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SPECIAL TOPIC — New generation solar cells

Preparation of Se-based solar cell using spin-coating method in ambient condition*

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A new hybrid organic-inorganic structure of FTO/TiO_2/Se/HTL/Au based selenium solar cell has been fabricated through a low-cost spin-coating process in air. In this process, selenium is completely dissolved in hydrazine, to form a homogeneous precursor solution. After spin-coating the precursor solution on the TiO_2 substrates, following by sintering at 200 °C for 5min, a uniform selenium film with crystalline grains is formed. The selenium based solar cell exhibits an efficiency of 1.23% under AM1.5 illumination (100 mW·cm^{-2}), short-circuit current density of 8 mA·cm^{-2}, open-circuit voltage of 0.55 V, and fill factor of 0.37. Moreover, the device shows a stable ability with almost the same performance after 60 days.

Keywords: spin-coating method, selenium, solar cells

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1. Introduction

Selenium (Se) based inorganic-organic heterojunction solar cells have been considered as one of the most promising candidates for solar energy harvesting.[1–3] Se can be used as a photoabsorber to generate photoelectrons in solar cells due to its stable nature and suitable band gap of 1.8 eV.[4] The maximum theoretical efficiency of selenium-based solar cells estimated to be about 20% under AM1 from the band gap energy of crystalline selenium.[5] Many studies on this type of selenium solar cell have been reported. ITO *et al.* assembled Se-based solar cells with a high efficiency of 5.01% and promising features early in mid-1980s.[6] Recently, a type of solar cell in ITO/compact-TiO_2/mp-TiO_2/Se/Au structure based on an extremely thin Se absorption layer on mesoporous TiO_2(mp-TiO_2) is successfully constructed with an over 3% power conversion efficiency (PCE) without any expensive organic parts.[7]

Although very impressive cell efficiencies have been achieved, the cell architecture, use of vacuum, or the two-step deposition process should be modified to improve efficiency and reduce fabrication costs since the high vacuum condition is high energy consumption and low production capacity. Evaporation process during fast spinning can induce the formation of well-crystallization between Selenium and the substrate for the fast crystallization rate of Se, which often leads to a poor coverage and morphology.[8,9]

Spin coating, as one of the cheapest film production methods, is widely used in solution-processed solar cells.[10] Alternatively, solution-based techniques have been proposed to fabricate thin films using a mixture of two precursors to form the complete absorption layer. Therefore, a high-quality Se films using mixing solvent is successfully prepared through spin-coating process in the ambient condition.[11] It is significative to synthesize Se film in the ambient condition without glove box involved.

Herein, we report a successful application of a solvent method for selenium film in heterojunction solar cell under air atmosphere. This solvent-engineering technology enabled fully solution-processed selenium based inorganic-organic heterojunction solar cells with a certified 1.23% PCE under standard reporting conditions. Comparing with the different hole transport materials (HTM) for this structure device, it provides important progress towards the understanding of the role of solution processing under air atmosphere in the realization of low cost and highly efficient selenium based inorganic-organic heterojunction solar cells.

2. Experimental section

2.1. Chemicals and reagents

The titanium (IV) isopropoxide (TTIP) was purchased from Aladdin. Other anhydrous solvent was purchased from Alfa Aesar. 4-tert-butypyridine and lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) were purchased from Kanto. Poly [bis(4-phenyl) (2,4,6-trimethylphenyl)amine] (PTAA) and Poly(3-

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hexylthiophene-2,5-diyl) (P3HT) were obtained from Sigma-Aldrich. 2,20,7,70-tetrakis-(N,N-di-4-methoxyphenylamino)-9,90spirobifluorene(spiro-OMeTAD) were obtained from Youxuan Trade and Toronto Technologies Co., Ltd, respectively. All chemicals and reagents were used as received without any further purification.

2.2. Preparation of TiO_2 substrate

Fluorine-doped tin oxide (FTO) glasses were etched by zinc powder and 2 M hydrochloric solution, following by ultrasonically cleaning in deionized water, detergent solution, ethyl alcohol and acetone for 30 min, respectively. Then the glasses were transferred to the ultraviolet-ozone (UV-O_3) cleaner and kept for 15 min. Subsequently, a titanium isopropylate (TTIP) solution including TTIP (369 μL) and 2.53 mL 2-propanol (IPO) was spin-coated on surface of the cleaned fluorine-doped tin oxide glasses (FTO), and calcined at 450 °C for 1 h, and the compact layer of TiO_2 (about 80 nm in thickness) was obtained. Lastly, a 200–300 nm thick mesoporous TiO_2 (mp-TiO_2) film was formed on the compact TiO_2/FTO substrate after spin-coating the pastes and calcining at 500 °C for 30 min.

