Design of solar cell materials via soft X-ray spectroscopy

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ABSTRACT

This overview illustrates how spectroscopy with soft X-rays can assist the development of new materials and new designs for solar cells. The starting point is the general layout of a solar cell, which consists of a light absorber sandwiched between an electron donor and an electron acceptor. There are four relevant energy levels that can be measured with a combination of X-ray absorption spectroscopy and photoelectron spectroscopy, as illustrated for an organic dye as absorber attached to a p-doped diamond film as donor. Systematic measurements of organometallic dyes (phthalocyanines and porphyrins) as a function of the metal atom are presented for the metal 2p and N 1s absorption edges. In combination with density functional theory one can discern trends that are useful for tailoring absorber molecules. A customized porphyrin molecule is investigated that combines an absorber with a donor and a linker to an oxide acceptor. The bridge to device fabrication is crossed by correlating spectroscopic features with the photocurrent in hematite photoanodes for water splitting. For speeding up the development of new materials and designs of solar cells a feedback loop between spectroscopy, theory, synthesis and device fabrication is envisioned.

1. Introduction

The search for clean energy is rapidly becoming one of the most pressing technological challenges. It is natural to tap into solar energy, the origin of most types of energy being used today, such as fossil, wind, and hydroelectric. Ideally, one would want to convert solar energy directly into electricity rather than using thermal energy as intermediate, such as in power plants and combustion engines. Electricity can be converted nearly lossless into any other type of energy, while conversion of thermal energy is limited by the Carnot efficiency. Such reasoning suggests solar electricity as the ultimate energy source.

Direct conversion of solar energy to electricity by photovoltaics is not yet financially competitive with traditional (polluting) energy sources, such as coal, oil, and gas, although photovoltaics has already obtained grid parity in specific locations [1]. Progress in photovoltaics has been achieved mainly by the Edisonian method of educated trial and error. Most of the R&D in industry has been restricted to the optimization of a specific design, such as silicon, CdTe, or CIGS (copper indium gallium selenide). Advances in cost per watt have been small compared to the rapid improvements in microelectronics exemplified by Moore's law, because solar cells cannot take advantage of miniaturization. Therefore, photovoltaics has not been a major contender for solving the energy problem, even though it is one of the cleanest possible sources of energy and has experienced enormous growth rates in favorable times, when fossil fuels became expensive. This situation calls for a new strategy, which accelerates the slow evolution of traditional concepts by considering a large variety of new materials and devices. They need to be winnowed down quickly to the most promising technologies.

This is where spectroscopy comes into the picture. It makes it possible to measure the energy levels that determine whether or
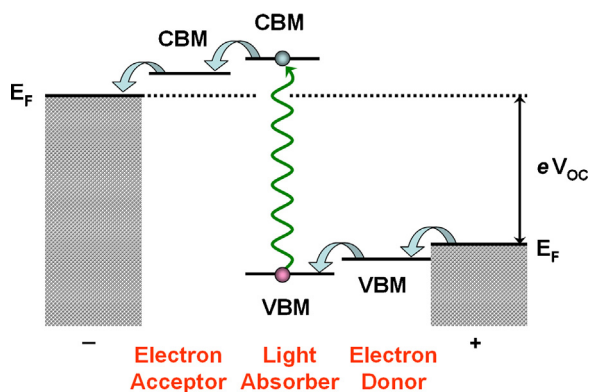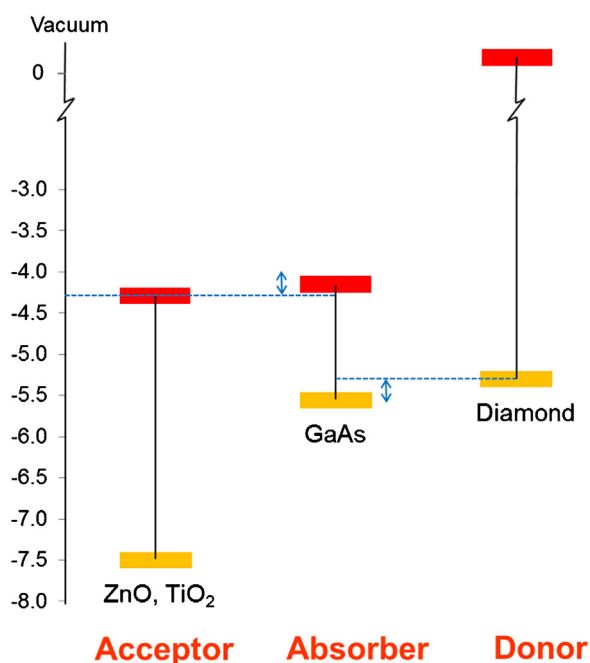
Fig. 1. Generic energy level diagram of a solar cell, consisting of a light absorber sandwiched between an electron donor and an electron acceptor. An example is the dye-sensitized solar cell. A traditional semiconductor solar cell combines all three functions in one material. Choosing three different semiconductors provides extra flexibility. A large energy drop between adjacent levels increases the photocurrent by speeding up carrier separation, but reduces the (open circuit) photovoltage V_{OC}.

