

Charge separation in nanoscale photovoltaic materials: recent insights from first-principles electronic structure theory

Yosuke Kanai,^a Zhigang Wu^b and Jeffrey C. Grossman^{*c}

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In this feature article we focus on the key problem of charge separation in nano-scale photovoltaic materials; in particular recent theoretical/computational work based on first principles electronic structure approaches is presented and discussed. We review applications of state-of-the-art electronic structure calculations to nano-scale materials that enable charge separation between an excited electron and hole in so-called excitonic photovoltaic cells. Emphasis is placed on theoretical results that provide insight into experimentally observed processes, which are yet to be understood and do not appear to obey a single unique model but rather depend on atomistic details. Examples are provided that illustrate how computational approaches can be employed to probe new directions in materials design for inducing efficient charge separation. We also discuss the computational challenges in electronic structure theory for reliably predicting and designing new materials suitable for charge separation in photovoltaic applications.

1. Introduction

The conversion of sunlight directly into electricity efficiently and inexpensively is considered one of the most promising approaches to provide renewable/clean electricity. However, the predominant technology in use today, based on materials made of large-grain silicon crystals, is at a significant economic disadvantage when compared to other sources of power generation.¹ It is therefore of great interest to explore whether comparable photovoltaic (PV) efficiencies can be achieved using

different types of materials that are inexpensive and have the potential for global-scale production. From the point of view of fundamental scientific understanding, this problem presents significant challenges since there remain a number of key gaps in our understanding of the basic PV conversion mechanisms that govern the efficiencies of these materials; filling these gaps will be critical for advancing the technology.

Nano-materials may be ideal for PV applications, as their optical and electronic properties can be tailored by controlling the material size, shape, and surface while maintaining low cost.² At the same time, there are a number of novel physical phenomena that occur in these materials that must be fully comprehended before optimal designs or even new basic concepts for the solar cell can be developed. One promising class of “nanoPV” is the excitonic solar cell where excitons are more strongly bound in the active material compared to

^aCondensed Matter and Materials Division, Lawrence Livermore National Laboratory, Livermore, CA, 94550

^bDepartment of Physics, Colorado School of Mines, Golden, CO, 80401

^cDepartment of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, 02139. E-mail: jcg@mit.edu



Yosuke Kanai

Dr Yosuke Kanai obtained his PhD in theoretical chemistry from Princeton University in 2006 under the supervision of Professor Annabella Selloni and Professor Roberto Car. He was subsequently a Berkeley Nano-sciences and Nanoengineering Institute postdoctoral scholar at the University of California, Berkeley, working with Professor Jeffrey C. Grossman. He joined Lawrence Livermore National Laboratory in 2009 as Lawrence fellow in the

Condensed Matter and Materials Division, belonging to the Quantum Simulation Group.



Zhigang Wu

Zhigang Wu is an assistant professor of the Physics department at Colorado School of Mines. He received his BS (1995) from Peking University and PhD (2002) from the College of William and Mary in physics. His research focuses on first-principles computations of the electronic properties of materials, in particular, nano-materials, materials for renewable energy and materials under extreme conditions.

conventional PV cells. These excitons must be dissociated in order for charges (excited electron and hole) to be generated for PV operation.³

Thanks to a number of significant advances in first-principles quantum mechanical calculations over the past several decades, it is now possible to investigate materials at a very fundamental level, fully taking into account atomistic details and in some cases to predict and design new materials with desired opto-electronic properties. Such calculations therefore have an important opportunity to play a substantial role in this global-scale challenge, working together with experimental teams, to provide basic understanding while concomitantly allowing for greatly accelerated materials design and discovery. In this feature article, we review how first-principles computational approaches have been employed in this relatively new area of research, particularly for investigating the process of charge separation, *i.e.*, the dissociation of strongly bound excitons in the nano- and organic materials that generate the charges.

We begin by discussing photovoltaic processes from the standpoint of their basic electronic structure, followed by a discussion of the levels of accuracy that can be expected from electronic structure calculations with present algorithmic and computational capabilities. We then highlight how such calculations have been used recently to shed light on charge separation processes in existing nano-scale PV materials, and discuss how such calculations can be employed to predict/design novel nano-materials with efficient charge separation. We conclude with comments on the key computational and theoretical challenges related to this subject and examples of how they are being addressed. It is important to note that our focus here is on a limited number of works based on first-principles quantum mechanical calculations, and the readers are referred to other more comprehensive reviews for organic PV, where semi-empirical quantum mechanical modeling has been quite successful (*e.g.*, ref. 4).

2. PV processes from an electronic structure standpoint

Before discussing the specific process of charge separation, which is the focus of this article, we briefly examine conceptually the fundamental physical processes involved in the operation of

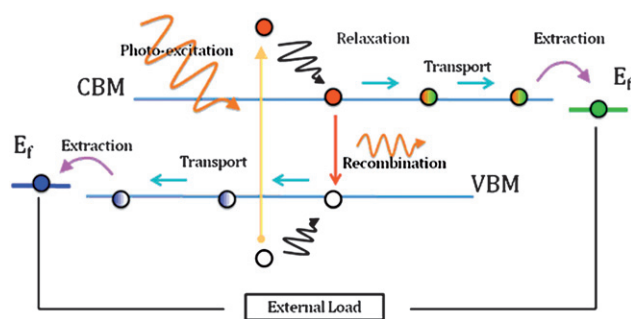


Fig. 1 Schematic of the physical processes involved in PV operation. See text for details.

photovoltaic cells from the standpoint of their fundamental electronic structure (Fig. 1).

