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Hierarchical $CuInS_2$ synthesized with the induction of histidine for polymer/$CuInS_2$ solar cells

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ABSTRACT

Hierarchical $CuInS_2$ (H-$CuInS_2$) was synthesized with the induction of histidine by the solverthermal method. The factors such as the category of the amino acid, the molar-quantity of histidine, the solvent, reaction time and reaction temperature were observed. The products were characterized by scanning electron microscope, X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy and ultraviolet-visible absorption spectrum. The results showed that, histidine is proven to be effect to synthesize the uniform flower-like chalcopyrite H-$CuInS_2$ in the solvent of N,N-dimethyl formamide at 180 °C for 24 h, which is originated from the strong coordinate ability of histidine. The change in the molar-quantity of histidine would result in the obviously different sizes and micro-structures of H-$CuInS_2$, contributing to the different light-harvesting ability and fluorescence quenching efficiency to poly (2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV). As a result, polymer solar cells with MEH-PPV and different H-$CuInS_2$ displayed structure-dependent device performances, device based on small-sized H-$CuInS_2$ obtained higher energy conversion efficiency of 0.59% under the monochromatic illumination of 15.85 mW/cm^2 with wide spectrum response from 300 to 900 nm.

1. Introduction

Chalcopyrite-based photovoltaic devices have become the focus in recent researches owe to their use in high efficient solar cells [1,2]. Copper indium disulfide ($CuInS_2$) is a material with small direct band gap of 1.5 eV, large absorption coefficient of 5×10^5 cm^{-1} and low toxicity, as a result, it is a promising material for solar cells [3–5]. Previously, it is used as light-absorbing materials to apply in the fabrication of thin solar cells [6–8], quantum dot-sensitized solar cells [9–11] and inorganic solar cells [12–17]. It could obtain the highest power conversion efficiency (PCE) up to 20% in the thin film solar cells [8]. However, the preparation of thin film solar cells demands high temperature process and high purity for the materials, resulting in the high cost. Hybrid polymer solar cells (HPSCs) consisting of polymer as the donor and inorganic nanoparticles as the acceptor are attractive owe to the integration of the advantages of inorganic materials in organic component. Therefore, the preparation of $CuInS_2$ nanoparticles receives much concern recently. Many methods such as solid state reaction [18], hot injection method [19], single-source precursor methods [20,21], solvothermal and hydrothermal routes [9,12,22–25], microwave assistant method [13,14,17,26] and ultrasonic assistant method [27,28] have been applied to fabricate various $CuInS_2$ nanostructures including nanoparticles [29,30], quantum dots [9], nanorods [22,24] and hollow nanospheres [31]. As to the HPSCs based on $CuInS_2$, it was reported previously that $CuInS_2$ in combination with poly(3,4-thylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) [32], Poly(3-hexylthiophene-2,5-diyl) (P3HT) [33–35] and poly(2-methoxy, 5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) [36–38] prepared bulk heterojunction solar cells, but the PCE is rather poor, which is far below 1%. Rath et al. synthesized $CuInS_2$ in a conductive polymer matrix without additional organic stabilizers to fabricate HPSCs, obtained PCE up to 2.8% [39]. However, it is difficult to control material morphology and structural property over device performance with the in-situ synthesis route.

It's well-known that the morphology of nanomaterials is one of the key factors that affect their properties. Three dimension (3D) micro/nanomaterials (namely hierarchical materials) which are assembled orderly from one or two nanoscale dimensions, they exhibits interesting properties such as the enhanced light absorption, facilitation of the exciton separation and carriers collection [40] which is originated from the presence of a large amounts of active sites and the combination of micro-nano scales to form unique multidimensional morphology [41].

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Therefore, hierarchical materials would be a candidate for effective solar cells. Previously, a bulk heterojunction photovoltaic device based on poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7- (2,1,3-benzothia-diazole)] (PCPDTBT) and CdSe tetrapods exhibits a PCE of ~ 3.2% [42], and the presence of tetrapods provides the electron a pathway to move away from the exciton dissociation site, contributing to the increased carrier lifetime [43]. Moreover, the use of hierarchical TiO_2 in HPSCs confirmed that it facilitates polymer infiltration and the intermixing of donor and acceptor phases for charge separation [44]. However, there are few reports on the HPSCs based on hierarchical $CuInS_2$ (H-$CuInS_2$) except our previous work, which applied 3D $CuInS_2$ in HPSCs for the first time and confirmed it is an effective electron acceptor for HPSCs in the future [40].

To fabricate HPSCs based on H-$CuInS_2$, it is no doubt that the synthesis of H-$CuInS_2$ is important. It's well known that the formation of hierarchical materials normally experiences three steps: the formation of nucleation seeds, growth of nanobuilding units, and the self-assembly of nanobuilding units in certain direction. Among these, the self-assembly of nanobuilding units is more important after the nucleation seeds formed, which needs ions releasing slowly to form the assembly along special orientation. Therefore, special templates are essential in the synthesis of hierarchical materials. Previously, flower-like CuS [45,46], micrometer-sized spinel $In_{3-x}S_4$ [47], In_2S_3 nanoplates [48] and flower-like In_2S_3 [40] were used as the template followed by the incorporation of the other element. But the synthesis procedure is complex, normally it needs two steps, which would lead to long reaction time and high energy cost. Another synthesis strategy is introducing special surfactant which coordinated with the metal ions to accomplish the self-assembly of nanobuilding units by releasing the metal ions slowly. Polyvinylpyrrolidone is the mostly used surfactant to synthesize H-$CuInS_2$ [49,50], however, the synthesized H-$CuInS_2$ is not uniform in size and morphology.