Fig. 2. Example illustrating the design of a solar cell based on spectroscopic input about the energy levels. H-terminated p-type diamond is selected as donor and n-type ZnO or TiO$_2$ as acceptor. The desirable range for the band edges of the absorber is indicated by double-arrows. The bands are referenced to the vacuum level of the isolated materials (adapted from Fig. 2 of [5], with H-terminated diamond data from [6–8]). When interfaces react, this simple picture breaks down. The actual band offsets have to be determined spectroscopically, because it is very difficult to predict the structure of a reacted interface theoretically.

not a solar cell design has a chance to separate electrons and holes and thereby provide a photovoltage. Consider a generic solar cell, as shown in Fig. 1. It contains three essential parts, a light absorber, an electron acceptor, and an electron donor. Four energy levels need to be arranged correctly to pull the excited electron toward the acceptor and refill the hole with a donor electron. Using semiconductors, the valence band maximum (VBM) acts as donor, and the conduction band minimum (CBM) as acceptor. In a molecule the VBM corresponds to the highest occupied molecular orbital (HOMO) and the CBM to the lowest unoccupied molecular orbital (LUMO). Both semiconductors and molecules will be considered here.

In order to separate the electron–hole pairs excited by the photons, a small energy drop is needed between the CBM of the absorber and the dye, as well as between the VBM of the donor and the absorber. The open circuit output voltage V_{OC} is maximized by minimizing this energy drop. But for maximizing the current one needs a large energy drop, which separates electrons and holes rapidly and thereby prevents recombination. Optimizing the voltage–current product requires a delicate trade-off in the spacing of adjacent energy levels. A desirable range of band offsets is indicated by blue double-arrows in Fig. 2.

In the generic solar cell of Fig. 1, each of the three parts can be optimized separately, but in a standard silicon solar cell these functions are all combined into one elemental material. That provides little room for innovations. Dye-sensitized solar cells (or Grätzel cells) are more flexible by separating the three roles [2–5]. Typically, TiO$_2$ nanoparticles act as acceptor, a redox electrolyte as donor, and organic dye molecules absorb sunlight. Those can be tailored in many ways by organic chemistry. Interestingly, the trade-off between maximum voltage and maximum current is handled asymmetrically in a typical Grätzel cell (see the energy diagram in Fig. 3 of [5]). The voltage drop between dye and acceptor is very small, but about half of the cell voltage is lost between the donor and the dye. The small voltage drop on the acceptor side keeps the excited electrons lingering near their holes. A large voltage drop is needed on the donor side to fill the holes before recombination takes place. It remains to be investigated whether a symmetric or asymmetric voltage drop is best for optimizing the power product.

Here we envisage an even more general design, where any of the three components can be molecular, liquid, or solid state. Although it is riskier to stray from proven avenues, such as semiconductor pn-junctions, this strategy opens up a much larger playing field for finding truly innovative combinations. It will take extra work, though, to refine a new design to the same level as traditional

pn-junctions. For example, dye-sensitized solar cells have not yet reached the efficiency of Si solar cells, despite their more flexible design. But they use much less energy during their fabrication and thus have an intrinsic cost advantage over silicon.

To be specific, we discuss in Fig. 2 the design of an all solid-state solar cell consisting of three semiconductors. It uses a p-type diamond film as inert donor, GaAs as absorber, and n-type ZnO or TiO$_2$ as acceptor. The conduction band minima are shown in red and the valence band maxima in yellow. The simplest model for obtaining the positions of the band edges uses their positions relative to the vacuum level in an isolated solid ("electron affinity model"). For ZnO, TiO$_2$, and GaAs these are taken from Fig. 2 of [5], and for diamond from [6–8]. This is equivalent to the Schottky Model for semiconductor–metal junctions. For Schottky barriers several more sophisticated models have been developed that take the specific nature of the interface states into account. These have counterparts for explaining band offsets at heterojunctions.

The main difficulty in predicting accurate Schottky barriers and band offsets is the unknown arrangement of the atoms near the interface. Growth and annealing conditions determine the interface bonds and cause interdiffusion. Interface dipoles are generated which create a potential step across the interface. Various spectroscopic methods make it possible to determine Schottky barriers and band offsets experimentally. The valence band maximum is obtained relative to the Fermi level by photoelectron spectroscopy. Likewise, the conduction band minimum can be determined relative to the Fermi level by inverse photoemission or two-photon photoemission. In addition, one can probe the band edges relative to a core level. The valence band maximum is probed by X-ray emission spectroscopy and the conduction band minimum by X-ray absorption spectroscopy. These results can then be combined with X-ray photoelectron spectroscopy of the core level to relate the band edges to the Fermi level.