The first step is the absorption of a solar photon by the active material, resulting in an electronic excitation in the material. From the representative Air Mass 1.5 solar flux spectrum,⁵ we note that photon absorption is a quite infrequent event on the nanoscale ($1\text{ }h\nu\text{ nm}^{-2}$ every \sim ms), even if a perfect absorption cross-section is assumed. It is therefore possible to describe the photo-excitation as primarily a single-photon absorption process. A useful conceptual framework for describing the physical processes operative in PV is the semi-classical description where the excited electron is viewed as a distinguishable particle with an explicit position. The subsequent physical processes are then also often described as a series of steps characterized by a single excited electron and the corresponding hole. It is important to remember, however, that quantum mechanical changes in the electron density upon excitation can only be identified as the probabilistic distribution of the “excited electron” (and the corresponding hole), which cannot be distinguished from other electrons.

In the next step, the excited electron and the hole are “relaxed” toward the conduction band minimum (CBM) and valence band maximum (VBM), respectively. This step corresponds to a process during which electronic energy is lost to thermal energy in the nuclei *via* electron–phonon interactions. In many bulk systems, such relaxation occurs quite rapidly; for example, in crystalline silicon this process occurs on the order of picoseconds or faster. The excited electron and hole interact with each other, screened by the surrounding electrons. The concept of an *exciton* is used to describe this attractive interaction, renormalizing the surrounding effects into an effective two-particle interaction. In many nano- and organic materials the excited electron and hole are tightly bound and therefore the exciton binding energy⁶ can be quite large (on the order of 1 eV), while in many bulk materials the exciton binding energy is small (a few meV in crystalline silicon⁷) compared to the thermal energy. An important consideration for PV cells based on nano- and organic materials is how the exciton can be dissociated into “free” charges, which can then be transported independently and in opposite directions through the active layer to the metal contacts. At the macroscopic scale and also in some interesting instances such as multi-exciton generation⁸ (an appealing theoretical concept yet to be realized in a working PV device⁹), one also needs to take into account the interaction among the excited electrons and holes,



Jeffrey C. Grossman

Jeffrey Grossman is a Professor of computational materials science in the Department of Materials Science and Engineering at the Massachusetts Institute of Technology. His research group develops and applies a wide range of theoretical approaches and computational methods to address problems in energy conversion, energy storage, nanomechanical phenomena, surface phenomena, and synthesis and assembly.

which inherently requires a treatment beyond independent excited electrons.

Once the excited electron and hole are separated (although the long-range electrostatic interaction may be still present), the next key step is charge transport. While effective mass theory often successfully describes charge transport in a crystalline material, a temperature-dependent hopping-type mechanism has been known to be operative in many organic materials¹⁰ and possibly also across interfaces between nano-materials. In some cases, as for the dye-sensitized solar cell (DSSC), the charges can also be transported by ions in electrolytes.¹¹

The last step is the extraction of the charges into the corresponding electrodes. Traditionally in semiconductor physics, concepts such as a Schottky barrier are used to measure how well the contact between the semiconductor and metal follows the ideal Ohmic behavior.¹² Another important consideration here is the selectivity of the electrodes for either the electrons or the holes, especially in PV cells based on a blend of two materials. In order to reinforce this specificity, charge blocking layers are employed in some cases to keep unwanted charges (*i.e.*, of the wrong sign) from going further toward the electrode by placing energetically unfavorable electronic states between the active material and the contact metal.¹³ In terms of electronic structure, alignment of the frontier energy levels (*e.g.* CBM/VBM) of the PV active layer with the Fermi energies of contacting levels dictates the current–voltage (*IV*) characteristic of such interfaces.

These physical processes compete with the undesirable recombination of the excited electron and hole in the active material. This presents a significant concern for PV cells based on nano- and organic materials where the exciton binding energy is considerably larger than in the case of bulk solids. The large exciton binding energy indicates a strong attraction in the active layer between the electron and hole, and the significant spatial overlap of the two results in a high recombination probability as long as the wave function symmetry does not prohibit such an electronic transition. Indeed in many organic materials the exciton travels as a single quasi-particle instead of the negatively charged excited electron and the positively charge hole independently.¹⁴ Concepts such as the exciton diffusion length, related to the lifetime of the excitons, play an important role in designing PV active layers. Therefore, one of the most crucial steps for excitonic solar cells, where the exciton binding energy is considerable, is *separating* the electron and hole efficiently so that recombination does not dominate. A “zeroth order” description of how such charge separation could be induced is illustrated in Fig. 2. This schematic represents a heterojunction interface of Type-II (staggered) energy-level alignment between two

