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Gang Lu

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California State University - Northridge
18111 Nordhoff Street

Northridge, CA 91330 -8232

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14. ABSTRACT
The objectives of the project are three-fold: (1) Development of first-principles simulator to understand the fundamental physical processes underlying the performance of the solar cells. (2) Identifying key physical quantities and materials parameters controlling the efficiency of the solar cells and translating the understanding to a set of materials design rules. (3) Providing theoretical guidance and computational screening for molecular design of materials to achieve high efficiency.

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Gang Lu
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Report Title

Final Report: Toward Computational Design of High-Efficiency Photovoltaics from First-Principles

ABSTRACT

The objectives of the project are three-fold: (1) Development of first-principles simulator to understand the fundamental physical processes underlying the performance of the solar cells. (2) Identifying key physical quantities and materials parameters controlling the efficiency of the solar cells and translating the understanding to a set of materials design rules. (3) Providing theoretical guidance and computational screening for molecular design of materials to achieve high efficiency.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
07/27/2015	4.00	Guangjun Nan, Xu Zhang, Gang Lu. Do “Hot” Charge-Transfer Excitons Promote Free Carrier Generation in Organic Photovoltaics?, The Journal of Physical Chemistry C, (07 2015): 0. doi: 10.1021/acs.jpcc.5b04652
07/28/2014	2.00	Zi Li, Xu Zhang, Cristiano F. Woellner, Gang Lu. Understanding molecular structure dependence of exciton diffusion in conjugated small molecules, Applied Physics Letters, (04 2014): 0. doi: 10.1063/1.4871303
07/28/2014	1.00	Guangfen Wu, Zi Li, Xu Zhang, Gang Lu. Charge Separation and Exciton Dynamics at Polymer/ZnO Interface from First-Principles Simulations, The Journal of Physical Chemistry Letters, (07 2014): 0. doi: 10.1021/jz500980q
07/28/2014	3.00	X Zhang, G Lu, Z Li. Exciton diffusion in disordered small molecules for organic photovoltaics: insights from first-principles simulations, Journal of Physics: Condensed Matter, (05 2014): 0. doi: 10.1088/0953-8984/26/18/185006
TOTAL:	**4**	

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received		Paper
TOTAL:		

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
WEi Ma	1.00	
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Guangjun Nan	1.00
FTE Equivalent:	**1.00**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Gang Lu	1.00	
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Wei Ma
Total Number: 1

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachement.

Technology Transfer

Award Information

Award Number	W911NF-13-1-0147
Title of Research	Toward Computational Design of High-Efficiency Photovoltaics from First-Principles
Principal Investigator	Gang Lu
Organization	The University Corporation (California State University Northridge)

Technical Section

Technical Objectives

The objectives of the project are three-fold: (1) Development of first-principles simulator to understand the fundamental physical processes underlying the performance of the solar cells. (2) Identifying key physical quantities and materials parameters controlling the efficiency of the solar cells and translating the understanding to a set of materials design rules. (3) Providing theoretical guidance and computational screening for molecular design of materials to achieve high efficiency.

Technical Approach

The PI has developed a first-principles method that can predict charge carrier mobility in organic semiconductors as a function of chemical structures, presence of defects, temperature, electric field, and carrier concentration entirely from first principles; i.e., there is no empirical input or adjustable parameter in the simulations. More specifically, this approach is based on the time-domain *ab initio* non-adiabatic molecular dynamics for simulating phonon-assisted electron transitions. The electronic energy levels and their transition rates are determined from the density functional theory (DFT), taking into account of both inter-molecule and intra-molecule contributions and treating dynamic and static disorder at an equal footing. This multiscale framework incorporates quantum mechanical determination of electron transition rates, mesoscale master equations for carrier mobility and continuum models for current-voltage characteristics tailored for experimental measurements. For interfacial exciton dissociation, we have developed a first-principle approach based on the time-dependent density functional theory (TDDFT) to describe exciton states, including energy levels and many-body wave functions. The non-adiabatic *ab initio* molecular dynamics (MD) is used to determine the phonon-assisted transition rates between localized exciton states. In conjunction with the Monte Carlo and surface-hopping methods, this approach can simulate exciton dynamics in organic semiconductors at different temperatures.

