Theoretical Study on Energy Conversion Processes of Perovskite Solar Cells

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Computational Materials Science For Energy Conversion

- Organic Photovoltaic Cells
- Dye-Sensitized Solar Cells
- Perovskite Photovoltaics
- Rechargeable Battery
- Interfacial Carrier Transport
- Photocatalysis
- Thermal Transport
- Molecular Electronics
- Automobile Catalysis
MAPbI$_3$ perovskite compounds as a light harvester

(Miyasaka et al., JACS 2009)

Key Properties:
- Ambipolar Charge Transfer
- Long Charge Carrier Lifetime and Diffusion Length

Xing et al., Science (2013)
MA induces the ambipolar (hole-transport) behavior

\[ m_e^* = 0.316 m_0, \quad m_h^* = 0.36 m_0 \]  (along the \( R \to \Gamma \) direction)

\[ m_e^* = 0.23 \quad m_0, \quad m_h^* = 0.29 m_0 \]  (with Spin-Orbit coupling)

This result clearly reveals the ambipolar nature of the material

Giorgi, Fujisawa, Segawa, Yamashita, JPCC(2014) 118, 12176
This 0.4-ps hot-hole cooling is much slower than that in most organic semiconductors (~100 fs).

Transient Absorption Measurement

Hot “Carrier (Hole)”
Carrier lifetime from MBPT

$$\tau_{nk}^{-1} = 2 \text{Im} \Sigma_{nk}^{\text{Fan}}(\varepsilon_{nk}, T = 0\text{K})$$

$$\approx \frac{2}{N_q} \sum_{q\lambda} \sum_{n' \in \text{CB}} \left| g_{nn'k}^{q\lambda} \right|^2 \delta(\varepsilon_{nk} - \varepsilon_{n'k-q} - \omega_{q\lambda})$$

$$+ \frac{2}{N_q} \sum_{q\lambda} \sum_{n' \in \text{VB}} \left| g_{nn'k}^{q\lambda} \right|^2 \delta(\varepsilon_{nk} - \varepsilon_{n'k-q} + \omega_{q\lambda})$$

- $N_q$: Number of q-points
- $g_{nn'k}^{q\lambda}$: e-ph coupling
- $\omega_{q\lambda}$: Phonon frequency

Generalized Eliashberg function:

$$g F_{nk}^2(\omega) \bigg|_{\text{Fan}} = \frac{1}{N_q} \sum_{n'} \frac{g_{nn'k}^{q\lambda} |g_{nn'k}^{q\lambda}|^2}{\varepsilon_{nk}^{KS} - \varepsilon_{n'k-q}^{KS}} \left[ 2N_q(T) + 1 \right] \delta(\omega - \omega_{q\lambda})$$

A reduction of the relaxation paths in the small valence DOS as being the origin of the slow hot-hole cooling.

Photophysical Processes and Loss Mechanism

Sum and Mathews, Ener. Env. Sci. (2014)

Long charge carrier lifetime and diffusion length

Combination of

- high charge carrier mobilities
- low charge carrier recombination rates

Free-carrier model

Yamada et al. JACS (2014)
PL and TA measurements
$E_b \approx 25-37\text{meV}$

Very high magnetic field
$E_b \approx 16\text{meV}$ (low temp)
reduced effective mass $0.104m_e$

Phase transition
at 160 K
orthorhombic $\rightarrow$ tetragonal
at 330 K \( (k_B T \approx 25 \text{ meV}) \)
tetragonal $\rightarrow$ cubic
MAPbI₃ is characterized by
• Strong absorption constant
• High photoluminescence quantum yield


1s cluster
MA$_{54}$Pb$_{27}$I$_{108}$ (567 atoms)
Cubic-like, MAI-terminated
organic/inorganic cation ratio = 2.00

2i cluster
MA$_{84}$Pb$_{45}$I$_{174}$ (891 atoms)
Tetragonal-like, MAI-terminated
organic/inorganic cation ratio = 1.87

3l cluster
MA$_{93}$Pb$_{60}$I$_{213}$ (1017 atoms)
[001] facet: PbI$_2$-terminated
[100], [010]; MAI-terminated
organic/inorganic cation ratio = 1.55

Top view
Lateral view

Gray, Pb; purple, I; brown, C; light blue, N; white, H
(a) Side and (b) top view of the VBM (2.05ps). (c) and (d) same for the CBM.