2.3. Device fabrication and characterization

300 mg·mL^{-1} selenium hydrazine solution was spin-coated onto the as-prepared mp-TiO_2/compact TiO_2/FTO substrates with the different hot casting temperature from 25 to 175 °C at speed of 2000 r.p.m. for 30 s. After sintering at 200 °C for 5 min, a black crystalline Se layer was obtained. Subsequently, the P3HT, spiro-OMeTAD and PTAA as hole transport materials (HTMs) were spin-coated on the Se layers respectively. Finally, a gold counter electrode was prepared by thermal evaporation deposition. The active area was fixed at 0.12 cm^2.

The morphology of Se films were characterized by field-emission scanning electron microscopy (FEI HELIOS NanoLab 600i). The crystal structure and phase purity of the Se films were investigated by x-ray diffraction (XRD) using a Empyrean Panalytical X'Pert Pro x-ray diffractometer with Cu Kα radiation 1.5418 Å. The band gap of Se films was studied through UV-visible (UV-vis) absorption spectra using a spectrophotometer equipped with an integrating sphere setup (UV-3600). The current density–voltage (J–V) characteristics of these devices were obtained on a comprehensive electrochemical power workstation (VersaSTAT3, Ametek, USA).The photovoltaic performance was recorded under AM1.5G illumination at a calibrated intensity of 100 mW·cm^{-2} with the Newport 94021A class ABB solar simulator equipped with a 150 W xenon lamp. The illumination intensity was standardized before each test by a standard Si solar cell (1218, Newport, USA).

3. Result and discussion

Schematic of the simple solution spin coating proceed methods of Se film and Se based solar cells deposition is shown in Fig. 1. In this study, a novel organic-inorganic solar

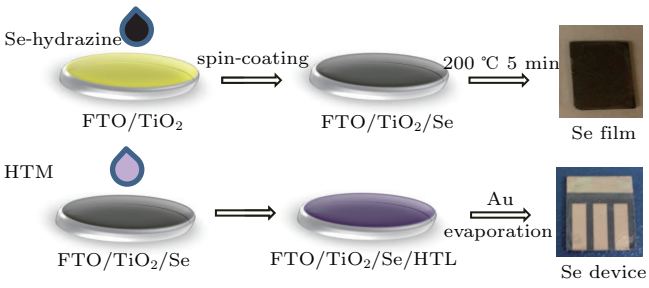


Fig. 1. (color online) Schematic illustration of different steps in solution processed methods for Se-based solar cells.

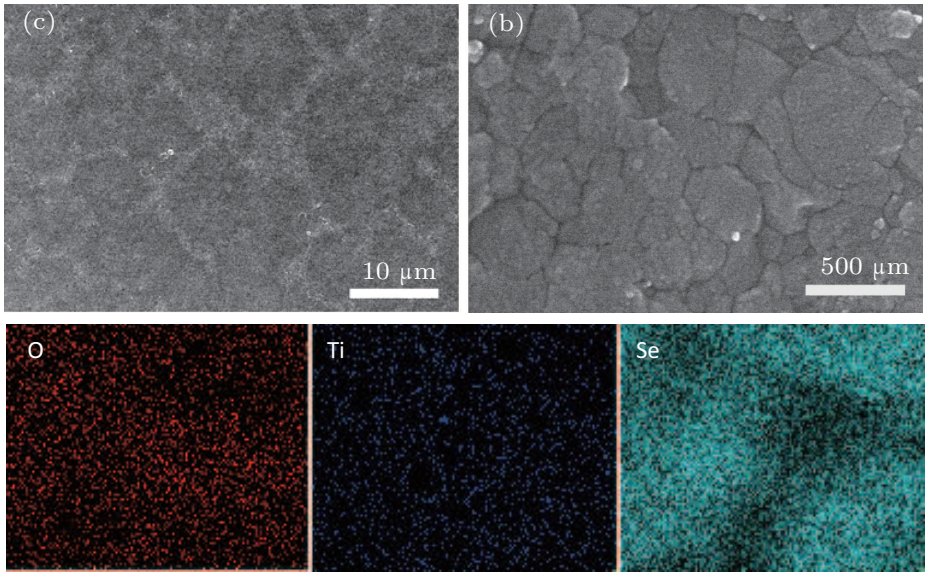


Fig. 2. (color online) Top-view SEM images of the Se crystalline film coated on FTO/TiO_2 substrate at (a) low and (b) high magnifications and EDX analysis of FTO/TiO_2/Se films with elemental mapping.

cell in FTO/compact-TiO_2/mp-TiO_2/Se/HTL/Au structure is designed using Se as the photo-absorbed layer. In the first step, Se layers were prepared on TiO_2-coated substrates by spin coating under air atmosphere. The high-quality crystallized Se film is formed after sintering at 200 °C for 5 min. The devices were successfully fabricated after depositing hole transporting materials (HTM) (PTAA, P3HT, Spiro-OMeTAD) and followed by the thermal evaporation deposition of a gold layer with a thickness of 80 nm.