Biomolecules display unique self-assembling properties which make them as good templates for the synthesis of materials with designed structures [51,52]. Large amounts of biomolecules such as amino acids, protein, polysaccharide have been used to synthesize different functional materials recently. Among them, L-cysteine is a mostly common amino acid which was used to synthesize metal sulfide [53–57] because of the sulfydryl group existed in its molecule. Previously, Cai et al. synthesized H-$CuInS_2$ using L-cysteine as the sulfur source for the first time [58]. As another important amino acid, histidine containing an imidazole group displayed a strong coordinate ability with metal ions. As a result, it could capture metal ions from a solution [59] to form a complex and prevent nanoparticles further growth or agglomeration. Previously, ZnS nanocrystal [60], CdS quantum dots [61] and CdS quantum dots [62,63] were synthesized with histidine as a stabilizing agent. Moreover, as one of the essential amino acid for the infant, histidine owed the traits of non-poison and environment friendliness. Therefore, histidine may be an important coordinate reagent in the material synthesis in the future. However, there are few reports on the synthesis of $CuInS_2$ nanoparticles with the histidine assistant-synthesis method.

In this paper, we synthesized H-$CuInS_2$ with histidine assistant-synthesized method successfully, observing histidine molar-quantity-dependent $CuInS_2$ morphology. Moreover, HPSCs based on different H-$CuInS_2$ blending with MEH-PPV were fabricated, and the relation between H-$CuInS_2$ structure and device performance was studied. It's noted that, the polymer used in previous HPSCs based on $CuInS_2$ is normally P3HT because P3HT displayed well-crystallized, wide absorption range and high hole mobility [64]. However, its high crystallization would result in the poor polymer chain flexibility, contributing to the poor interface contact between polymer and inorganic [65]. Compared to it, MEH-PPV is amorphous polymer with more flexible polymer chain which is beneficial to the better interface contact with inorganic. As a result, MEH-PPV was used to prepare the device in this work.

2. Experimental

2.1. Chemicals

Copper chloride dihydrate ($CuCl_2{\cdot}2H_2O$, AR), indium chloride tetrahydrate ($InCl_3{\cdot}4H_2O$, AR), thiourea (AR), ethanol (AR) and chlorobenzene (CP) were obtained from the Sinopharm Chemical Reagent Co, Ltd. MEH-PPV (M_n = 40,000–70,000, Aldrich), Lithium fluoride (LiF) (Alfa-Aesar, 99.99%) and PEDOT:PSS (Clevios P HC V4, H. C. Starck) were purchased directly. Glycine, tyrosine, serine, tryptophan, histidine and aspartic acid are biochemical reagents, which were obtained from the Sinopharm Chemical Reagent Co, Ltd. All the chemicals except chlorobenzene were used directly, and the chlorobenzene was used after the distillation under reduced pressure.

2.2. Synthesis of H-$CuInS_2$

In a typical procedure, 1 mmol $CuCl_2{\cdot}2H_2O$ and 1 mmol $InCl_3{\cdot}4H_2O$ were dissolved in 80 mL solvent (DI water, glycol or N,N-dimethyl formamide) with vigorous stirring to form a homogeneous solution, then a certain amount (0–1 mmol) of different kinds of amino acid (glycine, tyrosine, serine, tryptophan, histidine, aspartic acid) was added to the solution, followed by 4 mmol thiourea adding to above solution and keep stirring continually for 10 min. Finally, the mixture was transferred into a 100 mL Teflon-lined stainless autoclave. The

Table 1
Schematic illustration of $CuInS_2$ synthesis and the corresponding results.

No.	Experimental process	Results
1	$CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ → 80 mL DMF → $CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ DMF → 0.5 mmol different amino acid → $CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ DMF amino acid → 4 mmol thiourea → $CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ DMF amino acid thiourea → transfer to autoclave → 180 °C for 24 h	Fig. 2
2	$CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ → 80 mL DMF → $CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ DMF → different molar quantity histidine → $CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ DMF histidine → 4 mmol thiourea → $CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ DMF histidine thiourea → transfer to autoclave → 180 °C for 24 h	Fig. 3
3	$CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ → 80 mL different solvent → $CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ solvent → 0.5 mmol histidine → $CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ solvent histidine → 4 mmol thiourea → $CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ solvent histidine thiourea → transfer to autoclave → 180 °C for 24 h	Fig. 4
4	$CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ → 80 mL DMF → $CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ DMF → 0.5 mmol histidine → $CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ DMF histidine → 4 mmol thiourea → $CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ DMF histidine thiourea → transfer to autoclave → different temperature for 24 h	Fig. 5
5	$CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ → 80 mL DMF → $CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ DMF → 0.5 mmol histidine → $CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ DMF histidine → 4 mmol thiourea → $CuCl_2{\cdot}2H_2O$ $InCl_3{\cdot}4H_2O$ DMF histidine thiourea → transfer to autoclave → 180°C for different time	Fig. 6