is usually thick in part of the cell, will not be considered here.

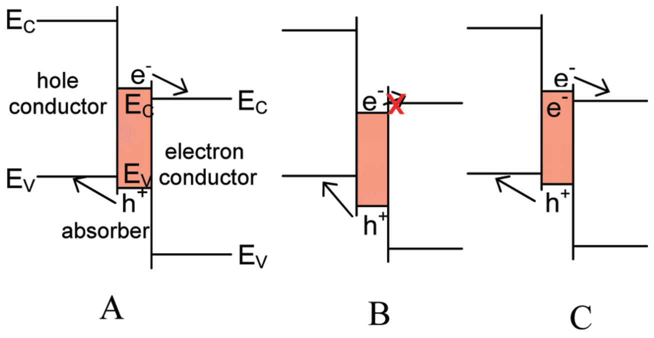

FIGURE 1. Schematic of a simplified electron energy level diagram of an ideal ETA cell. (A) Small energy offset between absorber and electron conductor conduction band bottoms (E_C) and absorber and hole conductor valence band tops (E_V) provides driving force for charge injection with minimal voltage losses. (B) Example where low absorber E_C apparently prevents electron injection into electron conductor E_C. (C) Possible steady-state equivalent of diagram B under illumination, where electrostatic effect of hole injection into the hole conductor results in upward movement of absorber energy levels until electron injection can occur.

Rationale for the ETA Cell and Potential Disadvantages

The main rationale for the ETA cell (and for SSSCs in general) is that the diffusion length of the electronic charges in the absorber can be much less than in a regular PV cell. The reason is that everywhere in the cell the semiconductor absorber is very thin, so that charge generation occurs on average much closer to an interface where charge separation occurs, than in a regular cell. This means that "poor quality" semiconductors that would not work well in normal PV cells might work for SSSCs. If this expectation is borne out, then not only should cell preparation be simpler (use less pure, smaller crystallite materials), but some semiconductors that would not be seriously considered for normal cells because of intrinsically low charge diffusion lengths may work in SSSCs.

There are, however, also potential disadvantages of the SSSCs. Energy, required to drive charge injection, is lost. This energy can be supplied by offsets between the bands/levels of the absorber and of the two charge conductors at the corresponding interfaces (see Figure 1A). While some offsets are needed to provide the driving forces, large offsets represent additional voltage loss without a proportionate gain in driving force (i.e., in photocurrent).

Another potential disadvantage is recombination due to the high surface area of the porous structure. This is not a problem for good DSSCs, which in principle would have the same disadvantage. However, in those, this recombination route is strongly suppressed. because of the very slow electron injection kinetics from TiO_2 to the liquid polyiodide hole conductor. Also it is likely that the dye molecules' chemical binding groups help to passivate the interface. Electron-hole recombination between TiO_2 and solid hole conductors is much faster than the equivalent route in liquid junction DSSCs. (We note that, in this short Account, we have neglected grain boundary recombination).

Mechanism of Operation of ETA Cells

Initially there was considerable controversy over how the DSSC operates. This was not trivial: Conventional (p-n, p-i-n and Schottky) cells depend on an electric field to separate charges. With the growing importance of nanoparticles and their applications to solar energy conversion, either in liquid junction solar cells or photoconversion or photocatalysis, it was realized that semiconductor nanoparticles in an electrolyte might be too small to support an appreciable space charge layer[9−11] and that charge separation might depend on other factors. Relatively high quantum efficiencies of photoelectrodes made of nanoporous light-absorbing semiconductor films, where both photogenerated electrons and holes are transported through the cell in the same semiconductor (in contrast to the DSSC and SSSC) were demonstrated. These were explained by surface charge separation related to charge transfer kinetics at the semiconductor−electrolyte interface,[12,13] that is, without invoking a space charge layer in the semiconductor. The liquid junction DSSC is understood in terms of very rapid injection of electrons from the excited dye to the nanoporous electron conductor on which the dye is adsorbed and rapid electron transfer from the electrolyte to regenerate the oxidized dye. Thus charge separation occurs due to energy level/band offsets that kinetically favor unidirectional charge transport. The cell's photovoltage is generated because the electron quasi-Fermi level (E_{Fn}) of the nanoporous oxide, which should be highly depleted in the dark (E_F far from the conduction band) shifts toward the conduction band.[14,15]

This picture is not necessarily valid for SSSCs and in particular not for ETA cells, although some elements of the DSSC model may hold for ETA cells. There are a number of fundamental differences. One is that the width of the typical absorbing semiconductor is at least 10 times more than that of a dye molecule and the presence of a macroscopic electric field across this absorber cannot be excluded. Furthermore, because liquid electrolytes are considerably more conducting than presently available solid hole conductors near room temperature, the photogenerated charges in the cell are screened electrically more efficiently by a surrounding liquid than by solid electrolytes.

