

Perspective: Hybrid solar cells: How to get the polymer to cooperate?

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Lately, a lot of attention has been paid to metal oxide-organic hybrid solar cells. In these devices, conjugated polymers replace the typically transparent hole transporter as usually used in solid-state dye-sensitized solar cells in order to maximize the photon absorption efficiency. However, to unleash the full potential of hybrid solar cells it is imperative to push the photocurrent contribution of the absorbing polymer.

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The tremendous success of dye-sensitized solar cells and organic photovoltaic as low-cost alternative to conventional silicon-based photovoltaic has led to the introduction of hybrid metal oxide-polymer solar cells.¹ Hybrid solar cells combine high surface area n-type metal oxide electrodes with hole transporting conjugated polymers. Most commonly, a thin film of sintered TiO₂ nanoparticles with diameters around 20 nm is used as n-type electrode, similar to the TiO₂ nanostructures employed in dye-sensitized solar cells. Frequently, ZnO is used instead of TiO₂, which is chemically less stable but exhibits similar energy levels and typically shows higher charge carrier mobilities. Besides particle films, also ordered nanostructures such as nanowire and nanotube arrays have been employed. The nanostructured metal oxide film can be decorated with a self-assembled monolayer of dye, which enables rapid electron injection into the metal oxide upon photon absorption. Alternatively, the metal oxide can be coated with a thin layer of an inorganic absorber like crystalline Sb₂S₃ or CdSe.² As polymeric compound of a hybrid solar cell, materials known from organic photovoltaic are employed, most commonly poly(3-hexylthiophene) (P3HT).

Metal oxide-polymer hybrid solar cells have reached power conversion efficiencies close to 4% with dye-sensitized TiO₂ and 6.2% with Sb₂S₃ as absorber coating on TiO₂ nanoparticle films.³ These efficiencies are impressive considering that hybrid solar cells are a relatively new technology. However, compared to dye-sensitized solar cells, which have reached efficiencies well above 12%, and organic polymer-fullerene solar cells with close to 10% there appears to be room for drastic improvements.⁴ In dye-sensitized solar cells the TiO₂ forms a highly connected network, which allows the charges to be transported to the electrodes after electron injection from the excited dye. However, the overall absorption is limited unless very thick TiO₂ electrodes are employed. Infiltration of the hole transporter into the TiO₂ electrode is challenging, which limits its thickness to a few μm. Higher extinction coefficients are provided by the active films of organic solar cells, which consist of a blended structure of conjugated polymers and fullerenes. However, the thickness of the active layers usually has to be about 100 nm in order to allow loss-free charge transport through the active layer due to its uncontrolled internal morphology.

The hybrid solar cell concept combines the advantages of dye-sensitized and organic solar cells, i.e., consistent charge transport pathways through a nanostructured metal oxide electrode and high extinction coefficients due to absorbing polymers as hole transporters. However, their full potential has not been unleashed. The main reason is that the advantage of the polymeric hole transporter is not exhausted yet. In many cases the polymer serves only as hole transporter and does

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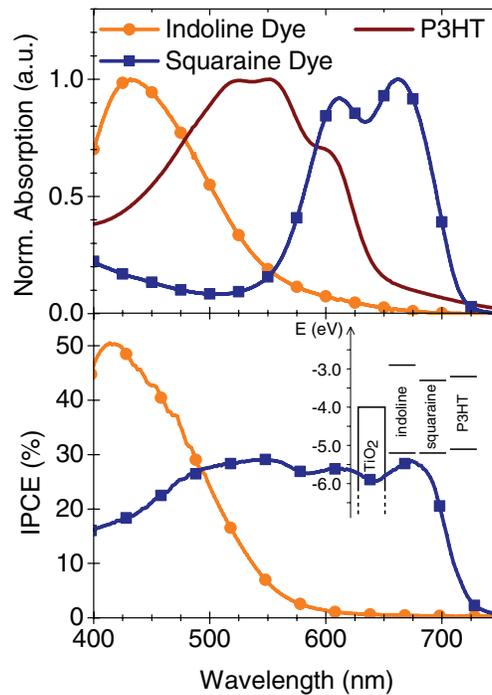


FIG. 1. The upper graph shows the normalized absorption spectra of the photoactive materials. Normalized incident photon to current conversion efficiency (IPCE) spectra (lower plot) for hybrid solar cells with dye-sensitized TiO₂ nanoparticle films infiltrated with P3HT as hole transporter.

not contribute to the photocurrent generation, although it is absorbing a significant fraction of the incident photons. The photocurrent is then mainly generated by the dye. This is reflected in only moderate photocurrents compared to other solar cell architectures. Although this issue has been addressed by different groups,⁵ literature is not always explicit about the origin of the photocurrent.