Progress:

1. The Lowest-Energy Charge-Transfer State and Its Role for Charge Separation in Organic Photovoltaics

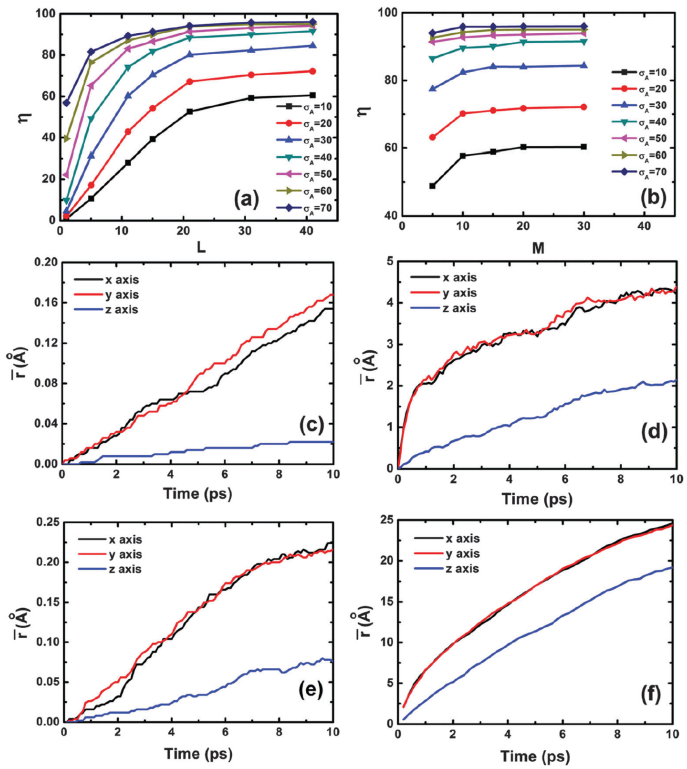

Figure 1: (a) Charge separation efficiency as a function of L with M = 40. (b) Charge separation efficiency as a function of M with L = 41. Hole (c) and electron (d) diffusion distance along x, y and z axes averaged over all KMC trajectories with energetic disorder of 10 meV. The diffusion distance for the hole (e) and electron (f) along x, y and z axes averaged over all KMC trajectories with energetic disorder of 70 meV.

Energy independent, yet higher than 90% internal quantum efficiency (IQE) has been observed in many organic photovoltaics (OPVs). However, its physical origin remains largely unknown and controversial. Hypothesis that the lowest charge-transfer (CT) state may be weakly bound at the interface has been proposed to rationalize the experimental observations. In this work, we study the nature of the lowest-energy CT (CT_1) state, and show conclusively that CT_1 state is localized in typical OPVs. The electronic couplings in the donor and acceptor are found to determine the localization of CT_1 state. We examine geminate recombination of CT_1 state and estimate its lifetime from first-principles. We identify the vibrational modes that contribute to the geminate recombination. With materials parameters determined from first-principles and experiments, we carry out Kinetic Monte Carlo simulations to examine charge separation of localized CT_1 state. We find that the localized CT_1 state can indeed yield efficient charge separation with IQE higher than 90%. Dynamic disorder and configuration entropy can provide energetic and entropy driving force for the charge separation. Charge separation efficiency depends more sensitively on the dimension and crystallinity of the acceptor parallel to the interface than normal to the interface. Reorganization energy is found to be the most important materials parameter for charge separation and lowering the reorganization energy of the donor should be pursued in materials design.

