



## Enhanced efficiency in organic solar cells via in situ fabricated p-type copper sulfide as the hole transporting layer



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### ABSTRACT

In this article, we in situ fabricated copper sulfide (CuS) on fluorinated tin oxide (FTO) substrate using a low temperature and low cost hydrothermal method and then organic solar cells (OSCs) were fabricated by using a thin layer of CuS film as hole transporting layer (HTL). Our CuS films, consisting of two-dimensional (2D) intersected hexagonal nanosheets, are stoichiometric and show p-type electrical conductivity, a good transparency and a high hole mobility. The Fermi level, valence and conduction band energies for CuS HTL are characterized in detail through photoelectron spectroscopy studies. The small energy barrier between the valence band of CuS and the HOMO of poly(3-hexylthiophene) (P3HT) and the high hole mobility and electrical conductivity of CuS nanosheet film benefit for the hole transporting. Therefore, CuS HTL to OSCs results in a power conversion efficiency of 3.4% with P3HT and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as the active layer, which is a 13.3% increase in performance than devices with a poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) HTL. Therefore, low-cost, environmental friendly and stable CuS is an appropriate choice for hole transporting materials (HTMs) in OSCs.

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## 1. Introduction

One of the great challenges in the 21st century is undoubtedly energy conversion and storage. At present, organic solar cells (OSCs) have been the spotlight due to their advantages of light-weight, low-cost, easy-making and high-efficiency [1–4]. OSCs with a blend of regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as the active layer have been made and studied by many groups. Lots of scientists have made their contribution to facilitating cheaper and more efficient organic or inorganic energy materials used in photovoltaic devices [5–7] or aiming at commercialization of OSCs [8–10]. In conventional OSCs, poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS) [11] is usually used to modify the anode interface to improve the hole collection ability. But the commercial available PEDOT: PSS has a negative effect on the device stability due to its acidity and hygroscopic property [12]. In order to overcome the challenges caused by PEDOT: PSS, many

transparent metal oxides (TMOs), such as molybdenum oxide ( $\text{MoO}_x$ ) [13,14], nickel oxide ( $\text{NiO}_x$ ) [15], chromium oxide ( $\text{CrO}_x$ ) [16], tungsten oxide ( $\text{WO}_x$ ) [17] and vanadium oxide ( $\text{VO}_x$ ) [18], are selected to be the hole transporting materials (HTMs) instead of PEDOT: PSS. These TMOs are good choices for high-efficiency OSCs. However, toxicity of some materials (such as  $\text{NiO}_x$  and  $\text{VO}_x$ ) and shortage of supply (such as molybdenum and tungsten) are two main problems for OSCs application. Therefore, we need devote to developing earth-abundant, low-cost, nontoxic and environmentally-stable HTMs for highly efficient OSCs.

Two-dimensional (2D) materials such as graphene and  $\text{MoS}_2$  have attracted a lot of attention because of their exotic electronic properties and high specific surface areas. Apart from those intensively studied materials, recently, 2D metal chalcogenide materials have been successfully synthesized and have drawn much attention because of their great potential applications in energy conversion and storage [19,20]. Copper sulfide (CuS) is an important p-type semi-conductor and has a wide range of applications such as gas sensor [21], cathode materials for lithium-ion batteries [22], solar radiation absorbers and nonlinear optical materials [23–25]. Many groups have utilized different ways to get CuS nanomaterials, like spray pyrolysis, microwave heating

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[26,27], the hydrothermal method [28], chemical deposition [29], ion exchange reaction [30] and so on.

In this work, we have in situ fabricated 2D copper sulfide nanosheet using the hydrothermal method. Compared with other approaches, this hydrothermal method has several advantages: (1) the solvent is ethanol, which is non-toxic, low-cost, and environmental friendly; (2) the reactant metal copper film and sulfur powder are both inexpensive and easy to be prepared; (3) the process is facile and low-temperature. Then, we used thin layer of copper sulfide film as the hole transporting layer (HTL) for OSCs. Compared with other HTMs such as PEDOT: PSS and transition metal oxides, our CuS is easier to get and has a lower cost and a higher environmental stability. Most importantly, it possesses a higher hole mobility due to its 2D layered structure. We made photovoltaic devices and such solar cells yield an open-circuit voltage ( $V_{oc}$ ) of 0.55 V, a short-circuit current density ( $J_{sc}$ ) of 10.96 mA/cm<sup>2</sup>, a fill factor ( $FF$ ) of 56% and displayed a power conversion efficiency ( $PCE$ ) of 3.4%. An obvious improvement of photovoltaic performance has been proved after the insertion of CuS layer between the transparent electrode and the active layer.

## 2. Experimental details

### 2.1. Material

Copper target (99.99%) was bought from Beijing InnoChem. The polymer donor P3HT was bought from Rieke Metals and acceptor PC<sub>60</sub>BM was purchased from Nano-C. Baytron P VP Al 4083 PEDOT: PSS was obtained from H.C. Starck. Sulfur powder (99.99%) was purchased from Aladdin. All the materials were used without future purification.