Both VBM and the CBM are spread along the surface edge.

VBM is mainly localized into a single PbI$_6$ octahedron at the surface. CBM is more spread along one of the \cdots Pb\cdots Pb\cdots I\cdots Pb\cdots edges in the z direction.

We can expect that an efficient electron (CBM)--hole (VBM) separation takes place, proving a reduced tendency of recombination once the cluster is excited.

(a) Lateral and (b) top view of the VBM after 2.65 ps (2.10 eV)
(c) and (d) for the CBM.
(e) Lateral and (f) top view for the VBM after 0.90 ps (1.46 eV)
(g) and (h) for the CBM

(a) Lateral and (b) top view of VBM (after 1.90 ps, 1.73 eV); (c) and (d) the same views for CBM

Rotational autocorrelation function $c(\Delta t)$:

$$c(\Delta t) = \frac{1}{N_{\text{cations}}} \sum_i \langle s_i(t) \cdot s_i(t + \Delta t) \rangle$$

where $i$ and $s_i(t)$ are the index of organic cations and unit vector aligned with the orientation of $i$-th organic cation, respectively.
Overlap integral $q$:

$$q = \int_{V_{\text{cell}}} |\psi_{\text{VBM}}(\mathbf{r})| |\psi_{\text{CBM}}(\mathbf{r})| d\mathbf{r} = \int_{V_{\text{cell}}} \sqrt{\rho_{\text{VBM}}(\mathbf{r}) \rho_{\text{CBM}}(\mathbf{r})} d\mathbf{r}.$$
High performance of lead halide perovskite-based photovoltaic devices

Remarkable carrier properties
- Long carrier diffusion length
- Long carrier lifetime
- Low electron-hole recombination rate

First-principles molecular dynamics simulations indicate that the charge separation is induced by the structural fluctuation of the inorganic lattice. The charge separation is attributed to the electrostatic potential fluctuation coupled to the inorganic lattice dynamics. The organic cations are unlikely to be essential for carrier properties.
Acknowledgements

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FIRST Project

Prof. Hiroshi Segawa
(UT, RCAST)
The localization of the wave function is more spread out and symmetrically distributed over the whole cluster as a consequence of the replacement of the A-site cation.

The comparison with inorganic halide perovskites supports the idea that the dipole and the rotation of the organic cation play a primary role in the localization of the wave function in MAPbI$_3$ clusters.

The charge localization causes electron-hole separation and reduces carrier recombination rates.

A) The effective masses of photogenerated electrons and holes were estimated to be $m_e^* = 0.23m_0$ and $m_h^* = 0.29m_0$, respectively, including spin–orbit coupling effects. This result is consistent with the long-range ambipolar transport property and with the larger diffusion constant for carriers.

B) A newly developed MBPT method is applied to analyze the carrier relaxation lifetime of MAPbI$_3$ perovskites.

C) Halide Perovskites other than CH$_3$NH$_3$PbI$_3$ are suggested featuring (1) zero dipole moment Guanidium cations, (2) aliovalent ionic pairs replace Pb cations.

D) We have introduced and discussed the properties of zero dimensional (clusters) of organic–inorganic halide perovskites. The present study represents the first analysis focused on the electronic and structural properties of OIHP clusters.

E) The dipole and the rotation of the organic cation play a primary role in the localization of the wave function in MAPbI$_3$ clusters. The charge localization causes electron-hole separation and reduces carrier recombination rates.

AIMD simulations
DFT GGA/PBE
NVE ensemble
Siesta code

Brus’s equation (1986):

\[ \Delta E_g \approx \left( \frac{2h^2 \pi^2}{\mu D^2} \right) - \left( \frac{3.6e^2}{\varepsilon D} \right) \]

\[ \frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*} \]

\[ D = \left( \frac{6V}{\pi} \right)^{1/3} \]

The coherent/random orientation of the MA cations thus seems to play a role on the wave function localization preferential sites at the surface.

A reduction of the relaxation paths in the small valence DOS as being the origin of the slow hot-hole cooling.

The 480-nm peak can be assigned to transitions from the VB states along the R-M path.