2. Interfacial Oxygen Vacancies as a Potential Cause of Hysteresis in Perovskite Solar Cells

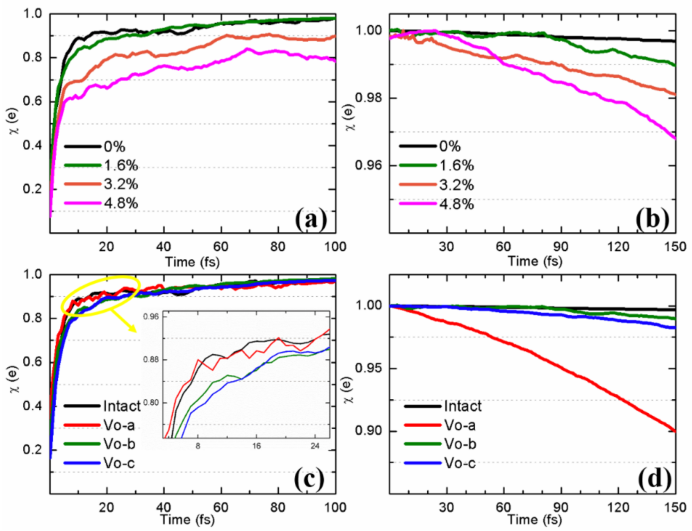

Figure 2: (a) Electron transfer fraction (χ) from the perovskite to the TiO_2 conduction bands as a function of time for different densities of oxygen vacancy (VO) in TiO_2. (b) Electron transfer as a function of time during the recombination process for different densities of VO in TiO_2. (c) Electron transfer fraction from the perovskite to the TiO_2 conduction bands as a function of time for intact TiO_2 and TiO_2 with VO at different sites. (d) Electron transfer as a function of time during the recombination process for intact TiO_2 and TiO_2 with different VO sites.

Organometal halide perovskite solar cells (PSCs) have emerged as one of the most promising photovoltaic technologies with efficiencies exceeding 20.3%. However, device stability problems including hysteresis in current−voltage scans must be resolved before the commercialization of PSCs. Transient absorption measurements and first-principles calculations indicate that the migration of oxygen vacancies in the TiO_2 electrode under electric field during voltage scans contributes to the anomalous hysteresis in PSCs. The accumulation of oxygen vacancies at the electrode/perovskite interface slows down charge extraction while significantly speeding up charge recombination at the interface. Moreover, first-principles non-adiabatic molecular dynamics simulations reveal that the charge recombination rates at the interface depend sensitively (with 1 order of magnitude difference) on the locations of oxygen vacancies. By intentionally reducing oxygen vacancies in the TiO_2 electrode, we substantially suppress unfavorable hysteresis in the PSC devices. This work establishes a firm link between microscopic interfacial structure and macroscopic device performance of PSCs, providing important clues for future device design and optimization.

3. Charge Stripe Formation in Molecular Ferroelectric Organohalide Perovskites for Efficient Charge Separation

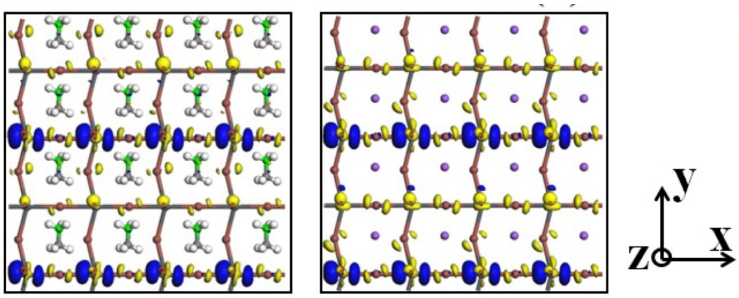

Figure 3: Charge density of the lowest energy exciton in $MAPbI_3$ (left) and $NaPbI_3$ (right) viewed along the *z* direction. The electron and hole density is colored in blue and yellow, respectively.

Despite rapid progress in the efficiency of organohalide perovskite based solar cells, physical mechanisms underlying their efficient charge separation and slow charge recombination still elude us. Here we provide direct evidence of spontaneous charge separation via first-principles simulations. The excitons are predicted to self-organize into stripes of photo-excited electrons and holes, spatially separated as effective channels for charge transport. The rotation of organic cations deforms the inorganic framework, and as the deformation reaches a critical value, a direct band gap transforms to an indirect one, and the photo-excited electrons rotate in alignment with the deformation-induced electric fields. The latter triggers Stark effect which in turn leads to the formation of charge stripes. The interplay between dynamic disorder, ionic bonding and polarization is responsible for the formation of the charge stripes and the indirect band gap, both of which could lead to efficient charge separation and reduced charge recombination in the organohalide perovskites.

Publications:

1. G. Nan, X. Zhang and **G. Lu**, "The Lowest-Energy Charge-Transfer State and Its Role for Charge Separation in Organic Photovoltaics", Phys. Chem. Chem. Phys. **18**, 17546 (2016).
2. F. Zhang, W. Ma, H. Guo, Y. Zhao, X. Shan, K. Jin, X. Lu, **G. Lu**, and S. Meng, "Interfacial Oxygen Vacancies as a Potential Cause of Hysteresis in Perovskite Solar Cells", Chem. Mater. 28(3), 802-812 (2016).
3. X. Zhang, M. Zhang and **G. Lu**, "Charge Stripe Formation in Organohalide Perovskites for Efficient Charge Separation", submitted to J. Phys. Chem. C (2016).