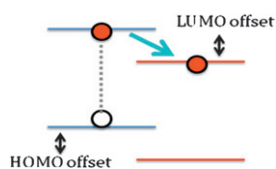


Fig. 2 Schematic of charge separation process in a Type-II (staggered) energy level alignment at a heterojunction of two different materials. The exciton, which strictly speaking cannot be presented in this single-particle description, undergoes dissociation across the interface. The red and white circles represent an excited electron and a hole, respectively.

materials, such that energetically the excited electron and hole prefer to spatially move to opposite sides of the interface. Understanding this charge separation process from experiments alone is a daunting task since only indirect information about the interfacial electronic structure can be obtained, and often the interpretation of the observation needs to assume a model. In this regard, first-principles calculations can provide much needed support in understanding the charge separation process *via* an accurate description of the electronic structure at these key interfaces.

3. Electronic structure calculations

Electronic structure calculations have been developed in both the condensed matter physics and quantum chemistry communities over many years. The maturity of so-called first-principles calculations, whose results do not depend on empirical parameters from experiments, has recently begun to allow their application in materials science. In particular, these methods are becoming indispensable where atomistic details are crucial for understanding and predicting the property–structure relations of a given material. Density functional theory (DFT) is arguably the most popular approach for investigating materials due to its balance between accuracy and applicability.¹⁵ In many research groups today, materials with several thousand electrons are routinely investigated and in some cases the properties of materials with more than 10,000 electrons have been computed using first-principles calculations based on DFT.¹⁶ An advantage of DFT is that the dynamical effects of both nuclei and electrons can be investigated within the existing frameworks of first-principles molecular dynamics¹⁷ and time-dependent extensions of DFT,¹⁸ respectively. These approaches can be combined together to address simultaneously the electronic structure evolution coupled with the motion of the nuclei.¹⁹ In recent years, there have also been significant advances in treating non-adiabatic couplings among different electronic states²⁰ and extended to first-principles molecular dynamics.²¹ As discussed below, such state-of-the-art calculations are beginning to play significant roles in advancing our understanding of excitonic PV materials.

However, it is important to emphasize that calculations based on DFT are not without shortcomings. A particularly important concern is that even though the so-called Kohn–Sham (KS) single-particle states of DFT are generally good approximations to the quasi-particle states (correctly describing the excitation due to electron addition or subtraction through the single-particle Green’s function by renormalizing the electronic many-body effects into a single-particle-like description²²), their single-particle energies are often considerably shifted such that the energy-gap is underestimated when standard approximations to exchange and correlation effects among electrons are employed.²³ It is therefore important to gauge the level of accuracy attained for a given calculated property, and whenever possible to validate the performance of DFT using the available experimental data. While understanding experimental observations and predicting *qualitative* behaviors are areas in which DFT can excel, designing novel materials with specifically tailored opto-electronic properties poses a challenge to the method because of the limited experimental comparisons available in such cases. In this regard, there are significant efforts to improve

upon traditional DFT calculations for obtaining accurate energy levels and excited state materials properties. Electronic structure calculations based on many-body perturbation theory (MBPT)²⁴ and quantum Monte Carlo (QMC)²⁵ are two examples of so-called “beyond-DFT” first-principles approaches, particularly relevant for obtaining accurate energy level alignments needed for understanding/predicting the optoelectronic properties of PV materials. These methods are considerably demanding computationally at the present time, although rapid advances in methodologies and computing platforms are encouraging for the prospect of employing such approaches more routinely in the future.

4. Understanding nano-scale PV materials

Herein, we first review several important first-principles theoretical works on the interfacial electronic structure in dye-sensitized solar cells (DSSC), which is one of the most widely investigated types of excitonic solar cell, both theoretically and experimentally. We then review our recent work on semi-conducting-polymer PV, emphasizing important differences with DSSC and their implication for designing materials interfaces for charge separation. In order to facilitate progress in the field from a theoretical standpoint, a thorough understanding of the existing interfaces that are known to be highly efficient for charge separation is an important asset. First-principles calculations are ideally suited for such investigations because an accurate description of the electronic structure can be obtained.

4.1 Dye-sensitized solar cell

The DSSC was proposed as a low-cost, high-efficiency alternative to conventional photovoltaic cells by O'Regan and Grätzel in 1991.²⁶ In DSSCs, a dye adsorbed on the surface of TiO₂ nanocrystals is photo-excited by a solar photon and the excited electron is transferred to the TiO₂ while the hole is left behind and subsequently transferred to a redox electrolyte (typically I⁻/I₃⁻). With some ruthenium complexes as the photon-absorbing dyes (such as tetraprotonated [*cis*-(dithiocyanato)-Ru-bin(2,2'-bipyridine-4,4'-di-carboxylate)]), an impressive power conversion efficiency of more than 10% has been achieved.²⁷

In most DSSCs, where dyes are weakly coupled to the TiO₂ nano-particles, the observed ultrafast electron transfer from the dye to the TiO₂ is often explained by a conventional non-adiabatic mechanism. This is because the unoccupied electronic states of the dye relevant for photo-excitation lie energetically deep within the conduction band (CB) of TiO₂. By invoking Fermi's golden rule, it is conceptually straightforward to realize that the excited electron within the dye has a very high total transition probability with semi-infinite accepting (final) states in the CB of the TiO₂, even if the coupling to each is small individually.²⁸ However, such a reasonable explanation does not necessarily mean that it is the unique model in general, and first-principles calculations have revealed that indeed the mechanisms involved in the charge separation process depend on atomistic details.

