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Fabrication of silver sulfide thin films for efficient organic solar cells with high short-circuit currents based on double heterojunctions

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HIGHLIGHTS

- Ag_2S nanoparticles are synthesized via a newly developed HRTD method.
- Efficient solar cells based on double heterojunctions are fabricated.
- High short-circuit currents for prepared solar cells are obtained.
- High conversion efficiency of 3.21% is achieved for prepared solar cells.

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ABSTRACT

Efficient solar cells based on Ag_2S/P3HT and PCBM/P3HT heterojunctions are fabricated, in which the Ag_2S nanoparticles are deposited on ITO glass via a newly developed high-speed rotating thermal decomposition method as an electron selective layer and a light absorption material. The ITO/$Ag_2S(n)$/P3HT:PCBM films have a complementary effect in the light absorption due to the narrow band gap of Ag_2S. The Ag_2S nanoparticles in the upper layer of Ag_2S film form a vertical nanotree-structure after many cycles of Ag_2S deposition and lead to the formation of Ag_2S/P3HT bulk heterojunction, which facilitates exciton dissociation at the P3HT/Ag_2S interfaces and made Ag_2S nanocrystals electron-transport materials in the active layers. Moreover, the Ag_2S make a contribution to the photocurrent as a light absorber. The maximum power conversion efficiency of 3.21% is achieved for the fabricated ITO/$Ag_2S(50)$/P3HT:PCBM/MoO_3/Au solar cell with high short-circuit current, which is 1.13 times the best efficiency (2.84%) of the ITO/dense-TiO_2/P3HT:PCBM/MoO_3/Au cell made by the high-temperature process and is also much higher than that of reported similar hybrid solar cells based on Ag_2S/conjugated polymer heterojunction. The improvement of the efficiency may result from the reduced charge recombination and increased light absorption due to the formation of Ag_2S.

1. Introduction

Organic bulk heterojunction (BHJ) solar cells have attracted great attention due to their potential as a low cost renewable energy source [1–4]. Over the past 10 years, considerable work has been done on the performance of organic BHJ solar cells and the power conversion efficiencies (PCEs) of 7–9% can now be obtained for small-area devices [5]. However, for commercial energy applications and competitiveness in the photovoltaic market, not only a higher module PCE (over 10%) but also a considerable reduction of manufacturing costs is required [6,7]. Compared with the further improvement in PCEs, the fabrication cost of organic BHJ solar cells is getting more and more attention [8–10]. For example, it has been noted that the consumption of considerable energy should be avoided in the fabrication process [8,10]. In other words, a very low input energy for manufacture should be required, which is the reason why solution processing organic BHJ solar cells are of particular interest. Compared with expensive vacuum-based coating techniques (thermal evaporation or sputtering) and/or high temperature sintering, the low-temperature solution-based technique allows lower energy consumption. Typically, for inverted organic BHJ solar cells, the transparent electron-selective layer between the ITO electrode and active film, such as TiO_2 film

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[11–14], generally requires high temperature sintering at about 500 °C. To reduce energy consumption, other electron-selective materials prepared by low temperature solution-based method, such as ZnO [15–17], tris(8-hydroxyquinolinato) aluminum [18], graphene quantum dots [19] and alkali carbonates [20], are used to replace the TiO_2 layer.

As an effective n-type semiconductor material for photovoltaic devices, Ag_2S has attracted much attention in the past few years due to its narrow band gap of 0.9–1.05 eV and its large absorption coefficient [21,22]. Therefore, as an electron-selective layer inorganic BHJ solar cells, Ag_2S is a potential replacement for commonly used TiO_2 due to its unique optical and electrical properties. It should be noted that, for the optimization of electron-selective layer, it is important to obtain high uniformity in low surface roughness (~ten nanometers) and film thickness, since electron-selective layer has an important influence on the PCEs of organic BHJ solar cells. So far, among several reported solution preparation technologies for Ag_2S nanoparticle films [22,23], chemical bath deposition (CBD) [24,25] and successive ionic layer absorption and reaction (SILAR) [22,26] are two widely used methods. Most attractive advantages of these two methods are low material cost, low preparation temperature and convenient for larger area deposition of thin films. However, both methods have their own disadvantages. For CBD method, it is difficult to achieve a full conformal coverage of quantum-dots layer onto the attached substrate. Moreover, the deposited QDs easily detach from the attached substrate after a certain amount of QDs are deposited. For SILAR method, it is not easy to deposit a sufficient amount of QDs, although a full conformal coverage of quantum-dots layer can be achieved. In particular, for these two methods, one common drawback is that the deposited QDs layer has a relatively large surface roughness (up to tens of nanometers), which does not accord with the requirement of low roughness of the electron-selective layer for efficient organic solar cells. Therefore, it is difficult to use low-temperature solution-based technique to directly deposit Ag_2S thin films with low surface roughness, high uniformity, and good adhesion on ITO substrates for organic solar cells. To overcome these disadvantages, we recently developed a novel method, i.e., high-speed rotating thermal decomposition (HRTD) method, for the preparation of inorganic nanoparticle films with high uniformity in low surface roughness and film thickness. This HRTD method can be carried at low temperature and therefore is a low cost and low-energy-consumption method. It is easy to control the deposition amount of inorganic nanoparticles by using HRTD method and the deposited nanoparticles do not easily detach from the attached substrate.