If we consider the simplest generic picture of an ETA cell (Figure 1A), a photogenerated electron in the absorber is injected into the E_C of the electron conductor, while the hole is injected into the E_V of the hole conductor. This picture demands suitable offsets between the respective bands of the absorber and electron and hole conductors. In principle, it might be possible for a cell to operate even if a suitable offset occurs only at one of the junctions. Figure 1B shows a case where the absorber E_C lies below that of the electron conductor (at least in the dark). Upon illumination, and assuming holes are removed by the hole conductor, electrons will accumulate in the absorber, and the extra negative charge will destabilize (bring closer to the vacuum level/move upward in the diagram) the absorber levels with respect to the two charge conductors, until electron injection occurs (Figure 1C, which is (energetically) identical now to panel A). A steady state is reached when the electron and hole injection rates are balanced (the extra negative charge on the absorber in this steady state could change the recombination kinetics, for example, Auger recombination is more likely to occur). Of course, the bandgap of the absorber must be sufficiently large to allow, after energy level adjustment, favorable overlap at both interfaces simultaneously. The converse, where the absorber valence band is above that of the hole conductor, can also occur. In the ZnO/In_2S_3/CuSCN cell, facile electron transport from In_2S_3 to ZnO allowed efficient hole transport from the In_2S_3 to the CuSCN, which did not occur in the absence of the ZnO.[16] Downward band shifting due to positive charging (as electrons are preferentially removed) could explain this observation.

Another possible scenario to explain electron injection from a Figure 1B-like energy scheme is injection of electrons into surface states in the electron conductor. If these states are shallow (close to E_C), photocurrent might be possible, either by thermal excitation of carriers from these states into E_C (in which case the current is likely to be low because the driving force is also low), or by electron hopping through surface states (in which case the photovoltage will be limited by the surface state level, rather than by E_C).

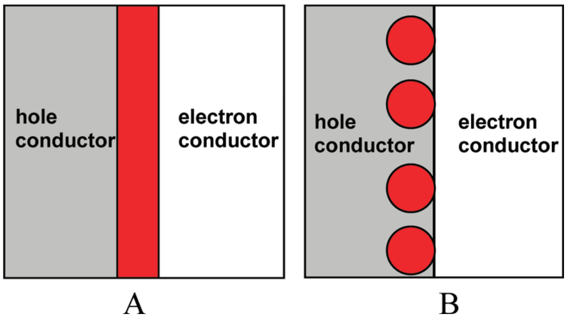

FIGURE 2. Schematic diagram of ETA cells. (A) The semiconductor absorber (red) forms a continuous film, separating the electron and hole conductors. (B) The absorber is in the form of isolated particles (e.g., quantum dots), embedded in the hole conductor at its interface with the electron conductor.

For ETA cells, a p-i-n mechanism (cf. a-Si solar cells in ref 17) is often invoked.[16,18] For a continuous absorber layer, this description is reasonable. In this picture (see Figure 2A), a relatively insulating thin semiconductor film (i) is sandwiched between an n- and p-type semiconductors (electron and hole conductor, respectively). The n- and p-type semiconductors should be heavily doped compared with the insulator, and therefore, the work function difference between them results in an electric field across the insulator. In some cases, it is quite possible that there is some field in the electron conductor, which often is itself lightly doped, particularly for relatively wide ZnO nanorods. The hole conductor is usually fairly heavily doped, but even here, some small contribution to the photovoltage may occur from "photodoping" by holes.