Figure 2(a) displays the top-view SEM image of Se film. The FTO/TiO_2 substrate is conformally covered by Se film with a few cracks in the Se layer. From the high magnification (Fig. 2(b)) image, a full coverage on the surface can be seen, indicating that Se shrinks after crystallization. Elemental mapping is also performed through energy dispersive x-ray (EDX) analysis (Fig. 2), which further confirms the uniform Se coated on the FTO/TiO_2 layer after sintering.

Photoabsorption and the transmission of electrons are significantly affected by the crystallinity and morphology of the inorganic photoabsorber. In this work, Se films annealed at 200 °C for 5 min, the crystal structure of the Se film annealed at 200 °C for 5 min is characterized by XRD (Fig. 3). Strong peaks are detected at the positions of 23.5°, 29.7°, and 51.7°, which are assigned to the (010), (011), and (021) crystalline planes of selenium, respectively.

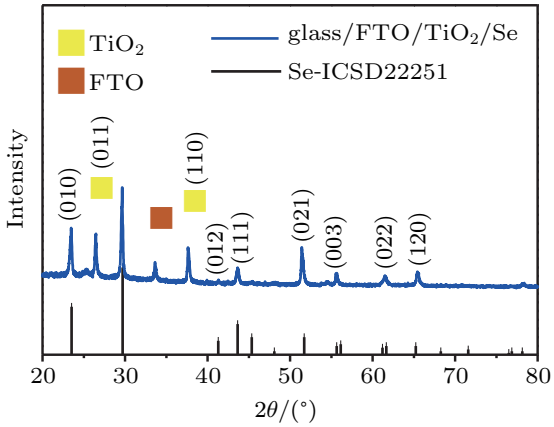


Fig. 3. (color online) X-ray diffraction data of FTO/TiO_2/Se.

In this study, we used Se as a photoabsorber to design organic-inorganic Se-based solar cells with a FTO/compact-TiO_2/mp-TiO_2/Se/HTL/Au structure (Fig. 4). Figure 4(a) shows a cross-sectional SEM image of the complete Se-based solar cell, in which each functional layer could be evidently distinguished. The energy level diagram of Se-based solar cells (Fig. 4(b)), the mesoporous TiO_2 as ETL collected the photo-induced electrons from Se and supported the Se layer in Se-based solar cells. Se as a photoabsorber generated electrons and holes. The HTL was used to collect and transport holes from Se to an external circuit.

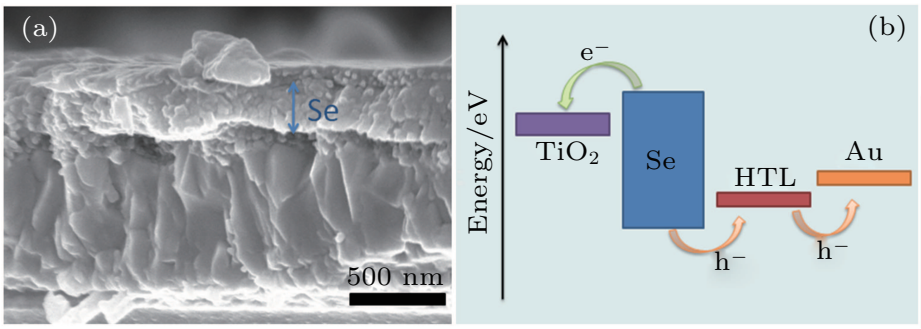


Fig. 4. (color online) Cross-sectional SEM image of a complete device (a) and energy level diagram of Se-based solar cells (b).

The ultraviolet visible (UV-vis) absorption spectra of selenium films deposited on TiO_2/FTO are shown in Fig. 5(a). The absorption wavelength of selenium ranges from 400 to 700 nm, almost covers the entire region of visible light. According to the conventional Tauc equation, the band gap of Se is calculated to be 1.79 eV, which is consistent with the result from previous research.[4] Therefore, Se is a suitable photoabsorber for solar cells.