In the present work, we use newly developed HRTD method to successfully fabricate Ag_2S nanoparticle film that has good uniformity and low surface roughness (~ten nanometers) on ITO substrates. On one hand, the deposited Ag_2S thin films are used as electron-selective layers to replace high-temperature sintered TiO_2 dense layers in P3HT:PCBM solar cells. On the other hand, Ag_2S thin films can act as long wavelength absorption material, which forms the complementary absorption of light with P3HT. In particular, due to the formation of Ag_2S/P3HT bulk heterojunction, the Ag_2S can act as an electron-transport material in the active layers of the fabricated cells, which is similar to the case of PCBM. To our knowledge, there are few reports in which Ag_2S thin films are directly deposited on ITO substrates as an electron-selective layer, a light absorbing layer and an electron-transport material in Ag_2S/polymer solar cells. Schematic diagram and energy diagram of the fabricated ITO/$Ag_2S(n)$/P3HT:PCBM/MoO_3/Au solar cells are shown in Fig. 1. The structural, morphological, and optical properties of prepared Ag_2S nanoparticle films are studied and the influence of prepared Ag_2S nanoparticle films on the performance of P3HT:PCBM solar cells is

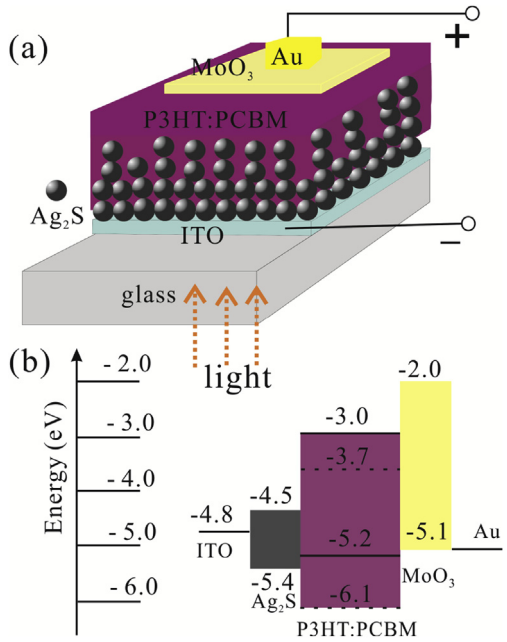

Fig. 1. (a) Schematic diagram and (b) energy diagram of the ITO/$Ag_2S(n)$/P3HT:PCBM/MoO_3/Au solar cells.

investigated. Under air Mass 1.5 Global (AM 1.5 G) illumination (100 mW cm^{-2}), the highest PCE of 3.21% of fabricated ITO/Ag_2S(50)/P3HT:PCBM/MoO_3/Au is much higher than that (2.84%) of prepared ITO/dense-TiO_2/P3HT:PCBM/MoO_3/Au, which shows the superiority of proposed HRTD method in terms of energy consumption during the manufacturing of solar cells. The more important thing is that this HRTD method may be used for the preparation of organic–inorganic hybrid solar cells and quantum dot-sensitized solar cells.

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$, 99%), silver acetate (AgOAc, 99%), thiourea (>99%) and sodium sulfide nonahydrate (Na_2S, 98.0%) were purchased from the Sigma–Aldrich. Poly (3-hexylthiophene) (P3HT, 95 + % regioregular, electronic grade) and [6,6]-phenyl-C61-butyric acid methyl esther (PCBM, 95 + %) were purchased from Luminescence Technology Co. All the reagents were used without further purification.

2.2. Formation of Ag_2S/ITO substrates

Ag_2S nanocrystals were synthesized through a HRTD method. Indium tin oxide coated glass slides (ITO, ≤15 Ω/square) were previously cleaned by successive sonication in deionized water, acetone, and isopropyl alcohol, then dried with nitrogen gas.

Firstly, $AgNO_3$ (0.5 mmol) and AgOAc (0.05 mmol) were dissolved in a mixture of ethanol (40 mL) and distilled (DI) water (10 mL). The mixture was then stirred for 40 min. Na_2S (0.25 mmol) and thiourea (0.01 mmol) were dissolved in a mixture of ethanol (40 mL) and distilled (DI) water (10 mL) and the mixtures were then stirred for 40 min. Secondly, the obtained $AgNO_3$ (and AgOAc) solution was spin cast onto the cleaned ITO substrates at 9000 rpm for 60 s. During the spin casting process, DI water and Na_2S (and thiourea) solution were sequentially dropped onto the substrates,