Prezhdo *et al.* explicitly addressed both adiabatic and non-adiabatic mechanisms of the electron transfer simultaneously using DFT.²⁹ In the adiabatic mechanism, the electron transfer

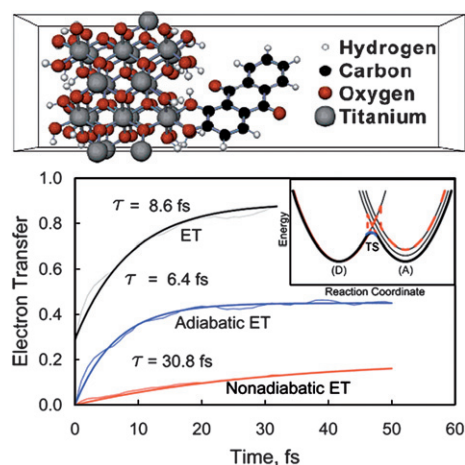


Fig. 3 An interface between alizarin and TiO₂ surface investigated in ref. 28 (top). Contributions to the excited electron transfer *via* adiabatic and non-adiabatic mechanisms as observed in first-principles dynamics simulations by Prezhdo and co-workers (bottom). Adapted with permission from ref. 28a.

takes place by remaining in the same (adiabatic) electronic state, and the electron transfer is sometimes accompanied with a small energy barrier associated with the nuclei motion. For the interface of alizarin/TiO₂, it was found that the adiabatic mechanism dominates over the non-adiabatic one, due to the strong coupling across the interface (Fig. 3). In this particular case, the LUMO of alizarin resides near the CB edge where the density of states is low, effectively repressing the non-adiabatic mechanism. As discussed in detail in their work,²⁹ such an understanding of the transfer mechanism is quite important for designing a new dye for DSSCs. In the conventional non-adiabatic transfer mechanism, the relaxation of the transferred excited electron within the TiO₂ CB toward the CBM results in the loss of electronic energy to heating of nuclei, thus a loss in the maximum obtainable open-circuit voltage (V_{oc}) for PV operation. However, if the adiabatic

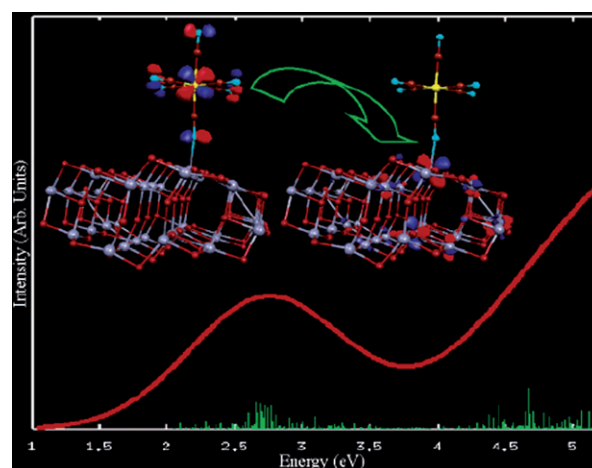


Fig. 4 The wavefunction change corresponding to a direct electron transfer upon photoexcitation from the molecule to TiO₂ surface and the optical spectrum obtained using time-dependent DFT calculations. The charge separation process does not involve photoexcitation within the molecule but results from the charge transfer excitation. Adapted with permission from ref. 29.

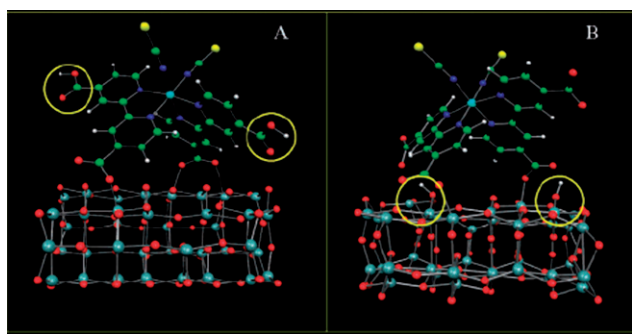


Fig. 5 An interface between TiO_2 and the N719 molecule without (left) and with (right) surface protonations. Hydrogen transfers from the molecule to the surface changes the excited electron transfer mechanism. See ref. 31 for details. Adapted with permission from ref. 31.

mechanism is operative, the LUMO of the dye does not have to be deep in the CB but rather near the CBM; therefore such a drop in V_{oc} can be prevented, potentially leading to higher power conversion efficiency.

