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GUEST EDITORIAL

Exceeding the Limit in Solar Energy Conversion with Multiple Excitons

Current solar cell technologies are economically not competitive with fossil fuels in electrical power generation; a game change demands the so-called third generation solar cells with both lower cost and higher efficiency. While extensive efforts are underway to meet the cost challenge with molecular and nanomaterials, the power conversion efficiency of a single junction solar cell is fundamentally constrained by the Shockley–Queisser limit.[1] *Can we use molecular and nanomaterials to exceed the Shockley–Queisser limit?* This question is one of the most exciting and provocative in solar energy research today. The most promising attempts in answering the above question are based on two photophysical processes originally discovered nearly 50 years ago: carrier multiplication (also called impact ionization) in inorganic semiconductors[2−4] and singlet fission in organic solids.[5,6] Both processes involve the absorption of a single high-energy photon to generate multiple electron–hole pairs and may be utilized to exceed the Shockley–Queisser limit theoretically. Champion solar cells made with low-cost molecular or nanomaterials but based on conventional photophysics have already shown power conversion efficiencies as high as 10%, approaching that of second-generation amorphous silicon technology. Additional gain in efficiency from carrier multiplication or singlet fission is perhaps what is needed to ring in the era of third-generation solar cells that can rival fossil fuel based electrical power generation.

The dominant power loss mechanisms in a conventional single-junction solar cell are the correlated below-bandgap and thermalization losses. The former comes from the transparence of the semiconductor material to solar radiation with photon energies below the bandgap (E_g), while the latter results from the cooling of hot carriers, initially generated by photon energies above E_g, to the band edges before they are extracted to do work. These two loss channels account for >55% of the total power from solar radiation[7] and are mainly responsible for the Shockley–Queisser limit of ∼31% in solar-to-electric power conversion efficiency. Carrier multiplication or singlet fission can be used to decrease the thermalization loss by converting part of the excess photon energy to multiple electron–hole pairs, thus increasing photocurrent. In the simplest implementation, a carrier multiplication or singlet fission chromophore absorbing at short wavelength may be combined with a conventional chromophore absorbing at longer wavelength for solar energy conversion with a theoretical power conversion efficiency as high as 44%.[8] This special issue presents the state-of-the-art in our understanding of carrier multiplication and singlet fission in nanomaterial and molecular materials, as well as initial efforts in the implementation of these processes to photovoltaics.

Since the early 1990s, carrier multiplication has been explored in crystalline semiconductor solar cells, and internal quantum efficiency as high as 130% has been reported.[9] However, such enhancement has little effect on the power conversion efficiency because significant carrier multiplication only occurs at photon energies as high as $4E_g$. Thus, "efficiency enhancement is found to be present but disappointingly small", as pointed out by Queisser in 2010.[10] One of the main reasons for the high photon energy threshold in carrier multiplication is the requirement for both energy and momentum conservation in crystalline semiconductors. In 2002, Nozik suggested that higher carrier multiplication efficiency may exist in semiconductor nanocrystals.[11] Since photogenerated electron–hole pairs in nanomaterials possess excitonic characteristics, carrier multiplication is often called multiexciton generation (MEG) in these systems. The enhancement of MEG in semiconductor nanocrystals may result from the relaxed requirement for momentum conservation, the possible presence of a phonon bottleneck, which slows the competing channel of hot carrier cooling, and the increased Coulomb coupling between excitons and multiexcitons due to spatial confinement. Over the past decade, MEG has been reported in a large number of semiconductor nanocrystals. While the reported efficiencies vary greatly in

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initial studies, the numbers have converged after problems with experimental measurements were identified and solved.

In this issue, Klimov and co-workers summarized the current understanding of MEG in semiconductor nanocrystals and discussed the important concept of e−h pair creation energy (ε_{eh}), which is determined by the ratio between the energy cooling rate and the carrier multiplication rate, in determining MEG efficiencies (η). These views are reinforced by the contribution of Beard et al., who also demonstrated solar cells based on MEG in semiconductor nanocrystals. Focusing on the issue of harvesting multiexcitons, Lian and co-workers used model systems of molecular electron acceptors anchored to semiconductor nanocystal surfaces and discussed the critical competition between multiexciton annihilation and multiexciton dissociation, as well as basic principles in controlling the interface for efficient multielectron transfer. Two papers discuss theoretical treatments of MEG in semiconductor nanocrystals. Efros and co-workers focus on the Coulomb coupling between single exciton and multiexciton states and emphasize the role of a high density of multiexciton states in this coupling. These authors use a spherical model and present a unified description of MEG based on the full quantum state evolution following initial coherent excitation of all the single and multiexciton states. Prezhdo and co-workers take the quantum coherent approach to a higher level and carry out *ab initio* time-domain simulations of MEG in the presence of classical nuclear motions. While limited to small clusters, great insights can be obtained from such a quantum chemical approach, e.g., the initial coherent excitation of single excitons and multiexcitons and the subsequent decoherence due to electron−phonon coupling, leading to the population buildup of multiple excitons.

