

論文の内容の要旨

論文題目 Functionalizations of single-walled carbon nanotubes and their application on solar cells
(単層CNTの機能化と太陽電池応用)

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Single-walled Carbon Nanotubes (SWNTs) have been widely explored in many fields to be integrated into new functional devices arising from their exciting optical, electrical, and thermal properties along with their mechanical and chemical stability. Photovoltaic application of SWNTs is one of the most promising application of SWNTs since they can be incorporated in various functional layers of photovoltaic devices as well as their earth abundance and stability. However, the main challenge regarding co-existence of metallic (m-SWNT) and semiconducting SWNTs (s-SWNTs) after synthesis has to be overcome to maximize SWNTs' potential in solar cell application, as small incorporation of either s-SWNTs into m-SWNTs or vice versa could seriously undermine the as-desired physical property of the SWNTs as functional material. While controlled synthesis for chiral specific growth of SWNTs has been extensively studied, functionalization of as-synthesized SWNTs has also been widely used for subsequent device application of SWNTs. In solar cell application, however, limited understanding of functionalization method as well as few exploitations of functionalized SWNTs into solar cell devices has hindered the further improvement of device performance of SWNT-based solar cells

compared to that of inorganic or organic counterparts. This doctoral thesis aims at exploring the new possibility of functionalized SWNT application on solar cell and understanding the functionalization method to achieve high performance solar cell device with SWNTs.

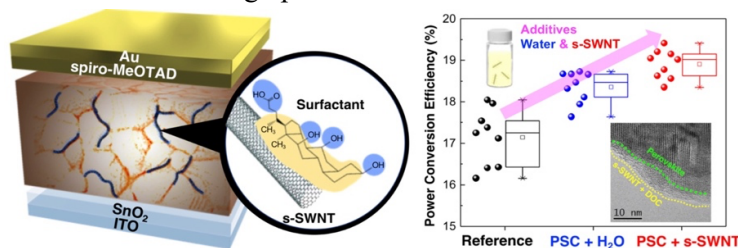


Figure 1 Schematics of purified-s-SWNT-added perovskite solar cells

Recently, perovskite solar cells (PSCs) are considered as promising next-generation solar cells. However, further breakthroughs in terms of realizing higher power conversion efficiency (PCE) are necessary to outperform conventional silicon solar cells. With regard to this, the engineering of grain size and passivation of defective boundaries of perovskite crystals are necessary to obtain high PCE. To enlarge the grain size, inducing homogeneous nucleation and retarding perovskite crystal growth are needed. Accordingly, polymer templates and various anti-solvents have been studied to obtain these. For the passivation of grain boundaries, Lewis-adduct formation of perovskite precursor at the grain surface has a beneficial effect as the structural disorder in the interface of the grains induces shallow trap states, leading to non-radiative recombination of localized charge carriers. Ideally, strategies for engineering the grain size and passivating the grain interfaces at the same time are required. Over the last two decades, CNTs have achieved a lot of excitement among researchers for their device applicability arising from their exceptional charge carrier transporting properties, and outstanding chemical and mechanical stability along with earth abundance. In particular, s-SWNTs with a direct bandgap of up to 2 eV have high conductivity along the tube axis, suitable for charge-transporting media in PSCs. Recently, fullerenes have been reported to function as charge-transporters in PSCs. However, fullerenes have lower carrier mobility and stability than that of SWNTs. So far, there has been one report on the application of purified s-SWNTs in PSCs, where s-SWNTs were used as a hole extracting material next to a perovskite photoactive layer. Another close application is sulfonated multi-walled carbon nanotubes as crystal growth templates during perovskite film formation, but the carbon nanotubes were not purified as semiconducting as they were multi-walled. Herein, we demonstrated purified s-SWNTs with sodium deoxycholate (DOC) surfactant dispersed in water acting as both the perovskite crystal growth templates and charge transporters inside a perovskite layer, increasing the PCE of PSCs from 18.1 % to 19.5 % (Fig. 1). DOC surfactants were used to collect s-SWNTs bound to agarose gel in the process of separation. The carbonyl groups in DOC surfactants formed Lewis adducts with perovskite precursors, PbI_2 to function as growth templates and passivators, inducing large crystal size and reducing trap sites, respectively. Since s-SWNTs

were dispersed in water for a purification step, a small amount of water was added into a $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) solution. To clarify the role of added water, we fabricated water-added PSCs for a comparison. The added-water enhanced the quality of the perovskite crystal grains in terms of homogeneity. With the presence of s-SWNTs with DOC surfactants, the size of crystal grains and mobility of the perovskite film increased. This was verified by microscopic techniques, such as scanning electron microscopy (SEM) and in-situ transmission electron microscope (TEM), and various charge kinetics measurements. However, there was a limitation in the use of s-SWNT_(aq); it was found that 2 wt% of s-SWNT_(aq) was the optimal amount and higher concentration resulted in the decrease in device performance. This is ascribed to the limited purity s-SWNTs and low mobility of DOC surfactants.