In another first-principles investigation of a DSSC, De Angelis *et al.* studied the $[\text{Fe}(\text{CN})_6]^{4-}/\text{TiO}_2$ nano-particle interface (Fig. 4).³⁰ They provided detailed insights for an experimental observation³¹ that photo-excitation may cause a direct electron transfer from the dye to the CB of TiO_2 , contrary to the conventional mechanism where the electron is transferred subsequent to photo-excitation within the dye. The optical absorption spectrum computed using time-dependent DFT revealed that the relevant low-energy electronic transitions indeed originate from the Fe atom of the dye to a few Ti atoms at the surface, confirming the so-called metal-to-particle charge transfer mechanism of the photo-excitation to be responsible for the charge separation.

The role of surface protonation on the charge separation mechanism was also investigated for the interface between $[\text{cis}-(\text{NCS})_2\text{-Ru}(\text{II})\text{-bis}(2,2'\text{-bipyridine-4,4'}\text{-dicarboxylate})]$ (N719) and a TiO_2 nano-particle (Fig. 5).³² Upon adsorption of the N719 dye on the TiO_2 surface, two protons can either remain as part of the dye or be transferred to the surface. Without the surface protonation, the LUMO of the dye is only weakly coupled to the CB of TiO_2 ; thus the conventional non-adiabatic electron transfer mechanism must be operative for efficient charge separation. However, the calculations showed that surface protonation induces a very strong electronic coupling between the two through the unoccupied electronic states, indicative of an adiabatic mechanism for the excited electron transfer from the dye to the TiO_2 surface. This is an excellent example of how atomistic details can dramatically change the electron transfer mechanism, forcing one to reconsider the naïve idea of one mechanism for one system.

4.2 Semiconducting-polymer/fullerene

A highly promising class of PV nano-materials is that based on semiconducting-polymer/fullerene blends.³³ In particular, the $\sim 5\%$ power conversion efficiency reported for a poly-3-hexylthiophene(P3HT)/fullerene device is quite encouraging,³⁴ especially given that the P3HT phase absorbs only approximately 20% of standard AM1.5 solar photons due to the spectral

mismatch.³⁵ In P3HT/fullerene blend cells, an exciton formed within P3HT upon photo-excitation must travel to and reach an interface with fullerenes (such as [6,6]-phenyl-C61 butyric acid methyl ester (PCBM)) in order for the excited electron to spatially separate from its corresponding hole. Efficient charge separation at the interface (in addition to a fast diffusivity of the exciton in polymers)³⁶ is crucial for suppressing undesirable exciton recombination. This design derives from the seminal work by Heeger and co-workers in 1992 where ultra-fast photo-induced electron transfer was experimentally observed when the fullerenes, which possess a very high electron affinity of ~ 2.7 eV, were mixed into semiconducting polymers.³⁷

There have been several different proposed mechanisms for explaining the observed ultra-fast electron transfer,^{37,38} which cannot be explained by the conventional non-adiabatic electron transfer mechanism as for the case of DSSC because the fullerenes, having a triply-degenerate LUMO, do not provide a semi-infinite CB as in the case of TiO_2 nano-particles. In some of our recent work, first-principles calculations based on DFT were employed to investigate the P3HT/fullerene interface to gain insights into how the exciton is split from its electronic structure.³⁹ The energy level alignment at the interface was found to be of Type-II with a very weak coupling between the LUMOs of the two phases in the electronic ground state. The interaction energy between P3HT and the fullerene was also found to be quite small. However, once the exciton is explicitly introduced in the lowest excited state, a strong overlap of the two states is observed in the calculations, leading to the formation of a so-called exciplex, or excited state complex asymmetric in character (the hole state being localized in the P3HT). By assuming that the lowest excited state is the relevant one for the P3HT exciton at the time it reaches the interface, the presence of a fullerene results in only about half of an electron transferred (*i.e.*, half of the electron probability density lies across the interface on the fullerene). Our analysis of the single-particle states revealed that this is a result of hybridization between the π^* LUMO state of P3HT and one of the triply-degenerate LUMO states of the fullerene, with the transferring excited electron occupying the itinerant state bridging across the interface. Critically, only a few meV in energy

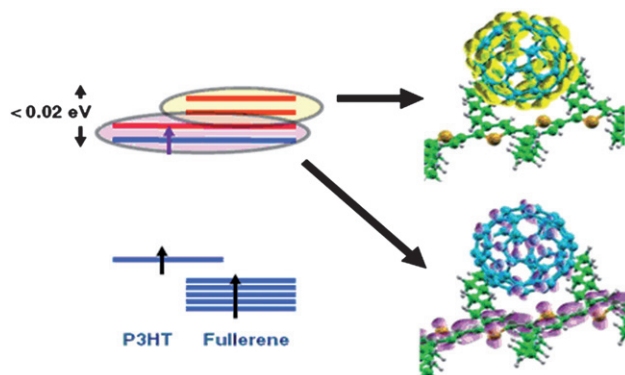


Fig. 6 Energy levels at P3HT/fullerene interface with an excitation, showing the quasi-degeneracy of the top four states along with their characters. The top two states are fully localized on fullerene while the bottom two are itinerant with the probability density bridging across the interface by approximately an equal amount. See ref. 39 for details.

above these two hybridized electronic states, lie two additional states that are completely localized on the fullerene and are quasi-degenerate (Fig. 6).