If the layer is discontinuous (e.g., the absorber is in the form of colloidal quantum dots or, as frequently occurs, a cluster-type deposition of the absorber; Figure 2B), then several fundamental differences to the previous (p-i-n) model apply. One is that the hole and electron conductor will be in contact to some extent. Whether or not this is a problem depends on the diode characteristics of the electron/hole conductor interface. We discuss this below for the TiO_2/CuSCN interface. Another difference is that screening of the absorber particles by the hole conductor will be more efficient, because of contact between the particles and hole conductor over much of the particle area. A third effect is that the fact that the hole conductor/absorber/electron conductor and hole conductor/electron conductor junctions acting in parallel can change the band picture from a (likely) p-i-n junction to a junction that is a mixture of the two or may be dominated by one or the other of the two extremes. As an example of a specific difference between the two morphologies, in the continuous layer model, a change of potential at the absorber interface with the hole conductor after deposition of the hole conductor will shift the absorber and the electron conductor energy levels equally (unless the absorber is very thin indeed). For the discontinuous absorber morphology, however, there may be no or little linkage between how bias on the hole conductor affects the absorber energy levels and those of the electron conductor.

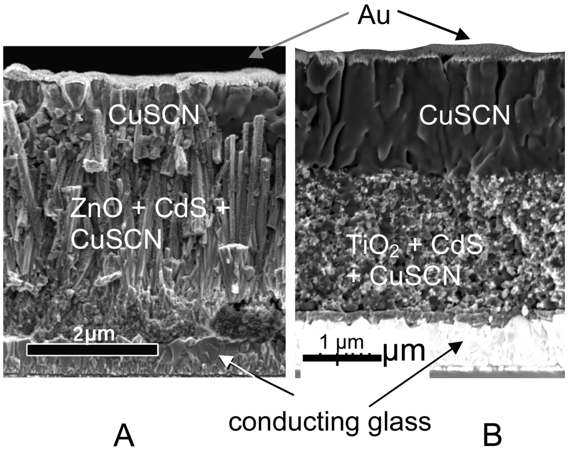

FIGURE 3. SEM cross-section images of (A) ZnO/CdS/CuSCN and (B) TiO_2/CdS/CuSCN cell. A dense ZnO or TiO_2 layer (not labeled) is deposited between the conducting glass and the corresponding nanoporous oxide layers.

Cell Assembly

As already noted, the main rationale for ETA cells (and SSSCs in general) is that semiconductors of lower quality (lower "cost") and of different composition (more readily available/composed of abundant materials) than those commonly used can serve as absorber. This rationale fits our long-term emphasis on cheap solar cell fabrication. Starting with commercial F-doped tin oxide (FTO) conducting glass, we use liquid processing methods for almost all the various stages of the cells. While at present we still use vacuum deposition for the final Au electrode evaporation, solution methods, such as electroless deposition, can replace this.[19] It is therefore worth briefly describing how we fabricate these cells in general.

Figure 3 shows cross sections of a ZnO nanorod-based cell (A) and a TiO_2 nanoparticle-based cell (B), both using CuSCN as hole conductor. Cell fabrication begins with the FTO substrate, through which the cell will be illuminated. A thin (typically ca. 100 nm) dense layer of the required oxide is deposited on the FTO. This is essential in ETA cells to prevent shorting between the *solid* hole conductor and the FTO; it is usually less critical for a *liquid* hole conductor, where shorting depends not only on physical contact but also on the electrochemical behavior of the liquid/FTO interface.

For TiO_2 cells, we deposit the dense TiO_2 layer by spin-coating five layers of a titanium isopropoxide sol, intermediate annealing between layers, and annealing in air.[20] For ZnO cells, we often deposit the dense ZnO layer together with the porous ZnO in a single deposition, and this will be discussed separately below.

Next the nanoporous TiO_2 is deposited, also by spin-coating, but this time from a paste of commercial TiO_2 particles of average size 25 nm (Degussa P25) and annealed again.[21,22] This is the same TiO_2 normally used for the DSSC, which is typically made in the same manner or by doctor blading. ETA cells made with such nanoporous TiO_2 have been reported to give poorer performance than those made with larger TiO_2 particles, a result that is attributed to poor penetration of the solid hole conductor into the small pores.[23] We find no improvement for cells made with the larger particle size. The porous ZnO layer, as noted previously, will be discussed separately.

