

Fabrication of the inverted bulk heterojunction organic solar cell on titanium oxide nanosheet

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1. Introduction

Organic solar cells (OSCs) with conjugated and fullerene based bulk heterojunction (BHJ) composites are considered promising candidate as one of the promising candidate for the solar cells because of their light-weight, low-cost, and simple fabrication for large area processing. Recent advances in polymer and fullerene based materials improved the power conversion efficiency of BHJ OSCs up to 5% in conventional device structures consisting of PEDOT-PSS as the anodic buffer layer, poly(3-hexylthiophene) (P3HT): phenyl-C₆₁-butyric acid methylester (PCBM) mixture as the active layer, and amorphous TiO_x as the cathodic buffer layer (not required always), and Al or Ag as the cathode. Since the more effective crystalline TiO₂ (anatase phase), requires high temperature heat-treatment at ~500°C, the inverted structure consisted of ITO/ TiO₂/ active layer/ MoO_x/ Ag or Au structure is preferable for fabricating the BHJ cell with titanium oxide. Since the interface between acidic buffer layer PEDOT-PSS, MoO_x, ITO and Al electrodes are unstable in air, especially under humid conditions, the improvement of the performance in inverted structure seems to be very important for the development of BHJ cells.[1,2,3] However, the high temperature process for fabricating crystalline TiO₂ is a severe disadvantage for the application of organic solar cell. Therefore, we considered that the development of the fabrication technique of high quality titanium oxide film at low temperature (below 150°C) is supposed to be one of the most important strategies for the development of inverted BHJ cells.

Recently, Sasaki et al. developed a set of transition metal oxides with 2 dimensional structure (called "nanosheet") including titania. [4]The nanosheet has several important features: (i) ultimate two-dimensionality with a thickness of ~1nm and a lateral size ranging from sub-micrometers to 10 micrometers, (ii) high crystallinity and well-defined composition, and (iii) novel and enhanced physical properties due to the quantum size effect.[3] For example, the band gap of titania nanosheet (~3.8eV) is much larger than that of conventional anatase titania (~3.2eV) which might be favorable for the transparent oxide buffer layer in solar cell application. Moreover, the exfoliated titania nanosheet can be deposited by low temperature process, such as electrophoresis, Langmuir-Blodgett technique, and the layer-by-layer deposition of the diluted dispersion of anionic titania nanosheet and cationic polymer in a pure water

etc. [5,6,7]

In this study, we have investigated the deposition condition of titania nanosheet onto ITO coated glass substrate and silica substrate. We have then investigated the electrical or photovoltaic properties of the inverted BHJ cell in ITO/ titania nanosheet/ P3HT: PCBM active layer/ MoO_x/ Ag multilayered structure.

2. Experimental

A layered titanate Cs_{0.7}Ti_{1.825}□_{0.175}·O₄ (□: vacancy) was prepared by solid-state calcination of an intimate mixture of Cs₂CO₃ and TiO₂ (1/1.825 in molar ratio) at 800 °C for 20 h. Interlayer Cs ions were removed by treating the Cs-titanate powder with a 1 mol/dm³ HCl solution for 3 days. The HCl solution was renewed each day to ensure complete exchange. The acid-exchanged phase (0.4 g), H_{0.7}Ti_{1.825}□_{0.175}O₄·H₂O, was agitated vigorously with 100 cm³ of a TBAOH solution at ambient temperature. The TBA concentration was 0.017 mol/dm³, and these conditions give an equivalent stoichiometry of the agent with respect to the exchangeable protons in H_{0.7}Ti_{1.825}□_{0.175}O₄·H₂O, which is favorable for delamination into single sheets. When the mixture was shaken for 14 days, it yielded a turbid colloidal suspension in which the unilamellar crystallites of Ti_{1-σ}O₂^{4σ-} (σ ~0.09) were dispersed. [5]

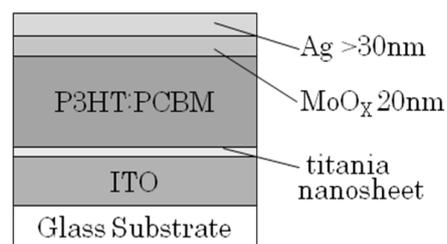


Fig.1. The cross sectional illustration of inverted BHJ cell used in this study

The devices were fabricated on 150nm-thick ITO coated glass substrates. The width of ITO layer was patterned to 2mm. After routine cleaning with detergent, deionized water, ultra-pure water (with ultra-sonication, 2-3 times), we deposited titania nanosheet by layer-by-layer deposition technique. Deposition cycles of the following four steps were repeated for a desired number of times (1~10 cycles) to obtain a multilayered nanosheet film at room temperature: (i) immersion of the substrate in 2wt% of polydiallyldimethylammonium (PDDA, cationic macromolecule) wa-

ter solution for 10 min, (ii) thorough washed with ultrapure water, (iii) immersion in the TiO₂ nanosheet sol solution adjusted to 1 mmol/dm³ for 20 min, and (iv) washed with ultrapure water. [3] After heat-treatment of the substrate at 110 °C for 30min, P3HT/PCBM mixture film was spin-coated onto titania nanosheet film from chlorobenzene solution. The sample was then heated at 150 °C for 5 min in nitrogen in order to obtain the micro-phase separation of crystalline P3HT/PCBM film. Finally MoO_x (20nm) and Ag (>30nm) layer film was evaporated in a vacuum chamber. The effective area was 4mm². Electrical characterization were performed in a groove box in argon atmosphere at ambient temperature with a source meter (ADCMT model 6241A) under 1 sun global AM 1.5 simulated solar illumination using a calibrated solar simulator (SAN-EL Electric model XES-40S1).