These results show that, first, the interfacial electron transfer is an adiabatic mechanism, occupying the itinerant bridging state across the interface. Next, the quasi-degeneracy of this state to those fullerene-localized states allows for efficient exciton dissociation, where the electron is spatially separated from the hole *via* a non-adiabatic process. Recent ultra-fast photo-induced spectroscopy experiments indicated a two-step process,⁴⁰ although the precise nature of the intermediate state is quite difficult to characterize experimentally. The fact that this two-step process is responsible for efficient charge separation has an important consequence to designing a better interface. While there have been proposals to “tune” the energy gap of the semiconducting polymer to increase the open-circuit voltage or short-circuit current,⁴¹ a two-step charge separation mechanism indicates that it is also important to retain this intricate interfacial electronic structure even when changing to other polymers.

4.3 Semiconducting-polymer/carbon-nanotube

An interesting direction for improving upon the P3HT/fullerene cell is the use of carbon nanotubes (CNTs) instead of fullerenes, since an important limitation of the semi-conducting-polymer/fullerene cell may be the degree of the percolation network formed by the fullerenes for efficiently transporting the electron after charge separation.⁴² In this regard, CNTs could provide a much more natural network for electron transport. Additionally, CNTs provide a dense CB for accepting the excited electron from P3HT at the interface *via* a non-adiabatic electron transfer mechanism, without the need for the intricate two-step process of the P3HT/fullerene interface for efficient charge separation. However, since it remains a major challenge experimentally to separate semiconducting from metallic CNTs,⁴³ it is imperative to understand the different roles played by each for charge

separation at the interface. While PV operation for P3HT/CNT blends has been demonstrated, the photocurrent is an order of magnitude smaller than for the fullerene blends.⁴⁴ Our DFT calculations showed that while it is possible for a semiconducting CNT to form an ideal Type-II heterojunction, the metallic tube undergoes significant charge redistribution with the P3HT polymer and the interaction at the interface is significantly enhanced.⁴⁵ Furthermore, the interaction does not result in the formation of interface states that could pin the CNT Fermi level within the P3HT gap as has been suggested.⁴⁶ As a result, the HOMO of P3HT lines up with the Fermi energy of the metallic tube, making the HOMO offset nonexistent at the interface. The charge neutrality level⁴⁷ of P3HT is only ~ 0.04 eV above its HOMO, and this essentially lines up to the Fermi level of the metal CNT (Fig. 7). This is far from being optimal for charge separation since a sizable offset between the HOMO of P3HT and CNT Fermi energy is the key driving force for the hole to drift away from the interface in the case of metallic tubes as discussed in ref. 44. When a mixed distribution of semiconducting and metallic tubes are present as inevitably is the case in experiments, the metallic tubes interact more strongly with P3HT because of the stronger electrostatic interaction due to the charge redistribution. This could result in a majority of the interfaces being inefficient PV heterojunctions with metallic tubes for which the P3HT excitons are unlikely to undergo charge separation. In light of these results, the very small photocurrent observed in experiments⁴⁶ may not be surprising. An alternative approach of using inorganic 1-D nanostructures (*e.g.*, nanopores and nanowires) instead of CNT has also been explored experimentally in this context,⁴⁸ free from the complexities associated with having both semiconducting and metallic structures. In such cases, surface modifications (*i.e.* surfactant molecules) appear to be quite important for designing an ideal Type-II heterojunction.⁴⁹

5. Designing nano-scale PV materials

Addressing materials challenges for improving PV cells will require collaborative efforts that span across both fundamental and applied scientific disciplines. Understanding the observed phenomena at a fundamental level is one of the keys to a rational approach for predicting and designing novel materials with desired behaviors. These new materials will demand from the applied scientific disciplines highly sophisticated and complex engineering approaches, which in turn require new or deeper understanding. As computational methodologies become more sophisticated and accurate, there exist exciting opportunities to effectively bridge this gap, by genuinely rising to the grand challenge of being able to predict and design new materials without resorting to empirical parameters from experiments. The computational materials science community is well positioned to address such an important challenge, and predicting/designing novel nano-materials for charge separation in PV cells constitutes one of these exciting directions with great potential benefits.

5.1 Controlling electronic structure of nano-materials

As we have discussed thus far, in most excitonic PV cells, charge separation of the exciton is induced by introducing another

