論 文 の 内 容 の 要 旨

論文題目　Tailoring SWCNTs and MoS_2 based nanomaterials for application in photovoltaic devices
（光電変換デバイス応用に向けた単層CNT及びMoS_2由来ナノ材料の開発）

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1. Introduction and motivation of this dissertation

As energy is closely related to our human society development, how to obtain energy and how to guarantee sufficient energy have become important issues for a long time. Traditional energy sources such as fossil fuels and nuclear energy suffer from the significant issues of shortage, pollution, and unsafety. In order to solve these issues, renewable energy has attracted much attention in recent years, within which the solar energy has been regarded as a promising next-generation energy source. Photovoltaic (PV) devices, especially solar cells, which are used to cultivate solar energy, are being vibrantly developed. Although several kinds of solar cells have achieved high efficiency of over 20%, the current issues in these solar cells include high cost, inflexibility, heavyweight, and so on. There is an urgent need for the development of next-generation PV devices.

On the other hand, the diversity of low-dimensional nanomaterials has been enriched by both the dimensionalities and new compounds. The 1-dimensional (1D) single-walled carbon nanotube (SWCNT) and 2-dimensional (2D) MoS_2 are both the representatives of their dimensions and elements, with excellent physical, chemical, and mechanical properties. Moreover, the diversity of low-dimensional nanomaterial world has also been enriched by the method of "tailoring". As the properties of these materials can be tuned by carrier doping and structural transformation, we can develop different tailoring methods for different application purposes, such as nanomaterial PV devices. For PV device applications, the low-dimensional nanomaterials can reduce the usage of high-cost materials, and they have tunable physical properties with flexible and lightweight nature. These advantages enable them to be promising candidates for next-generation PV devices.

2. Purpose of this dissertation

This dissertation focuses on the tailoring methods of SWCNTs and MoS_2 based nanomaterials for the application purpose of PV devices, especially solar cells.

The SWCNT transparent conductive film (TCF) in SWCNT-Si solar cells is one of the crucial factors for improving performance. Both the conductivity and transmittance of SWCNT film need to be high in order to have excellent performance in SWCNT-Si solar cells, but this always includes a trade-off. Moreover, SWCNT shows a hole-transporting property in solar cells, which is tunable by carrier doping. As a result, the first purpose of this dissertation is to explore novel and outstanding tailoring methods for SWCNT TCF, and to apply the tailored SWCNT TCF to SWCNT-Si solar cells to achieve higher performance than the state of the art. Furthermore, this process can shed some light on the mechanisms of SWCNT-Si solar cells.

The second purpose of this dissertation is to explore the possibility of applying SWCNTs and MoS_2 based nanomaterials in PV devices. Although MoS_2 only has a thickness of nanometer level, its light-absorbing efficiency has been calculated to be about one order of magnitude higher than that of traditional PV materials. Thus, using MoS_2 as the light-absorbing material in PV devices can have the advantages of cost-reduction, flexible applications, and gaining insights for developing low-dimensional nanomaterial PV devices. On the other hand, MoS_2 may also contribute to other functional layers of solar cells after tailoring. In order to achieve the second purpose, tailoring SWCNTs and MoS_2 based nanomaterials by synthesis and structural transformation methods are discussed in this dissertation, as well as the application of the synthesized SWCNTs and MoS_2 based nanomaterials in PV devices.

3. Organization and contents of this dissertation

In Chapter 1, this dissertation begins with a brief introduction of the world of low-dimensional nanomaterials, followed by the discussions of the structures and structure-related properties of SWCNTs and MoS_2, which are the two basic low-dimensional nanomaterials that this dissertation focuses on. Then, renewable energy resources are introduced, with a specific emphasis on solar cells for solar energy harvesting. Subsequently, the development of next-generation solar cells is discussed, of which the nanomaterial solar cells are the applications that this dissertation studies for low-dimensional nanomaterials. The application of low-dimensional nanomaterials in solar cells are introduced in a general manner, with the detailed and specific introductions provided in the following experimental chapters. The motivation and purpose of this dissertation are also introduced in Chapter 1.

The general experimental methodology is introduced in Chapter 2. The first part is about the metrology for the low-dimensional nanomaterials and nanomaterial solar cells, with the discussions of the mechanisms of these methods. The second part is about the fabrication of SWCNT-Si solar cells and the properties of the as-fabricated pristine SWCNT-Si solar cells. We applied the randomly-oriented SWCNT films that can be dry-transferred onto arbitrary substrates. The pristine SWCNT-Si solar cell showed the best power conversion efficiency (PCE) with 90%-transparency SWCNT film and was stable in air for over one month. The third part is about the structure of a semi-automated low-pressure chemical vapor deposition (LPCVD) system that I constructed for synthesizing MoS_2 based nanomaterials, and about the reactions during the CVD process. The specific experimental methodology will be introduced in the following experimental chapters.