Figure 5(b) shows the *J*–*V* curves under AM 1.5 G irradiation (100 mW·cm^{-2}) of the corresponding device. Different HTL layers including Spiro-MeOTAD, P3HT, and PTAA are employed on Se-based solar cells for parallel comparison. The device based on P3HT as HTL presents much lower PCE of 0.62% with low open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF) (Table 1). Spiro-MeOTAD-based solar cell exhibits a high PCE of 1.23% coupled with high V_{oc} of 0.52 V, J_{sc} of 6.39 mA·cm^{-2} and FF of 0.37. The unoptimized solar cell in FTO/TiO_2/Se/PTAA/Au structure delivers a low PCE of 1.08% due to its low J_{sc} and FF, while the PTAA-based Se solar cell shows a higher V_{oc}. The V_{oc} value depends on the difference between the conduction band of TiO_2 and highest occupied molecular orbital (HOMO) level of HTM. The photonic properties of solar cells based on the solution processed Se film prepared in ambient condition are comparable to those devices fabricated in the glove box reported previously. The device using spiro-MeOTAD as HTL exhibits the best photovoltaic performance among the three samples produced in air condition. Built on all the above re-

sults, this solution proceed Se-based solar cells possess great potential in the future application.

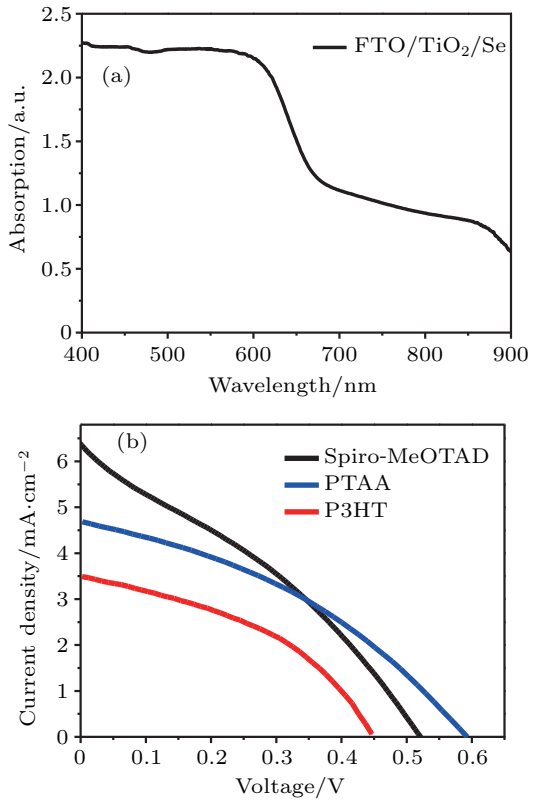


Fig. 5. (color online) UV-vis absorption spectra of Se film (a) and *J*–*V* curves of Se-based solar cells (b).

Table 1. Photovoltaic parameters of the optimized Se-based solar cell with different HTL under AM 1.5 G irradiation (100 mW·cm^{-2}) of the corresponding device.

HTM	V_{oc}/V	J_{sc}/mA·cm^{-2}	FF	PCE/%
Spiro-MeOTAD	0.52	6.39	0.37	1.23
PTAA	0.59	4.71	0.39	1.08
P3HT	0.45	3.50	0.39	0.62

Figure 6 shows the results of stability tests of the corresponding Se solar cells in an ambient environment with 40% relative humidity without encapsulation. We note that the cell characteristics improved with aging owing to stress release, and stabilized after 60 days at room temperature in air.

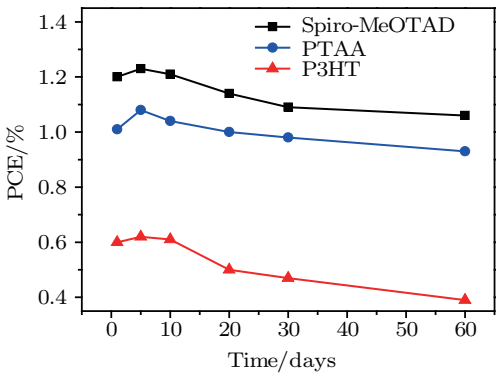


Fig. 6. (color online) Long-term stability of the cell stored in ambient atmosphere at room temperature without encapsulation and measured under one sun illumination.

4. Conclusion and perspectives

In summary, inorganic-organic heterojunction solar cells have been fabricated employing a Se film as the photoabsorber layer, which is prepared by facile spin-coating method in ambient condition. A new selenium thin-film solar cell has been developed. The unoptimized selenium based thin-film solar cell in FTO/TiO_2/Se/HTL/Au structure exhibits PCE of 1.23%, AM1 of 100 mW·cm^{-2} and an efficiency of 1.07% after aging for 60 days. This new type of Se-based solar cell from a facile spin coating method under ambient condition with satisfied performance make it possible to fabricate competitive solar cell in low cost process.

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