Despite all the developments on MEG, the ε_{eh} values measured in semiconductor nanocrystals to date remain too high (or η too low) to contribute in a substantial way to the power-conversion efficiency in solar cells. The challenge is to find critical material properties that may lower ε_{eh} and increase η. In this regard, the discoveries of increased MEG efficiency due to enhanced single-exciton/multiexciton Coulomb coupling in nanorods and platelets suggest an exciting possibility of lowering ε_{eh} using such pseudo-one-dimensional and two-dimensional structures. We will return to this scene with carbon nanomaterials discussed below.

The MEG process in molecular materials is called singlet fission. With quantum yields as high as 200% at threshold photon energies in, for example, pentacene and tetracene, singlet fission is positioned to make significant impact to organic or hybrid organic/inorganic solar cells. One of the main reasons for the high quantum yield is that singlet fission is both energy- and spin-allowed. The excitation energy of a triplet can be half or less than that of a singlet due to the large quantum mechanical exchange energy specific to molecules. The conversion of a singlet exciton to two triplet excitons occurs via a multiexciton state[12] (i.e., a correlated triplet pair) with total singlet spin and is a spin-conserved process. However, there are only a handful of organic materials where high singlet fission yields are known. The challenges are evident: the mechanism of singlet fission is not well established and even less is known about how to extract multiple carriers from a singlet fission chromophore. Such mechanistic understanding is essential to the development of design principles for the synthesis of more singlet fission materials and the implementation of singlet fission to solar cells.

In this issue, Johnson, Nozik, and Michl discussed two design principles for molecular materials with high singlet fission yields: an ideal electronic energy structure and appropriate interchromophore coupling. These authors demonstrate a successfully designed molecule, 1,3-diphenylisobenzofuran, with high singlet fission yields verified in experiments. Other papers all deal with singlet fission in the two best-known model systems: crystalline pentacene and tetracene. Chan et al. analyze singlet fission in pentacene and tetracene using a quantum coherent formalism. The similarity of this theoretical framework to those of Efros and co-workers and Prezhdo and co-workers for MEG in semiconductor nanocrystals underscores the commonality of the underlying physics in both processes. In comparing experimental findings from time-resolved two-photon photoemission spectroscopy with density matrix simulation based on calculated matrix elements, Chan et al. conclude that indirect coupling between singlet and multiexciton states via charge transfer excitons is the dominant mechanism for efficient singlet fission in crystalline pentacene and tetracene. In contrast, Zimmerman et al. emphasize the importance of direct singlet/multiexciton coupling to singlet fission in pentacene and tetracene based on high-level electronic structural calculations. Burdett and Bardeen report direct experimental observation of spin coherence in the manifold of triplet pair states for singlet fission in crystalline tetracene. Wilson et al. use transient absorption spectroscopy to probe in great detail the ultrafast conversion of singlet to triplet pair in 80 fs and the subsequent dissociation of triplets at an interface with electron acceptors over time scales as long as microsecond. These authors also summarize successful attempts in building model singlet fission solar cells with pentacene as the

short wavelength absorber and PbSe nanocrystals as the electron acceptor and longer wavelength absorber. Baldo and co-workers take a device perspective, focus on the issue of multiple charge extraction from singlet fission in pentacene and tetracene, and demonstrate unambiguously the harvesting of singlet fission in solar cells based on the magnetic field dependence of solar cell efficiency.

Graphene and carbon nanotubes offer exciting potentials for high MEG efficiency;[13−15] this may be attributed to the extremely efficient electron−electron scattering but inefficient electron−phonon (particularly acoustic phonons) scattering in carbon nanomaterials. Gabor presents a summary of our understanding on the optoelectronic properties of graphene and carbon nanotubes based on elegant device measurements. These experiments provide unambiguous support for the exceptionally strong electron−electron interaction expected from the unique electronic structures in this class of materials. Kanemitsu takes a spectroscopic view of MEG and the reverse process of Auger recombination in carbon nanotubes and compares these to corresponding processes in inorganic semiconductor nanocrystals. While the actual implementation of MEG in carbon nanomaterials to solar cell technologies may be limited by the lack of low cost manufacturing, graphene and carbon nanotubes continue to serve as excellent playgrounds for the exploration of many electron physics essential to multiexciton generation.

It is an encouraging sign that solar cells based on both MEG in semiconductor nanocrystals[16] and singlet fission in organic semiconductors[17] have shown external quantum efficiency exceeding 100%. However, power conversion efficiencies of these cells are still too low to compete with champion solar cells made with either molecules or semiconductor nanocrystals. Engineers building the next generation solar cells must have access to a tool box of widely available materials that possess not only novel attributes, such as MEG or singlet fission, but also many other complementary physical properties, for example, strong light absorption, favorable charge carrier mobility, and long-term chemical stability. In this regard, the study of fundamental MEG and singlet fission mechanisms in a few materials and the successful demonstration of solar cells based on these model material systems are just the beginning. It is our hope that this special issue will inspire more researchers to bring new understanding to this exciting field, to design and discover new MEG and singlet fission materials, and to ultimately implement multiple excitons in third generation solar cell technology with power conversion efficiency approaching or exceeding the Shockley−Queisser limit.

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FOOTNOTES

Views expressed in this editorial are those of the author and not necessarily the views of the ACS.

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