Controlled Redox of Lithium-Ion Endohedral Fullerene for Efficient and Stable Metal Electrode-Free Perovskite Solar Cells


†Department of Mechanical Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
‡KU-KIST Green School Graduate School of Energy and Environment, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Korea
§Nanomaterials and Nanotechnology Department, Advanced Materials Division, Central Metallurgical R&D Institute (CMRDI), P.O. Box 87, Helwan, Cairo 11421, Egypt
×SKKU Advanced Institute of Nanotechnology (SAINT) and Department of Nanoengineering, Sungkyunkwan University, Suwon 16419, South Korea
○Department of Materials Science and Engineering and California Nano Systems Institute, University of California, Los Angeles, California 90095, United States
©Department of Mechanical Engineering, National University of Singapore, Block EA #07-08, 9 Engineering Drive 1, Singapore 117576, Singapore
×Department of Applied Physics, Aalto University School of Science, P.O. Box 15100, Aalto, Espoo FI-00076, Finland
◇Energy NanoEngineering Lab., National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8564, Japan
○Institute of Materials Innovation, Institutes of Innovation for Future Society, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Supporting Information

ABSTRACT: High efficiency perovskite solar cells have underpinned the rapid growth of the field. However, their low device stability limits further advancement. Hygrosopic lithium bis(trifluoromethanesulfonyl)imide (Li‘TFSI’) and metal electrode are the main causes of the device instability. In this work, the redox reaction between lithium-ion endohedral fullerenes and 2,2,7,7‘-tetrakis(N,N-di-p-methoxyphenylamine)-9,9‘-spirobi-fluorene (spiro-MeOTAD) was controlled to optimize the amount of oxidized spiro-MeOTAD and antioxidizing neutral endohedral fullerenes. Application of this mixture to metal-free carbon nanotube (CNT)-laminated perovskite solar cells resulted in 17.2% efficiency with a stability time of more than 1100 h under severe conditions (temperature = 60 °C, humidity = 70%). Such high performance is attributed to the uninhibited charge flow, no metal-ion migration, and the enhanced antioxidizing activity of the devices.

Perovskite solar cells (PSCs) have become an established photovoltaic technology owing to the exceptional power conversion efficiency (PCE).1 Despite high PCE, the device stability needs to be substantially improved if PSCs are to be commercialized.2 There are two factors responsible for the low stability of PSCs: Li‘TFSI’ and metal electrodes. Use of hygrosopic Li‘TFSI’ results in an uncontrolled oxidation of spiro-MeOTAD as well as moisture-driven degradation.3 In the same vein, metal electrodes induce a metal ion-migration, which degrades the perovskite material, lowering the device stability.3

We previously reported the use of lithium-ion containing [60]fullerene trifluoromethanesulfonylimide salt ([Li‘@C60]-TFSI) instead of Li‘TFSI’ in PSCs.5 [Li‘@C60]-TFSI’ induced an instant oxidation of spiro-MeOTAD and produced neutral [Li‘@C60]2’− (= Li@C60), which functioned as an antioxidant, protecting the device from intruding oxygen. With the instant generation of spiro-MeOTAD**TFSI’ and the antioxidation activity of Li‘@C60’−, the stability of PSCs improved by 10-fold. However, the reported PCEs were relatively low due to the small amount of spiro-MeOTAD**TFSI’ and rough morphology of endohedral fullerene species.

Replacing metal electrodes by carbon conductors has been reported to be one of the most effective ways to improve the

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In PSCs was novel yet presented limited PCE (Figure 1A).5a

Combining those two technologies and controlling the redox reaction of $[\text{Li}^+@\text{C}_{60}]\text{TFSI}^-$ offer an outstanding synergistic solution to the instability and low efficiency of PSCs. Because HTLs are typically spin-coated onto the CNT network in solution to the instability and low efficiency of PSCs.10 the CNT electrode functioned as a HTL are typically spin-coated onto the CNT network in solution to the instability and low efficiency of PSCs.9c

We found that the reaction time between spiro-MeOTAD and $[\text{Li}^+@\text{C}_{60}]\text{TFSI}^-$ is crucial because not all $[\text{Li}^+@\text{C}_{60}]\text{TFSI}^-$ dissolves in CB. This means that the equilibrium of reaction 1 will depend on the concentration of the reactant $[\text{Li}^+@\text{C}_{60}]\text{TFSI}^-$ and the product Li@C$_{60}$. Since the solubility of Li@C$_{60}$ (<0.1 mg mL$^{-1}$ in CB, newly found in this work) is even lower than that of $[\text{Li}^+@\text{C}_{60}]\text{TFSI}^-$, the reaction equilibrium will constantly shift to the right, producing spiro-MeOTAD$^*\text{TFSI}^-$ and Li@C$_{60}$ (3) (Figure S7):

$$\text{spiro - MeOTAD} + [\text{Li}^+@\text{C}_{60}]\text{TFSI}^- \rightarrow \text{spiro - MeOTAD}^*\text{TFSI}^- + [\text{Li}^+@\text{C}_{60}]^*^-$$  

$$[\text{Li}^+@\text{C}_{60}]^*^- + O_2 or O_2^* \rightarrow \text{Li}^+ @ \text{C}_{60} O_2^*$$ etc.