However, in order to take advantage of the hybrid solar cell concept it is imperative to seek combinations of dyes and polymers which allow both absorbing compounds to play an active role in the photocurrent generation. To illustrate this, we fabricated hybrid solar cells from sintered TiO₂ nanoparticle films (thickness 500 nm) using an indoline and a squaraine dye as sensitizer in combination with P3HT as the polymeric compound. As shown in Figure 1, the incident photon to current conversion efficiency (IPCE) spectrum for the hybrid solar cell with the indoline dye clearly shows that the polymer does not contribute any photocarriers. The reason is that electron injection from the polymer into the dye is energetically unfavorable due to its higher lowest unoccupied molecular orbital. In contrast, for the squaraine dye the IPCE clearly features dye and polymer contribution. Note that even though the peak IPCE is higher with the indoline dye the resulting short circuit density under AM 1.5G illumination is 4.6 mA cm⁻² compared to 3.4 mA cm⁻² for the squaraine and the indoline dye, respectively.

The generally higher potential of such a dye-polymer couple is directly apparent as the incoming light is converted into current over a broad spectral range. High short circuit currents can only be achieved if both dye and polymer contribute, ideally in complementary spectral regions. In contrast, if the dye blocks photocurrent contribution from the polymer, photons absorbed by the polymer are lost for charge generation and any spectral overlap between polymer and dye absorption reduces the short circuit current.

Therefore, the first approach to boost the photocurrent contribution of the polymer is to directly match energy levels of the polymer and the dye. This fosters charge separation via electron injection into the dye and hole transfer to the polymer. The tremendous potential of energy level tuning has been demonstrated using a model system of cyanoacrylic acid-based interfacial modifiers in TiO₂-P3HT hybrid solar cells.⁶ By shifting the energy levels of the sensitizer the photocurrent contribution

of the polymer can be directly switched on and off and the device efficiency is boosted from 0.6% for a blocking sensitizer to 2.9% for a sensitizer allowing polymer photocurrent contribution.

As an alternative to direct charge transfer, the photocurrent contribution of the polymer can also be activated via an energy transfer from the polymer to the sensitizer. Upon photon absorption in the polymer the excitation energy can thus migrate to the dye, followed by electron injection into the metal oxide and hole transfer to the polymer. Such a mechanism has been proposed for a combination of P3HT with a porphyrine dye, which allows outstandingly high short circuit current densities beyond 12 mA/cm^2 , four times more than with a transparent hole transporter.⁷

Furthermore, for crystalline polymers like P3HT the orientation of the polymer at the interface plays an important role in the charge generation process, since it influences the contact between the photoactive materials as well as local charge carrier mobilities. Recently, it has been shown that face-on orientation of P3HT on TiO_2 can be achieved by modification of the hybrid interface with mercaptopyrindines, which directly enhances the photocurrent contribution of the polymer.⁸

With a tremendous amount of research concerned with hybrid solar cells there is the potential that optimized dye-polymer combination will be found, allowing efficiencies exceeding 10%. As discussed, an ideal dye for hybrid solar cells has to be matched to the employed polymer and plays multiple roles. For a high efficiency solar cell the sensitizer should

- exhibit a high extinction coefficient and absorb complementary to the polymer;
- have suitable energy levels to foster photocurrent contribution from the polymer, either via charge injection or energy transfer from the polymer to the sensitizer;
- induce favorable orientation of the polymer at the interface.

If these requirements are kept in mind when searching for new dye-polymer combinations, efficiencies outperforming dye-sensitized solar cells and organic photovoltaic are a realistic goal.

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