The absorber layers (we used CdS, CdSe, Sb_2S_3, and $Cu_{2-x}S$) are mostly deposited by chemical bath deposition (CBD).[24] CdSe is often deposited also by electrodeposition from a selenosulfate bath.[25] $Cu_{2-x}S$ is prepared by simple solution ion exchange between the CB-deposited CdS and a Cu^+ solution.[21] The absorber layers on the nanoporous oxide may be further annealed. When CuSCN is used as hole conductor, the absorber is treated with an aqueous solution of KSCN or LiSCN before deposition. Larramona et al. described this treatment for TiO_2/CdS/CuSCN cells and showed that the treatment reduces the cell resistance.[23] We confirm this finding, not just for that cell, but for both TiO_2 and ZnO electron conductors and for all absorbers that we used. The SCN- treatment has no effect on cells using spiro-OMeTAD as hole conductor and was not needed in these cells.[26] While practically this is an important beneficial step, how it works is not clear-cut. Several possible reasons were suggested,[23] one of which was doping of the CuSCN, which we view as the most likely reason.[22] Unpublished experimental work of ours supports this explanation. More specifically, we find the doping effect in the CuSCN inside the cell pores rather than in the ~1 μm bulk CuSCN on top of the cell (see below).

In many cases, a "buffer" layer is deposited between the absorber and oxide, the function of which varies, as discussed below. We mostly use CBD In(OH)S for TiO_2 cells and ZnS (formed by ion exchange) for ZnO cells.

The hole conductor (mostly CuSCN) is deposited by slowly dripping a di-*n*-propyl sulfide solution of CuSCN into the absorber/oxide composite on a hot plate.[27] The CuSCN infiltrates into the porous structure, and enough is added to also form a ~1 μm layer on the oxide/absorber/CuSCN composite. Finally the Au top contact is evaporated onto the CuSCN.

ZnO Layer

In contrast to the nanoporous TiO_2, for which we follow standard procedures, we developed a special CBD technique for ZnO deposition, which gives us better performance than more standard techniques. The method is based on an alkaline ammonia/ethanolamine bath and $KMnO_4$-treated substrates, forming manganese oxide nuclei on the substrate, acting as nucleation promoters for ZnO.[28] ZnO does not nucleate readily and most reports on CBD ZnO nanorods describe nucleation on a nanocrystalline ZnO layer, previously deposited by a different method. We showed how certain "impurities" (Fe, Mn) in the deposition solution, can *in situ* form iron or manganese oxide nuclei on the substrate, which act as efficient nucleation centers for ZnO growth,[29] and extended this to pretreatment of the substrate with $KMnO_4$. Adding a Sb salt to the ZnO deposition solution results in ZnO nanorod deposition on a very effective dense ZnO layer with ~5 nm particle size.[30]

Buffer Layers

"Buffer" layers between the oxide and absorber have often been found to be beneficial for ETA (and other nanoporous) cells, in particular for low bandgap absorbers. They were used effectively for $CuInS_2$,[31] PbS,[32] and by us for $Cu_{2-x}S$[21] absorbers. The purpose of these layers was, at least initially, to reduce recombination. There are various ways in which they could do this and these are discussed by Grasso and Burgelman (for $CuInS_2$-based cells, but their arguments are general).[33] In_2S_3 or In(OH)S have been used most commonly for this purpose. In the case of our $Cu_{2-x}S$-based cells, the CBD In(OH)S buffer layer resulted in a major improvement in all three cell parameters. The exact reason for this improvement is still open for discussion: We originally thought that it reduced recombination by preventing direct contact between the TiO_2 and CuSCN, but we now consider it more likely that the larger distance between the electrons injected into the TiO_2 and holes remaining in the $Cu_{2-x}S$ reduces the recombination by decreasing the Coulomb attraction between them. An additional adsorbed dodecylphosphonate monolayer further improved the total cell efficiency somewhat by reducing surface recombination (as measured by increased electron diffusion length in the TiO_2), although with a small reduction of V_{OC}, caused by a decrease in the system work function, presumably because of interface dipole effects of the monolayer.