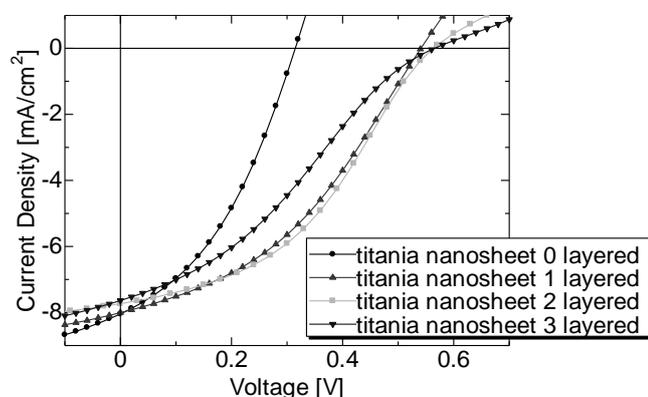


Fig.2. Photovoltaic properties of ITO/titania nanosheet/P3HT:PCBM/MoO_x/Ag devices under white light illumination

Table 1

Photovoltaic parameters of fabricated BHJ solar cells which deposited different number of titania nanosheet under 100 mW/cm² simulated solar radiation

Number of titania nanosheet	J _{SC} (mA/cm ²)	V _{OC} (V)	FF	η(%)
0 layered	8.04	0.31	0.39	0.97
1 layered	8.00	0.54	0.39	1.70
2 layered	7.73	0.56	0.42	1.80
3 layered	7.64	0.56	0.32	1.35

3. Result and discussion

Figure.2. shows the current density-voltage (J-V) characteristics for ITO/titania nanosheet/ P3HT:PCBM/MoO_x/Ag devices under white light illumination. Table 1 summarizes the J_{SC}, V_{OC}, FF and conversion efficiency η for each device. The device fabricated without tinania nanosheet showed J_{SC}, V_{OC}, FF and η in the device without titania nanosheet are 8.04 mA/cm², 0.31 V, 0.39 and 0.97 % respectively. On the other hand, those values in the device with titania nanosheet mono-layer becomes 8.00 mA/cm², 0.54 V, 0.39, 1.70%. Similarly, V_{OC}, FF and η in the device with two

layers of titania nanosheet increased to 0.56 V, 0.42 and 1.80 % respectively. However, those parameters in the devices with thicker decrease with the increment of titania nanosheet thickness.

From these result, one or two nanosheet layers could markedly suppress the leakage current because the ITO surface is covered by a few titania nanosheet layers deposited by layer-by-layer deposition technique.

On the other hand, the decrement of FF and JSC in the device with thicker nanosheet is attributable to the increment of series resistance across the titania nanosheet. Since PDDA is considered as a polymeric insulator the insertion of PDDA reduces the electron transport across the titania/PDDA multi-layers. And it is preferable to remove PDDA layers by the additional new technique in the near future.

4. Conclusion

In this study, we investigated the deposition condition of titania nanosheet onto ITO coated glass substrate and silica substrate and then investigated the electrical or photovoltaic properties of the inverted BHJ cell in ITO/ titania nanosheet/ P3HT:PCBM active layer/ MoO_x/ Ag multilayerd structure.

Only one or two nanosheet layer could markedly suppress the leakage current. That is we could obtain the pin-hole free nanosheet film by the layer-by-layer technique. The open circuit voltage, therefore, increased from 0.31 V to 0.56 V by the insertion of only 2~3nm thick titania nanosheet successfully. On the other hand, the use of PDDA might be increase the contact resistance across the titania nanosheet. This disadvantage might be overcome by the improvement of nanosheet deposition technique or the device architecture. The detail will be discussed during the conference.

Acknowledgements

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References

- [1] N. Kudo, S. Honda, Y. Shimazaki, H. Ohkita, S. Ito : *Appl. Phys.* **90** (2008) 183513.
- [2] C. Waldauf, M. Morana, P. Denk, P. Schilinsky, K. Coakley, S. A. Choulis, C. J. Brabec : *Appl. Phys.* **89** (2006) 233517.
- [3] J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T. Nguyen, M. Dante, A. J. Heeger : *Science*, **31** (2007) 222.
- [4] T. Sasaki, M. Watanabe : *J. Am. Chem. Soc.* **120** (1998)4682
- [5] T. Sasaki, Y. Ebina, T. Tanaka, M. Harada, M. Watanabe, G. Decher: *Chem.Mater.*,**13** (2009)4661
- [6] L. Xue, K. Kajiyoshi, Y. Yan: *Thin Solid Films*, **518** (2009) 10
- [7] K. Akatsuka, M. Haga, Y. Ebina, M. Osada, K. Fukuda, T. Sasaki: *Acs nano*, **3** (2009)1097