Chapter 3 presents the results of tailoring SWCNTs for application in SWCNT-Si solar cells. We report a polymeric acid, which can induce a multi-effect of permanent and strong *p*-doping, anti-reflection, and encapsulation of SWCNT-Si solar cells. Nafion, the polymeric acid was reported to dope carbon electrodes effectively and exhibit a permanent doping effect in organic light-emitting devices and organic solar cells. Interestingly, when Nafion was used in SWCNT-Si solar cells to dope the SWCNT top electrode, its effect was not only limited to a *p*-dopant but led to a favorable anti-reflection effect and an encapsulation effect as well. The device PCE increased from 9.5% to 14.4% owing to the increases in all the three photovoltaic parameters, specifically, short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), and fill factor (FF) upon a simple spin-coating of the polymeric acid. The increase in J_{SC} came from the inaugurated light absorption from the anti-reflection effect as evidenced by both empirical and computational analyses in this work. The anti-reflection effect was greater than that of PMMA owing to the intrinsically low refractive index of Nafion. The improvement in FF came from the improved conductivity of SWCNT films by the strong *p*-doping of the polymeric acid. There was a significant increase in V_{OC} as well, which is attributed to the strong Fermi level downshift and the densification effect of SWCNTs, thanks to the highly electronegative fluorinated chains and the viscous nature of the polymeric acid, respectively. The polymeric acid functioned as an excellent encapsulation layer as well. The polymeric acid-coated SWCNT-Si solar cells withstood submersion to chloroform, HNO_3, and water for more than 10 days, which was by far more stable than the PMMA-coated SWCNT-Si solar cells. The obtained stable PCE of 14.4% currently stands the highest among the reported carbon nanotube-based Si solar cells with similar active areas.

In Chapter 4, the investigations of tailoring SWCNT and MoS_2 based nanomaterials and their application to PV devices are discussed. First, the results of the controlled synthesis of 2D MoS_2 nanomaterials are presented. Through the LPCVD system that I constructed, a 2D MoS_2 monolayer film with over 99% coverage was synthesized after tuning various synthesis parameters to the optimal conditions. Second, we tried to synthesize 1D MoS_2 nanotube (MoS_2NT) onto 1D nanostructures. With the optimized synthesis parameters for 2D MoS_2 monolayer film, a heterostructure of an SWCNT wrapped with a single-walled MoS_2NT has been discovered, which is also the first evidence of a single-walled MoS_2NT. Furthermore, with the heterostructure of 1D boron nitride nanotube (BNNT)-SWCNT, a novel type of 1D semiconductor-insulator-metal (MIS) van der Waals (vdW) heterostructure of MoS_2NT-BNNT-SWCNT has been synthesized with MoS_2NT as the semiconducting tubular layer. Third, the possibility of applying the as-synthesized SWCNTs and MoS_2 based nanomaterials in PV devices are discussed with various device structures. For the light-absorbing layer function, C_{60}-MoS_2NT-BNNT-SWCNT PV device showed higher photocurrent than that of C_{60}-MoS_2NT-SWCNT because of the charge separation facilitation of BNNT. For the electron transport layer (ETL) and cathode multifunction, we have substituted two layers of PCBM and SWCNT in inverted-type perovskite solar cells with one multifunctional layer of MoS_2NT-(BNNT)-SWCNT. The integration of ETL and cathode in one layer can allow easier fabrication than the layer-stacking, and thus reduce the size of the device and the amount of used materials. The BNNT again facilitated the charge separation, resulting in the improvement of V_{OC} and PCE. Moreover, there is a trade-off between the tunneling and blocking effects of BNNT for electrons and holes. For the hole transport layer (HTL) and anode multifunction, MoS_2NT-SWCNT was applied to normal-type perovskite solar cells and improved the PCE by the excellent hole-extraction ability of MoS_2NT. A PCE of 15.0% has been achieved after the application of spiro-MeOTAD. These results have demonstrated prototypes for the promising application of 1D vdW heterostructures in PV devices.

Finally, the summaries, my vision for next-generation solar cells, and the future perspectives of the research in this dissertation are presented in Chapter 5.

4. Conclusions and future perspectives of this dissertation

First, SWCNT film has been tailored by Nafion to improve SWCNT-Si solar cell performance successfully. The performance of SWCNT-Si solar cell has been improved to record-high efficiency and stability. Mechanism discussions show that Nafion has the superior multifunction of *p*-type doping, anti-reflection, and encapsulation.

Second, MoS_2 monolayer film has been synthesized by a home-made LPCVD system. A heterostructure of an SWCNT wrapped with a single-walled MoS_2NT has been discovered, which is also the first evidence of a single-walled MoS_2NT. Furthermore, a 1D MIS vdW heterostructure of MoS_2NT-BNNT-SWCNT has been synthesized for the first time.

Third, the MoS_2NT-BNNT-SWCNT 1D vdW heterostructures have shown promising applications in PV devices with different multifunctions of light-absorbing layer, ETL/cathode, and HTL/anode. The further improvements of the tailoring methods and the device structures will lead to novel applications of both the SWCNT and MoS_2 based nanomaterials and the 1D vdW heterostructures in PV devices.