

論文の内容の要旨

論文題目 Design and Functionalization of Fullerenes for High-Performance Perovskite Solar Cells

(高性能ペロブスカイト太陽電池のためのフラーレンの設計と機能化)

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Buckminsterfullerene (C_{60}), a perfectly symmetric soccer ball shape molecule, has been widely investigated in multiple disciplines since the successful gram-scale production achieved in 1990. In the past several decades, thanks to the rapid development of organic chemistry, tremendous methodologies have been well demonstrated for the functionalization. Then, versatile fullerene materials have been synthesized and presented in a wide range of applications, including biomedicine, cosmetics, and photovoltaic. Among these applications, fullerene materials have been mostly demonstrated in the photovoltaic field, thanks to their remarkably excellent electric properties such as ultrafast photo-induced charge transfer, the low reorganization energy, *etc.* Accordingly, considerable efforts have devoted to developing fullerene materials in both organic solar cells (OSCs) and perovskite solar cells (PSCs). The first fullerene-utilized OSC was reported in 1995 using fullerene as an electron-acceptor in the active layer, which obtained a power conversion efficiency (PCE) of 3.5%. Since that, the energy level and solubility were elucidated to be the key for the design and functionalization of fullerenes, owing to fullerenes take the role in the active layer of OSCs. Different from fullerenes in OSCs, fullerenes are commonly used as electron-transport layers (ETLs) in PSC. So, merely transferring the strategies of fullerenes in OSCs to PSCs understandably results in poor performance. Although fullerene-applied PSC achieved an impressively excellent PCE of 21.3% compared with the first device in a PCE of 3.9% in 2013, most examples were obtained by a try-and-error method, which typically exhibited difficult in

reproducibility. Consequently, the design and functionalization of fullerenes for high-performance PSCs remain unclear.

Herein, this thesis mainly discussed how fullerenes influence the performance of PSCs and how to design a good fullerene material for high-performance PSCs. Unlike to fullerene materials in OSCs, this thesis found that fullerene materials in PSCs should be more concerned regarding the electron-carrier mobility, interlayer morphology, and passivation effect, as fullerene materials were utilized as the ETLs or dopant instead the electron-acceptors in OSCs.

- **Interlayer morphology:** fullerene materials that can form a uniformly amorphous ETL film improve the perovskite film quality. Accordingly, thermal-deposited C₆₀ and mixed C₆₀/C₇₀ ETLs exhibited a higher PCE than solution-processed fullerene ETLs’.
- **Electron-carrier mobility:** there are more pristine C₆₀ and fullerene derivatives with 1,2-addition pattern applied in PSCs, as multi-adducts have poor electron mobility because of the large molecular size, and thusly discrete molecule packing.
- **Passivation effect:** fullerene materials that installed alkoxy (RO-), amine (RNH₂-), carbonyl (C=O) groups can function as the Lewis base to passivate the Pb²⁺ to improve the stability and performance by reducing the defects in perovskite cell.

However, conventional fullerene-anion and fullerene-radical chemistry produced fullerene materials failed to achieve fullerene molecules that having all the demands mentioned above. Accordingly, this thesis developed fullerene-cation chemistry to obtain the designed fullerene materials, which achieved the up-to-date highest PCE of 20.7% in an NH₃PbI₃-type PSC. In short, this thesis deeply discussed the design of fullerene materials applied in PSCs, and the functionalization of fullerene materials through fullerene-cation chemistry.

In chapter 3, this thesis deeply discusses how interlayer morphology of fullerene ETL influences the performance of PSCs. Through the electron microscopy, typical thermal-deposited C₆₀ showed an amorphous morphology, which conclusively resulted in a highest performance among pristine fullerenes applied PSCs. On the basis of this finding, a mixed C₆₀/C₇₀ with mass ratio of 9/1 was fabricated as ETL by spin-coating process, which provided a PCE as high as thermal-deposited C₆₀ ETL. Moreover, a vacuum-dry treatment was specifically designed for the spin-coated C₆₀/C₇₀ ETL, which further promoted the PCE up to 18.0%.

In chapter 4, this thesis focuses on finding the best fullerene molecular size for high-performance PSCs. Although C₆₀ can provide the best electron-transport ability thanks to its smallest molecular size for compacted packing, C₆₀ cannot provide other beneficiary functions if without chemical modifications. However, once pristine fullerenes are functionalized, the molecular size is inevitably enlarged. Through applying the designed full-carbon indano[60]fullerene in PSCs, this thesis concluded that the most favorable fullerene molecular size is the fullerene mono-adduct rather than fullerene multi-adduct in OSCs. Therefore, the fullerene mono-adduct can effectively provide many functions such as passivation

site with the minimum compensation of electron-transport ability.

In chapter 5, this thesis comprehensively demonstrates the methodology how to introduce the Lewis base structures such as alkoxy, amino, into fullerene structure. To effectively passivate the perovskite, both dopant method and single passivation layer were investigated. The FIF passivation layer exhibited excellent passivation ability, enabling perovskite cell grow with enlarged crystal size, decreased grain boundaries, and reduced the trap sites at surface. Accordingly, a record-high PCE of 20.7% is achieved among fullerene-applied MAPbI₃ type PSCs. The amino[60]fullerene was applied as dopant in perovskite layer, achieving a slightly better performance. Therefore, the single passivation layer strategy is much more efficient compared with the doping strategy for high-performance PSCs.

In chapter 6, this thesis successfully combined all dominant points previously discussed, synthesizing [60]fullerene-fused ketones for being as ETL in PSCs. This fullerene ketone is the first fullerene derivative that tolerate the thermal-deposition process. ETL fabricated through the thermal-deposition can produce amorphous fullerene film for perovskite formation, which affords a significant improved performance compared with widely applied deposition C₆₀ ETLs. Moreover, the synthesis of [60]fullerene-fused ketone also provide the breakthrough among the fundamental organic chemistry. This is the first example demonstrating the one-step direct oxidation of alkoxy groups to ketones, which is mainly thanks to the excellent electric property of fullerene. This thesis found that fullerene can function as an electron-pool to control the electron transfer so that facilitate the direct oxidation of alkoxy.

In chapter 7, which is positioned after conclusion as an appendix, this section presents several promising non-fullerene materials that can also effectively promote the performance of PSCs. One is the newly designed s-SWNT surfactant helps CNT applied as perovskite crystal bridge to improve the PSCs's performance. The other is denatured M13 bacteriophage applied as large-crystal perovskite growth-template in high-performance PSCs.

Moreover, the ultimate purpose of this thesis, titled "Design and functionalization of fullerenes for high-performance perovskite solar cells", is to provide 1) the efficient synthetic fullerene chemistry on the basis of unconventional fullerene-cation-mediated synthesis; 2) fundamental design and application knowledges for fullerene materials achieving high-performance PSCs to scholars and scientists that currently work in this area and will work in near future.