Dual nature of excited states


Excited state behavior of PbI$_x^{n-}$ complex in solution

Absorption spectra of 250 μM PbI$_2$ solution in dimethylformamide (a) with increasing concentration of MAI from 6mM(b) to 24mM(e)

Excited state behavior of perovskite films

760nm

\[
\text{CH}_3\text{NH}_3\text{PbI}_3 + h\nu \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3 [h + e] \rightarrow \text{CH}_3\text{NH}_3\text{PbI}_3
\]

480nm

\[
\text{CH}_3\text{NH}_3\text{PbI}_3 + h\nu \rightarrow [\text{CH}_3\text{NH}_3\text{PbI} \cdots \text{I}_2]
\]
$\text{Pbl}_4^{2-}$, $\text{MA}_4\text{Pbl}_6$, $\text{Pbl}_3^-$, $\text{MA}_7\text{Pb}_2\text{l}_{11}$

B3LYP/6-311G++, MWB46(halides), MWB78(Pb)

FMO overlap integral

\[ S = \int \text{d}r \left| \psi_{\text{HOMO}} \right| \left| \psi_{\text{LUMO}} \right| \]

Poster Presentation

4669 Charge Carrier Trapping at Surface Defects of Perovskite Solar Cell Absorbers: A First-Principles Study

Hiroki Uratani, Koichi Yamashita


ACS Editor’s Choice Selection
**Nanostructured OIHPs**

**Colloidal Nanoplates**

Sharp excitonic absorption
Tyagi, Arveson, Tisdale

**Nanowires, nanorods, nanoplates**

Long carrier lifetime
Fu, Jin et al.

**Colloidal Nanoplates**

Enhanced excitonic nature
Im, Grätzel, Park et al.
*Nano Lett.* 2015

**Nanocrystals**

Bandgap tunability
Protesescu, Kovalenko et al.
*Nano Lett.* 2015

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Long photoluminescence times
Zhu, Petrich, Smith, Vela et al.
*ACS Nano* 2015
Ion Migration in Organometal Trihalide Perovskite and Its Impact on Photovoltaic Efficiency and Stability

Ambipolar charge transfer
• Absorber (Kim et al. 2012, Heo et al. 2013) TiO$_2$/MAPbI$_3$/HTM
• Electron transporter (Lee et al. 2012) Al$_2$O$_3$/MAPbI$_3$/HTM
• Hole transporter (Etgar et al. 2012) without HTM

Xing et al., Science (2013)
MAPbI$_{3-x}$Cl$_x$, >1 µm,
Stranks et al. Science (2013)

Huang et al. JPCL (2015)
Superior point defect properties


Vacancies \(V_{MA}, V_{Pb}, V_{I}\), interstitials \((MA_i, Pb_i, I_i)\), cation substitutions \((MA_{Pb}, Pb_{MA})\) and antisite substitutions \((MA_{I}, Pb_{I}, I_{MA}, I_{Pb})\)

Electrically benign structural disorder


(a–i) are (partial) DOS of pristine \(\text{CsPbI}_3\) and polycrystalline \(\text{CsPbI}_3\) with \(\Sigma 3(111)\) and \(\Sigma 5(310)\) GBs. (j) and (k) are atomic structures at \(\Sigma 3(111)\) and \(\Sigma 5(310)\) GBs respectively.
A large hysteresis in the current-voltage curves may be attributed to the motion of organic cations with a permanent dipole moment in response to the applied electric field.

Organic cations that have a zero dipole moment and a molecular size qwell fitted to the lead iodine cavity.

Effective mass of carriers (A-Γ direction)

\[ FAPbI_3 \]
\[ m_h^* = 0.302 m_0, \quad m_e^* = 0.403 m_0 \]
\[ GAPbI_3 \]
\[ m_h^* = 0.385 m_0, \quad m_e^* = 0.359 m_0 \]

\[ \text{Ratio: } m_h^*/m_e^* \]

\[ FAPbI_3 \ (0.75), \quad GAPbI_3 \ (1.07) \]

\[ \text{GAPbI}_3 \text{ has a more marked ambipolar behaviour than } FAPbI_3 \]

We speculate that guanidinium ions serve to suppress formation of iodide vacancies and passivate under-coordinated iodine species at grain boundaries and within the bulk through their hydrogen bonding capability.