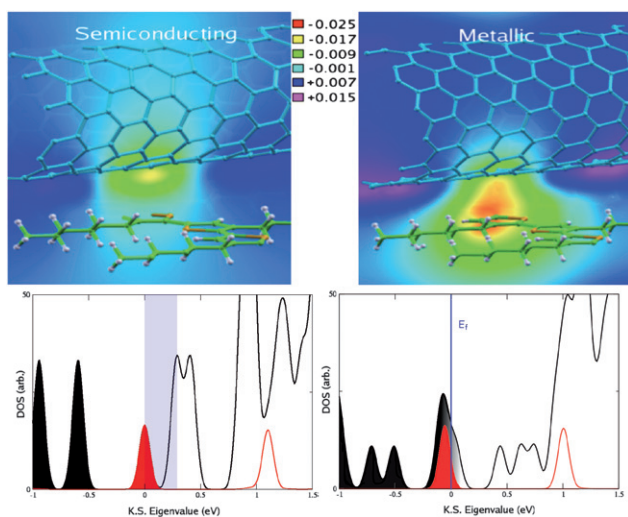


Fig. 7 Induced change in the electrostatic potential (a.u.) by the interface formation for semiconducting (10,2) CNT and metallic (12,3) CNT with P3HT, and the corresponding projected density of states deriving from CNT (in black) and P3HT (in red). See ref. 45 for details.

material to form a Type-II level alignment across the interface. Since the electronic structure of nanomaterials can be tuned (*e.g.*, by quantum confinement and topological symmetries), it is also possible to control the intrinsic properties of a *single* nanomaterial to induce charge separation without doping the material or introducing an interface with other materials. Thus, an interesting question is whether one could take advantage of nanoscale effects to design new PV cells based on novel charge separation schemes.

We have investigated silicon nanostructures as a proof-of-principle demonstration to answer such a question since Si nanostructures have shown enormous potential in terms of tunability of their electronic properties. In particular, Si nanowires^{50,51} are appealing because they provide a physical path for transporting charge carriers and can be synthesized routinely and controllably, even well within quantum confinement regimes.⁵¹ Motivated by the experimental observation of tapering⁵² of Si nanowires grown *via* the vapor–liquid–solid technique, we began to explore the fundamental aspects of how the inherent electronic structure of Si nanowires can be modified by controlling their nanoscale morphology. A key aspect of this work is that broken translational symmetry along the wire axis could affect the LUMO and HOMO electronic states distinctively and might lead to separate locations of these states in real space. As shown in the upper panel of Fig. 8, our DFT calculations suggest that the LUMO and HOMO states are mainly located at the opposite ends of a small-diameter tapered Si nanorod.⁵³ This is because in a narrow tapered Si nanowire, the quantum confinement strength varies significantly along the wire axis, and the surface morphology changes substantially as well, causing local near-gap energy levels along the axis to shift differently. On the other hand, the states deeper into the unoccupied and occupied manifolds are delocalized, and photoexcitation of the silicon nanorod would primarily occur across the higher excitation energy states into these levels. Thermal relaxation of the excited electron and hole to the near-gap frontier states naturally separates them spatially along the axis within such a tapered silicon nanorod. Thus, the calculations point to the possibility of spontaneous charge separation induced, without the need of doping, in a single nano-material by controlling the morphology.

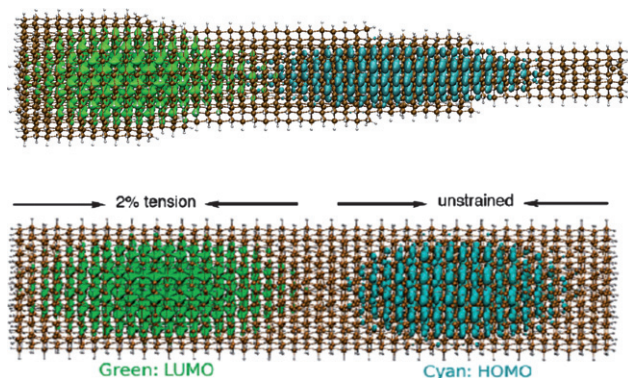


Fig. 8 Separation of the frontier orbitals in a single nano-material by morphology control in a tapered nanorod (top) and strained nanorod (bottom). See ref. 53 and ref. 54 for details.

Charge separation by morphology control could also be realized in a number of ways apart from tapering. For example, the lower panel of Fig. 8 shows that an untapered (straight) silicon nanorod can be partially strained along the axis to induce its LUMO and HOMO states to be localized in separate regions spatially. The reason for this effect is that axial tensile strain brings down the frontier energy levels of a Si nanowire, while axial compressive strain lifts these levels higher, due to the characteristic symmetries of these wave functions.⁵⁴ Consequently, in a partially strained Si nanorod, the frontier energy levels of the strained part are simultaneously higher or lower than the unstrained part, effectively forming a type-II junction in a single nano-material. We note that this phenomenon results mainly from the crystal structure of the Si nanowire, and quantum confinement effects strengthen the energy-level offsets. Experimentally, axial strain on Si nanowires has been investigated for the purpose of enhancing the charge carrier mobility,⁵⁵ and partially strained Si nanowires have been experimentally realized as well.⁵⁶ Our calculations show that controlling the opto-electronic properties of a single nano-material by modifying its intrinsic symmetries could be an interesting direction for designing novel PV cells.