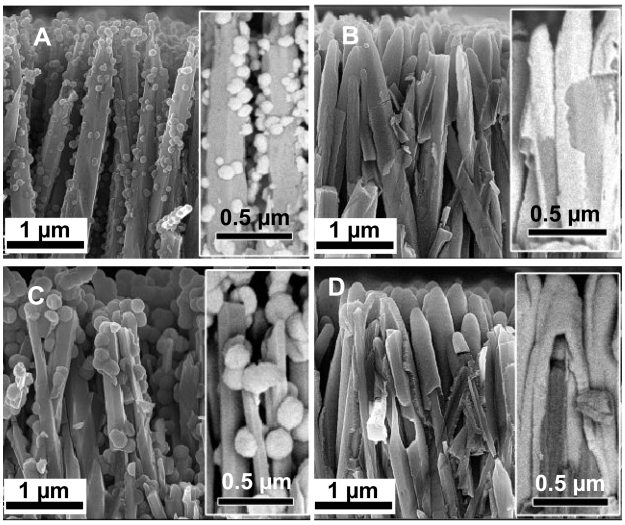

FIGURE 4. SEM cross sectional images showing the effect of sulfide treatment on ZnO surface coverage by (A,B) CBD CdS or (C,D) CBD CdSe. Insets are higher magnification backscattered images to show element contrast. (A,C) non-treated; (B,D) treated. The insets for the sulfide-treated samples have been deliberately chosen to show broken CdS(e) layers because the coverage is so conformal that the layers would not be readily visible. Adapted from ref 37.

The buffer layer between oxide and absorber can also act as a nucleation enhancer for deposition of the absorber. We employed CBD In(OH)S for this purpose in Sb_2S_3/TiO_2-based cells, using both CuSCN[22] and spiro-OMeTAD[26] as hole conductors. CBD on In(OH)S allows for faster and more homogeneous Sb_2S_3 than Sb_2S_3 deposition directly on bare TiO_2. However, there is no evidence that it influences the cell performance, except possibly increasing its long-term stability because we made comparable cells without this buffer (actually nucleation) layer. Larramona et al. made very good TiO_2/Sb_2S_3/CuSCN cells without this nucleation layer.[34,35] They do note that the Sb_2S_3 forms as relatively large (100–200 nm) clusters in the porous network, but this does not appear to impact the cell performance negatively. In fact, we made similar large cluster ETA cells using CdSe instead of Sb_2S_3 (unpublished) and obtained $V_{OC} > 800$ mV, indicating that the TiO_2/CuSCN direct contact is not a problem, because if it were, it should degrade V_{OC}. We also used a nucleation layer of CdS for $TiO_2/CdSe/S_x^{2-}$ liquid junction SSSCs,[36] although it is possible that the CdS performed additional functions in these cells. A CdS buffer layer is now commonly used in liquid junction CdSe-based SSSCs.

In our ZnO-based ETA cells (also in liquid junction cells), the ZnO nanorod films that comprise the nanoporous substrate in these cells are treated with a sulfide solution to form a coherent, controlled-thickness (several angstroms to several nanometers) ZnS layer on the ZnO nanorod surface.[37]

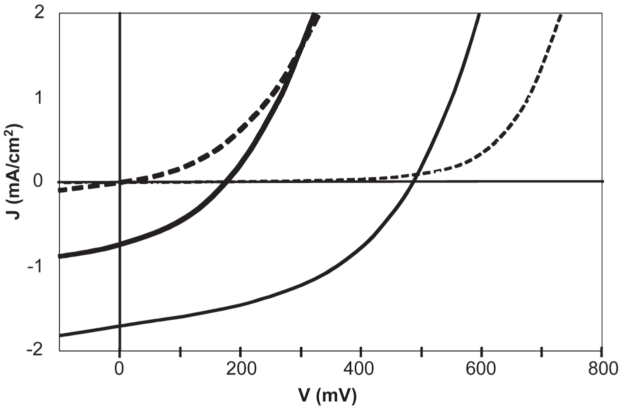

FIGURE 5. Best current–voltage curves of sulfide-treated (thin lines) and nontreated (thick lines) ZnO/CdS/CuSCN cells in the dark (dashed lines) and under 1 sun illumination (full lines). Reproduced from ref 37. Copyright 2010 American Chemical Society.