In theory, reaction 3 should cease when most of $[\text{Li}^+@\text{C}_{60}]\text{TFSI}^-$ is dissolved and reverse the equilibrium like eq 4 (Figure S8):

$$\text{spiro - MeOTAD}^*\text{TFSI}^- + [\text{Li}^+@\text{C}_{60}]^*^- \rightarrow \text{spiro - MeOTAD} + [\text{Li}^+@\text{C}_{60}]\text{TFSI}^-$$
to the CNTs (Figures 2A–D, S9, and S10). Figure 2A shows that the CNT films are intact with the Fe catalysts visible from the magnified inset when the 0 h-stirred solution was applied. The 2 h-stirred solution applied CNT appears to be coated with a thick layer and the catalyst particles are invisible from the magnified layer (Figure 2B). The 5 h-stirred solution-applied CNT appears rough on the surface and the magnification shows less pronounced CNT shapes with newly formed particles (Figure 2C). The 10 h-stirred solution-applied CNT films have large aggregations greater than 300 nm from the inset image (Figure 2D). This trend tells us that the reaction between spiro-MeOTAD and [Li@C60]TFSI leads to a cumulative formation of aggregations over time.

The reaction mixtures of spiro-MeOTAD and [Li@C60]TFSI in three conditions over the reaction time were analyzed (Figure 2E). The three conditions were the whole solution (supersaturation), a filtered solution using a 0.2-μm-pore-filter to simulate the CNT (filtered supernatant), and a dilution of the filtered residue (diluted precipitates). We used o-dichlorobenzene (ODCB) to dilute the residue (the solubility of [Li@C60]TFSI− in ODCB is reported to be 15 mg mL−1).6a Vis−NIR spectroscopy can identify the composition of the HTL solution, specifically, spiro-MeOTAD peak at 390 nm, spiro-MeOTAD**TFSI− peak at 500 nm,11 and Li@C60 peaks at 800 nm12 and 1035 nm.13 The absorption of the spiro-MeOTAD at 390 nm was too strong in all solutions, indicating that there is an excess amount of spiro-MeOTAD constantly present during the reaction (Figure 2F–H). The Vis−NIR spectra of the supernatant solution show that the spiro-MeOTAD**TFSI− concentration increases over time (3) (Figure 2F). Stirring for 10 h did not decrease the amount of spiro-MeOTAD**TFSI−, which means that reaction 4 does occur. The humps at 800 nm indicate oxidized Li@C60 according to Campbell et al.12a Yet, our calculation shows that it may also indicate spiro-MeOTAD**TFSI− (Figure S11). This peak gets stronger and blueshifts with the increase in the stirring time, indicating that leaving the reaction for a long time may results in the formation of unwanted Li@C60 species (Figure S12). The antioxidant Li@C60 peak at 1035 nm did not appear due probably to an insufficient amount of Li@C60 after the filtration. The supersaturation showed almost no change in the spiro-MeOTAD**TFSI− and the oxidized Li@C60 after 2 h (Figure 2G). The magnified peaks of Li@C60 at 1035 nm showed that the peaks increased in intensity from the 0 h-stirred to 2 h-stirred solution, then decreased for the 5 h- and 10 h-stirred solutions (Figure 2G inset). This alludes that Li@C60 produced in reaction 3 turns into something else when left stirred for more than 2 h. From the diluted precipitates, we could see that the amounts of spiro-MeOTAD**TFSI− were small and similar in all samples (Figure 2H). Whereas, the hump at 800 nm increased with the stirring time, which indicates an increase in the amount of oxidized Li@C60. There was no neutral Li@C60 peak at 1035 nm, which we ascribe to the ODCB solvent.14 Additional experiments using XPS (Figures S13 and S14), and dynamic light scattering measurement (Figure S15) corroborate the reaction mechanism as well, which are discussed in detail in the Supporting Information.