5.2 Quantitative prediction of energy-level alignment

As mentioned earlier, the KS single-particle energies from DFT are erroneously shifted such that the energy gap is considerably underestimated. For semiconductor interfaces of similar electronic characters, the resulting errors in level alignment within DFT may not be severe due to error cancellation.⁵⁷ However, for materials of distinctly different electronic structures, the extent of such shifts could naturally be quite different across the interface, which could result in completely incorrect predictions of the HOMO and LUMO offsets in addition to the energy gap at the interface (Fig. 2). Therefore, as is done in many theoretical studies (*e.g.*, ref. 30), comparisons with experiment are highly valuable for assessing the performance of DFT for investigating well-known interfaces. However, designing novel interfaces is much more challenging for this reason because in such cases minimal experimental comparisons can be made to check the reliability of the DFT results. Thus, it is important to invest effort into the development of efficient first-principles methods with higher accuracy that go “beyond DFT”.

The most straightforward way of correcting KS single-particle energies is to use many-body perturbation theory (MPBT).^{25,58} Given that KS single-particle states are quite similar to quasi-particle states, they can be utilized to compute the so-called many-body correction that renormalizes the missing electronic many-body effects in this single-particle-like description. This is a quite convenient and straightforward approach for extending the applicability of DFT; however, it is not without some computational and methodological difficulties. As recently discussed by Shaltaf, *et al.*, the accuracy of this approach could depend significantly on how the so-called self-energy operator is evaluated,⁵⁹ and the computational cost also does not scale as favorably as DFT (N^3) but rather N^{4-5} , where N is the number of electrons in the calculations.

We recently proposed an alternative approach for improving upon the accuracy of DFT to predict energy level alignment,

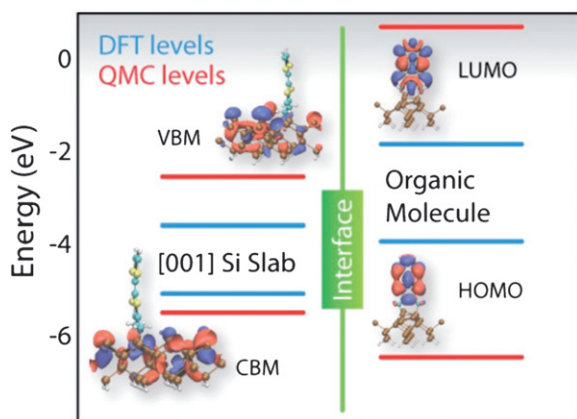


Fig. 9 The calculated energy level alignment of a representative organic–inorganic hybrid interface from single-particle energies of DFT and also with electronic many-body corrections obtained using QMC. See ref. 60 for details.

employing quantum Monte Carlo (QMC) calculations. In this approach, the many-body correction is obtained by relating KS single-particle energies to the derivatives of the total energy of the system, which can be obtained accurately using QMC.⁶⁰ The advantages of this approach are the high level of accuracy of QMC for a wide range of materials and the favorable scaling (N^3) of the method.

The importance of electronic many-body effects could show up in a number of places. For example, as a way of designing a desirable Type-II heterojunction using organic–inorganic interface, we investigated how the quantum confinement of a silicon slab could be used as a tuning parameter to line up the energy levels suitably with a specific organic molecule of interest. Even though DFT calculations predict a desirable Type-II heterojunction with the slab thinner than ~ 16 layers, accurately taking into account the missing electronic many-body effects using the QMC scheme completely modifies the prediction as seen in Fig. 9, revealing that this interface is instead Type-I in character. This is an extreme case where the qualitative optoelectronic character of a heterojunction is incorrectly predicted using DFT calculations, exemplified by a heterojunction composed of two electronically very different materials. Still, such results warrant caution in using DFT for predicting such novel interfaces to obtain targeted optoelectronic behavior, and provides a glimpse into the necessary developments that need to occur of more efficient approaches for obtaining many-body corrections.

6. Conclusion

In this feature article, we have reviewed how first-principles electronic structure approaches can be employed to understand, predict, and ultimately design new charge separation mechanisms in PV cells. It has been our aim to convey both the excitement of how such approaches can be important in this field as well as what technical and methodological challenges need to be overcome in order to make further significant progress.

Regarding computational approaches, we believe that there are two important directions relevant to the problem of charge

separation to be pursued. One is further development of non-adiabatic first-principles dynamics simulations. There have been substantial efforts in treating non-adiabatic processes within a first-principles molecular dynamics framework. Yet, there are many remaining challenges in terms of both theoretical developments and numerical efficiencies, which are important for generating a statistically accurate ensemble of trajectories for investigating the time evolution of the electronic structure. The other direction is in more efficient and accurate calculations of electronic excited states, including the quasi-particle energies. While the time-dependent extension of DFT is a promising approach, the underlying approximation to electronic exchange and correlation effects poses a challenge. In this regard, parallel efforts in developments of MBPT and QMC methodologies are encouraging as complementary approaches to the DFT framework.

While there are still a number of outstanding challenges, the first-principles calculations are revealing many important insights for charge separation processes in nano-scale photovoltaic materials. Further developments of the computational methodologies and collaborations with experimentalists are likely to foster more detailed understanding and novel designs of nano-materials optimal for photovoltaic applications. It is our hope that game-changing breakthroughs in PV materials discovery can be realized and indeed accelerated with these types of computational efforts, particularly when they are tightly coupled with experiment.

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