The effect of this treatment can be seen in Figure 4, which shows CBD CdS and CdSe deposited on ZnO nanorods before (A,C) and after (B,D) sulfide treatment. The CdS or CdSe deposited on the untreated ZnO form isolated clusters, while the deposits on the treated ZnO yield very homogeneous CdS and CdSe coverage. This difference is reflected in ETA cell behavior. Figure 5 shows our *most* efficient CdS cells for both nontreated and treated ZnO. The difference, seen in all parameters and also in the dark characteristics, is outstanding. There is clear contrast between the clustered absorber cells on TiO_2, where clustering is not necessarily a problem, as noted earlier, and those on (untreated) ZnO. The ZnO/CuSCN junction is substantially less blocking (in terms of diode behavior) than the TiO_2/CuSCN junction. Quite possibly the sulfide treatment may have other effects on cell performance, apart from the better absorber coverage. For example, the ZnS layer might act as a conventional buffer layer to reduce recombination by reducing electron (in ZnO)/hole (in absorber) recombination through reduced Coulomb attraction.

While the improvement we find in absorber coverage for sulfide-treated ZnO is valid for absorbers made by CBD, one of the most common methods of absorber deposition, this is not necessarily the case for other methods of deposition. For example in SILAR (dip-coating, where deposition occurs by sequential anion and cation dips with intermediate rinsing), the anion (usually sulfide) dip is qualitatively the same as the sulfide treatment, and therefore good coverage on untreated ZnO is also found by this method.

Semiconductor Absorber

We used four different absorbing semiconductors in our research: CdS, CdSe, Sb_2S_3, and $Cu_{2-x}S$. Each of these absorbers was chosen for specific reasons. In keeping with emphasis on low-cost methods, and using our expertise in deposition techniques, all of these absorbers are deposited by solution methods.

CdS was chosen specifically for most of our work on ZnO, as a reproducible absorber while learning how to deposit the ZnO layers by CBD, as well as a good standard absorber in general. It was also used as a precursor for our $Cu_{2-x}S$ cells.[21] While CdS has a relatively high bandgap and is not suitable for (single bandgap) high-efficiency solar cells, it has the advantage of reproducible preparation by a variety of solution methods.

CdSe was an obvious choice, both because of our long-ranging experience with this material for solar cells and its deposition by solution methods, going back to the mid 1970s,[38] and because it has a reasonable bandgap for solar cell use. It was used commonly in liquid junction cells long before the advent of the nanoporous cells. CdSe was the semiconductor used for our first ETA cell, then using electrodeposited ZnO (with the group of Claude Levy-Clement)[25] and for our first liquid junction SSSC.[36]

Sb_2S_3, with a bandgap similar to CdSe, was initially chosen as a buffer layer for ETA cells. This was because CBD Sb_2S_3 as-deposited is normally amorphous and we thought that it might form a homogeneous coating on TiO_2 for use in $Cu_{2-x}S$ cells, since there should be no issues of lattice mismatch. While it behaves very poorly as a buffer layer (although as-deposited, it does form a homogeneous coating) and also as an absorber as-deposited, after annealing, it gives very good cells, in particular, high photon-current quantum efficiencies (up to ~80% external and essentially 100% internal) with high short circuit photocurrent densities.[22,26] A likely major reason for this high performance is that Sb_2S_3 melts at the annealing temperature of 300 °C (see Figure 1 of ref 26). While the bulk melting point of Sb_2S_3 is 550 °C, this temperature is obviously strongly depressed due to the small particle size of the as-deposited material and the fact that a relatively large fraction of the material is surface and surface melting can occur considerably below bulk melting, the Tammann temperature, which is roughly 2/3 of the bulk melting point in degrees Kelvin (~275 °C).

Another important issue we found with Sb_2S_3 is that surface oxidation (to antimony oxide) forms a passivation layer, reducing recombination,[22] although the mechanism of the passivation is not clear; we are presently investigating which of the several possible explanations for this passivation is the correct one(s). Improvement in cells was reported after light soaking and attributed to oxygen, with passivation of the Sb_2S_3 through oxidation one of the potential causes.[35] Our cells usually improve with aging (with or without light), even though the Sb_2S_3 is deliberately oxidized from the start.