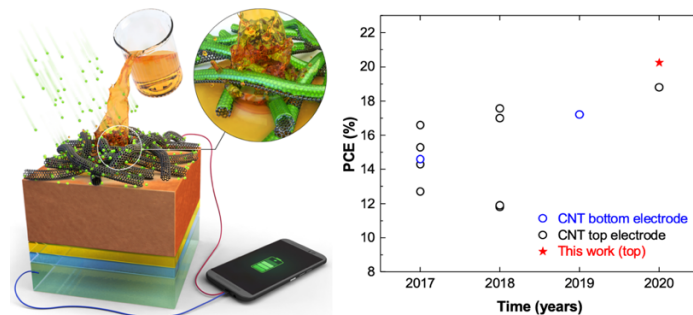


Figure 2 Schematics of PSCs with SWNT top electrodes doped with evaporated MoO_3

Today, the certified PCE of PSCs on a laboratory scale reads over 25%. To supersede the commercially available silicon solar cells (SiSCs), thin-film photovoltaics such as PSCs should extend the application to solar panel windows and tandem solar cells. In addition, by combining PSCs with SiSCs in a tandem structure, the theoretical Shockley-Queisser (SQ) of $\sim 33\%$ can be surpassed thanks to the larger band gap of PSCs compared with that of SiSCs. However, both of those applications require PSCs to be semi-transparent while having high PCE.

To achieve highly transparent and efficient semi-transparent PSCs, the transparent top electrode plays a crucial role. To date, transparent conductive oxide (TCO) electrodes, such as indium tin oxide (ITO), indium zinc oxide, and Al-doped zinc oxide have been widely used. Nevertheless, they are deposited by a magnetron sputtering in which high energetic particles often damage the underlying layers and high-cost vacuum atmosphere is necessary. Metal nanowires could provide a solution to this, but their reflective nature and metal-migration-induced device degradation deter them from being the alternative.

Recently, single-walled carbon nanotube (CNT) transparent electrode has been reported as the top electrode in semi-transparent PSCs and demonstrated high PCE surpassing even that of the metal electrode-based PSCs. Use of CNT electrodes drastically reduces the fabrication cost as they are made from abundant carbon sources and can easily be laminated onto devices by a simple mechanical transfer. The prospect of such CNT top electrode-based PSCs will be boosted if the

efficiency and the transparency of the devices improve even further. The most effective strategies to achieve this is threefold: (1) tuning the work function of the CNT electrode to align with the energy levels of the active perovskite layer and hole-transporting layer and thereby maximizing the open-circuit voltage (V_{OC}), (2) increasing the conductivity of the CNT electrode to maximize the fill factor (FF) and the short-circuit current (J_{SC}), (3) reducing the optical loss between the layers to maximize the transparency of the device. Chemical *p*-doping of the CNT electrode can tune the work function as well as boosting the conductivity. However, it is an extremely challenging task as applying dopants to CNT top electrode can damage the underlying sublayers.

Herein, multifunctional effects of MoO₃ doping on CNT electrode in semi-transparent metal electrode-free PSCs (CNT-PSCs) will be discussed. MoO₃ is thermally deposited onto the CNT top electrodes. The MoO₃ doping boosts the conductivity of the CNT electrode without damaging the sublayers nor reacting with the spiro-MeOTAD solution. This is attributed to the fact that the stable nature of MoO₃, which is solvent-free and non-acidic. The controllability of the *p*-doping strength enables tuning of the CNT work function. By optimizing the thickness of MoO₃, 8-nm-thick MoO₃ layer was found to give the highest PCE of 20.25% when deposited on CNT-PSCs, in which 70% transparent CNT electrode at the wavelength of 550 nm was used. The devices showed increases in all of the photovoltaic parameters upon MoO₃ doping, namely, V_{OC} of 1.162 V, J_{SC} of 23.09 mA/cm², and FF of 0.755. All of which are ascribed to the better aligned energy level, the enhanced electron-blocking ability and the conductivity of the CNT electrodes. The achieved PCE is the highest among the reported CNT-PSCs to date as far as concerned. In addition to this, the presence of MoO₃ heightens the device transparency owing to the reduced parasitic optical loss at the CNT interface. The full potential of the MoO₃-doped CNT-PSCs were assessed by stacking them to SiSCs using a computational model and simulating the 4-terminal tandem solar cells. The enhanced transparency in both visible and near-infrared region through the minimum parasitic absorption of MoO₃ demonstrated expected higher performance of the MoO₃-doped CNT-PSCs compared with ITO-based semi-transparent PSCs as well as the other semi-transparent PSCs reported thus far.

To sum up, this doctoral thesis has made novel contributions on exploring application of functionalized single-walled carbon nanotubes (SWNTs) into solar cell devices and identifying their role as functional material to achieve high-performance solar cell devices : (1) purified s-SWNTs with DOC surfactant can form Lewis-adduct with perovskite precursor, which leads to larger and uniform crystal formation of perovskite film and enhancement of charge extraction from perovskite photoactive layer thereby achieving 19.5% PCE compared to control device. (2) Evaporated MoO₃ can efficiently dope top SWNT electrodes of PSCs resulting in the most efficient SWNT-based PSC of 20.2% PCE for the first time.