These results present a simple method for suppressing nonradiative carrier loss in hybrid perovskites to further improve performances toward highly efficient solar cells.
### Band Structures

<table>
<thead>
<tr>
<th>Lattice constant /Å</th>
<th>CH$_3$NH$_3$PbI$_3$</th>
<th>CsPbI$_3$</th>
<th>PbI$_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a=c=5.99$, $b=6.02$</td>
<td>$\alpha=\gamma=86.5$, $\beta=91.0$</td>
<td>6.13</td>
<td>6.72</td>
</tr>
<tr>
<td>Bandgap /eV</td>
<td>0.93</td>
<td>0.89</td>
<td>1.51</td>
</tr>
</tbody>
</table>
Only CsPbI$_3$ has long lifetime region of holes.

Long lifetime comes from the small DOS.

Phonon modes contributing to the carrier relaxation

Holes are decayed through the motions of Pb and I, not Cs.

Difference of A-site cation does not alter the decay mechanism.

Electronic band structure of CsPbI$_3$ along the R-M path.

Optical strengths of the transitions

Carrier lifetimes at the electronic states

(a) PAO/PBE band structure, (b) DOS/PDOS ($E_g=1.57$ eV at $\Gamma$)
(c) Lateral and top view of VBM, (d) CBM
Together with high radiative recombination yields and long carrier lifetimes, these properties raise the question of whether absorption and reemission of excited carriers can occur during the transport. “Photon recycling” does indeed play a central role, allowing considerable increases over current descriptions in the characteristic lengths for charge and energy transport.
Pb-free Perovskites

- Replacing Pb with other group IVA elements, Ge, Sn.
- Mixed-(Sn, Pb) perovskites
- Aliovalent ionic pairs replace Pb cations
  \[ \text{MATI}_{0.5}\text{Bi}_{0.5}\text{I}_3 \text{ (MTBI)} \]
  \[ \text{MAIn}_{0.5}\text{Bi}_{0.5}\text{I}_3 \text{ (MIBI)} \]

Bandgap with SOC
0.84 eV for MTBI.

Reduced effective mass
0.31 (0.33)
Ratio between the two carrier effective masses
0.83 (0.89)
for MAPbI$_3$ (MTBI)

(e) lateral and (f) top view of the optimized MTBI cell. Bandstructure without (g) and with (h) SOC effect inclusion for MTBI.

(b) VBM and (d) CBM wavefunctions of MTBI

Band Gaps of the Lead-Free Halide Double Perovskites Cs₂BiAgCl₆ and Cs₂BiAgBr₆ from Theory and Experiment  

Marina R. Filip,† Samuel Hillman,‡ Amir Abbas Haghighirad,‡ Henry J. Snaith,‡ and Feliciano Giustino*†

Indirect band gap (eV)

\[ \text{GW} \quad \text{Exp} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>GW</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs₂BiAgCl₆</td>
<td>2.2</td>
<td>2.4</td>
</tr>
<tr>
<td>Cs₂BiAgBr₆</td>
<td>1.8</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Giustino et al (JPCL 2016)
Woodward et al (CM 2016)
Botti et al (JMCC 2016)

(MA)₂KBiCl₆
Indirect band gap 3.02 eV(calc)
3.04 eV(exp)

Cheetham et al
(Mater. Horizons 2016)
The rotational motion of methylammonium cations is considered responsible for phonon transport suppression.

Suppression Mechanism:
the rotations are coupled with translational motions of cations, via which inorganic lattice vibrations are coupled and scatter each other.

**Nanowires, nanorods, nanoplates**

*Long carrier lifetime*

Fu, Jin et al.  

**Colloidal Nanoplates**

*Sharp excitonic absorption*

Tyagi, Arveson, Tisdale  

**Nanowire**

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**Nanocrystals**

*Long photoluminescence times*

Zhu, Petrich, Smith, Vela et al.  
*ACS Nano* 2015
The calculated average band gap (~1.58 eV) recovers that of the bulk (1.57 eV); an average diameter of 32.7 Å recover the electronic properties of the bulk.

Nanoscale Charge Localization Induced by Random Orientations of Organic Molecules in Hybrid Perovskite CH$_3$NH$_3$PbI$_3$


**Figure 6.** Charge densities of the CBM and VBM states of an equilibrium structure, which is taken from a snapshot of the Monte Carlo simulation at $T = 300$ K in the 20 736-atom supercell. Both the CBM and VBM are still strongly localized and separated, although the localization sizes increase.