Raman spectroscopy was used to identify the generated Li@C60 species. Figure 3 shows the Raman spectra of spiro-MeOTAD (black), [Li@C60]TFSI− (red), and the 5 h-stirred mixture of both (blue) in the low and high wavenumbers (Figure S16). The A1(2) and H2(8) modes of the [Li@C60]TFSI− spectrum shifted to lower wavenumbers in the mixture. This confirms the reduction to Li@C60 (indicated by green).15 The spiro-MeOTAD peaks still remain after the reaction (closed star). The positions of the H2(1) and A1(2) and the downshift of the A1(1) indicate the formation of (Li@C60)2, arising from the reduced symmetry of the covalently bonded C60.12a The increasing intensity of the peak at 1419 cm−1 is typical of fullerene dimerization (Figures S17 and S18).17 The splitting of H2(1) and A1(1)18 indicates a possible polymerization of fullerene.19 The new peaks near the H2(1) and A1(1) (closed circles) probably come from the mixing of vibrational modes caused by symmetry perturbation. This reveals that Li@C60 undergoes further reaction not only with oxygen (2) but with other Li@C60 to form dimers and polymers (5) (Figure S19).

\[ n\text{Li}^+@\text{C}_{60} \rightarrow (\text{Li} @ \text{C}_{60})_n \]  

PSCs were fabricated in a configuration of glass/indium tin oxide (ITO)/SnO2/[P(phenylethylamine]
(PEA)$_2$PbI$_4$]$_{0.97}$Cs$_{0.03}$PbI$_3$]$_{59}$ (formamidinium (FA)$_{0.97}$Cs$_{0.03}$PbI$_3$]$_{59}$ (2D-3D FACsPbI$_3$)/CNT, onto which the mixture of spiro-MeOTAD and [Li +@C$_{60}$]TFSI$^{-}$ were applied (Figure 4A). It is worth noting that 4-tert-butylpyridine (t-BP) was necessary for PSCs to work and there was no reaction between [Li+@C$_{60}$]TFSI$^{-}$ and t-BP (Table S2 and Figure S20). The initial PCEs of the [Li+@C$_{60}$]TFSI$^{-}$-applied CNT-laminated PSCs showed that the photovoltaic performance increased with the increase in the stirring time of the HTL (Figures 4B and S21, Tables 1 and S3). We surmise that the initial PCE is proportional to the amount of spiro-MeOTAD•TFSI$^{-}$. It should be mentioned that the reproducibility of the initial PCEs of PSCs was relatively low for the long hour-stirred HTL solutions. This is due to the reaction rate being dependent on the stirring condition such as temperature and stirring speed. Continuous illumination on the PSCs in air improved the performance of the devices for a certain period of time, then decreased slowly (Figures 4C and S22). The maximum PCEs, the time taken before reaching the maximum PCE, and the PCE attenuation rates all depended on the HTL reaction time (Figure S23). This is also supported by our oxygen transmittance rate (OTR), in which the change of OTR values follow the predicted degrees of antioxidation activity (Figure S24). The 2 h-stirred HTL-applied CNT-PSCs exhibited the highest PCE of 17.2% with a slow PCE attenuation rate, which implies the optimal balance of spiro-MeOTAD•TFSI$^{-}$ and Li@C$_{60}$ (Figures 4D and S25, Table 1). By encapsulating the device at the right timing, the long-term stability time of more than 1100 h stability under constant illumination in a severe condition (60 °C, 70% humidity) was recorded (Figures 4e and S26). The data reveal that the [Li'@C$_{60}$]TFSI$^{-}$-used CNT-laminated PSCs show by far greater device stability than those of the metal electrode-based PSCs (Table S4) and the Li'TFSI$^{-}$-used CNT-laminated PSCs.

In summary, we fabricated metal electrode-free CNT-PSCs with the mixture of spiro-MeOTAD and [Li'@C$_{60}$]TFSI$^{-}$. The CNT electrode functioned as a natural filter for the endohedral metallofullerene aggregations. This prevented the aggregations from interfering the charge flow, enhancing PCE of the PSCs greatly. It was found that the redox time control of spiro-MeOTAD and [Li'@C$_{60}$]TFSI$^{-}$ was crucial, and 2 h of reaction time was optimal for the maximum efficiency and stability. With the new reaction mechanism found, this work demonstrates metal electrode-free PSCs with unprecedented high stability.
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b06418.

Experimental details, morphology investigation, computational study, reaction mechanism, vis–NIR spectroscopy, XPS analysis, dynamic light scattering measurement, Raman spectroscopy, device performance tests (PDF).

Corresponding Authors
*il.jeon@spc.oxon.org
*maruyama@photon.t.u-tokyo.ac.jp
*matsuo@photon.t.u-tokyo.ac.jp

ORCID
Il Jeon: 0000-0002-4220-8374
Hao-Sheng Lin: 0000-0003-1947-4954
Seungiu Seo: 0000-0002-1676-7172
Hiroshi Okada: 0000-0002-0809-8167
Yang Yang: 0000-0001-8833-7641
Shigeo Maruyama: 0000-0003-3694-3070
Yutaka Matsuo: 0000-0001-9084-9670

Author Contributions
These authors contributed equally.

Notes
The authors declare no competing financial interest.

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