$Cu_{2-x}S$ was chosen because it is normally considered to be a "poor quality" (high recombination) semiconductor. This may be connected with the difficulty in obtaining (and maintaining) a high (Cu) stoichiometry for this material. As such, it appeared, to us, to be an ideal choice to test the concept that ETA cells would allow such poor quality material to give good cells. In fact, we were unable to make cells above 0.07% overall efficiency.[21] However, the fact that by interface engineering using buffer layers and adsorbed monolayers, we were able to effect major improvements in this cell indicates that further major improvements may be forthcoming with a dedicated effort.

Present State of ETA Cells and Prognosis for the Future

Table 1 gives a list of relatively high efficiency ETA cells, showing how they have developed over the past years. The acceleration in the rate of improvement over the past few years is clearly visible. In this aspect, the ETA cell parallels the more established and more studied organic PV cells but at a lower efficiency level. CuSCN has been the most popular hole conductor as this list shows. However, there is an increasing tendency to use alternate hole conductors, in particular organic ones. The variety of suitable hole conductors is limited at present, and this is one area where research is needed, both to identify new hole-conducting materials and to make those that are presently used more conducting. Electron conductors remain limited to TiO_2 and ZnO, a situation that leaves this part of the cell open to creative new ideas, but the fact that these are cheap and environmentally benign materials will complicate finding competitive alternatives. While understanding of ETA cells is improving, there is still much that is not known. Experimentally measured energy level diagrams of actual cells, taking into account the possible effects of one layer on the ones buried under it, are badly needed and this is a major effort of ours these days. Kinetic measurements to determine charge transport properties and charge lifetimes in the various phases, commonly used for the DSSC, are less common for ETA cells. Also, we need more emphasis on operational stability studies, that is, stability under actual operating conditions because only a few studies have treated this aspect until now. From the cell design aspect, while all present cells are made by depositing the oxide electron conductor on an FTO substrate, followed by absorber and then hole conductor deposition, there is no fundamental reason why this should not be reversed; that is, a porous hole conductor is deposited first, followed by absorber and then electron conductor. This would allow a wider range of processing conditions to be used. For example, transparent hole conductors that require (at present) relatively high-temperature processing in air that is likely to degrade the absorber (e.g NiO or, even more so, $CuAlO_2$ and related delafossite compounds) could be more readily used, since the absorber would be deposited after the hole conductor processing. Since good three-phase cells have been reported with light-absorbing hole conductors and a separate absorber,[4] one can envision using light-absorbing electron conductors. Indeed, depending on the cell geometry, all three phases might be absorbing. All these options can significantly widen the choice of the charge-conducting phases, which at present is rather limited.

The combination of better understanding of the operation of these cells, together with increased experimental expertise and experience, both of present groups in the field and new ones entering it, presents a positive outlook for progress in the cells. However, there are still plenty of challenges. We consider two of these to be the following:

- Can appreciably lower quality absorber material be used, that is, does the central idea behind these cells hold? This question has yet to be conclusively answered.
- Will small offsets ($0.1-0.2$ eV) between absorber conduction and valence bands and corresponding electron and hole conductor bands, to minimize voltage losses, provide sufficient driving forces to allow high photocurrents?

We thank Leeor Kronik for useful discussions. We thank the Wolfson Family charitable Foundation, a research grant from Monroe and Marjorie Burk (D.C.) and from Rowland and Sylvia Schaefer (G.H.), the Nancy and Stephen Grand Center for Sensors and Security (D.C.), and the GMJ Schmidt Minerva Centre for Supramolecular Architecture. We acknowledge the Harold Perlman family's historic generosity. D.C. holds the Schaefer Chair in energy research.

BIOGRAPHICAL INFORMATION

Gary Hodes (B.Sc. and Ph.D. in Chemistry from Queen's University, Belfast) is a professor at the Weizmann Institute of Science. He studies semiconductor-sensitized solar cells and solution deposition of semiconductors, with emphasis on the use of these semiconductors in the solar cells.

David Cahen (B.Sc. Chemistry & Physics, Hebrew University; Ph.D. Materials chemistry, Northwestern University, postdoctoral studies in photosynthesis at the Hebrew U. and Weizmann Institute of Science) is a professor at the Weizmann Institute of Science. He works on solar cells, hybrid molecular/nonmolecular materials, how (bio)molecules can serve as electronic current carriers, and what possibilities they provide for novel science.

FOOTNOTES

*To whom correspondence should be addressed. E-mail: gary.hodes@weizmann.ac.il.

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