### 2.2. Preparation of thin CuS films on FTO glass

Fluorinated tin oxide (FTO) coated glass with a sheet resistivity of 15 Ω/sq was used as the substrate. The substrates were firstly cleaned with aqueous detergent, and then were cleaned by ultrasonic agitation in deionized (DI) water, acetone and alcohol sequentially for 10 min each. Finally, the substrates were dried by N<sub>2</sub> gas and put into a temperature controlled drying oven for use. Copper films were prepared on FTO substrates by a radio frequency (RF) magnetron sputtering system using a metal copper (99.99% pure) target in Ar atmosphere. The base vacuum chamber was pumped down to a pressure below 10<sup>-4</sup> Pa. The Ar gas flow rate was retained at 12 standard-state cubic centimeter per minute (sccm). The deposition progress was carried on under a pressure of 1 Pa at 60 °C and RF power of 60 W. By controlling the sputtering time, we could achieve copper films of various thicknesses.

The FTO/Cu was placed in a 100 ml Teflon-lined autoclave immediately after the sputtering. Then, 0.03 g of sulfur powder and 70 ml of anhydrous ethanol were added separately into the autoclave. The temperature of the autoclave was maintained at 90 °C for 6 h. After it cooled down to room temperature (RT) naturally, the FTO with the product was taken out of the autoclave and washed with ethanol and DI water for several times. Finally, the FTO/CuS was dried in an oven at 60 °C for 3 h.

### 2.3. Fabrication of solar cells

The solution was prepared by dissolving 20 mg of P3HT and 20 mg of PCBM in 1 ml of chlorobenzene. The blend was heated to 40 °C with vigorous magnetic stirring for 24 h before use. For control devices, a layer of PEDOT: PSS was spin-coated on FTO substrates at 600 rpm for 10 s and then 2000 rpm for 30 s (about 40 nm) followed by annealed at 150 °C for 20 min. Subsequently,

the active layer was spin-coated from the solution onto CuS or PEDOT: PSS film at 500 rpm for 6 s and then 1000 rpm 20 s (thickness about 200 nm). And then the samples were put into the evaporator immediately. A 1.5 nm LiF and a 100 nm Al top electrode were thermally evaporated sequentially through a shadow mask under a pressure of about 10<sup>-4</sup> Pa. Finally, the fabricated devices were thermal annealed on a hot plate at 150 °C for 10 min in an argon-filled glove box. The active area of our device is 0.04 cm<sup>2</sup> defined by our shadow mask.

### 2.4. Materials and device characterization

The crystal structure of the CuS films was characterized by X-ray diffraction (XRD). Conventional XRD in Bragg–Brentano configuration has also been performed by the same Bruker D8 Advance diffract meter using Cu Kα radiation at 40 kV and 40 mA. Line traces were collected over 2θ values ranging from 20° to 80°. The transmittance of the films was measured by a UV–VIS–NIR spectrophotometer (CARY5000, Varian) in the 200–800 nm wavelength range at RT. Scanning electron microscopy (FEI XL-30), transmission electron microscopy (JEOL JEM 2010) were used to observe the morphology of the samples. The energy dispersive spectroscopy (EDS) measurement was made in a scanning electron microscope (FEI XL-30) equipped with an X-ray analyzer and an EDS spectrometer. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were performed using a XPS/UPS system (Thermo Scientific, ESCLAB 250Xi, USA). The compositions and chemical states of the CuS films were examined by XPS. Before been tested, samples were sputtering-cleaned, to remove atmospheric contamination in the XPS chamber for approximately 30 s, by the lower energy of Ar<sup>+</sup>, and the Ar<sup>+</sup> gun was operated at 0.5 kV, at a pressure of 1 × 10<sup>-7</sup> Pa. The vacuum pressure of the analysis chamber was better than 1 × 10<sup>-8</sup> Pa. The whole survey scan to identify the overall surface composition and chemical states were performed, using a monochromated Al Kα X-ray source (=1486.68 eV), detecting photoelectrons at a 150 eV pass energy and a channel width of 500 meV. The surface carbon signal at 284.6 eV was used as an internal standard. The work function and band energy position were calculated by UPS. UPS was carried out using Helium I<sub>α</sub> radiation from a discharge lamp operated at 90 W, a pass energy of 10 eV, and a channel width of 25 meV. A -9 V bias was applied to the samples, in order to separate the sample and analyze low-kinetic-energy cutoffs. The conductivity, carrier concentration and mobility were measured by a Hall effect measurement system (Lake Shore 7704A). The morphology of the active layer spin-casting on top of CuS was characterized by atomic force microscopy (AFM SPM-9500J3, Shimadzu, Japan). The current–voltage ( $J$ - $V$ ) curves of the devices were obtained using a computer-controlled Keithley 2400 Source Measure Unit and the device test was carried out in a glove box under illumination of AM 1.5G, 100 mW/cm<sup>2</sup> (The light intensity was calibrated using a Si photodiode) at RT using a solar simulator. The corresponding incident photo-current efficiency (IPCE) spectrum was measured with a QE/IPCE Measurement Kit system (Newport, USA).

## 3. Results and discussion

Fig. 1 shows the schematic diagram of the in situ growth of copper sulfide nanofilms on FTO coated glasses. At the early stage, the FTO substrate is covered by plenty of copper nanoparticles after the radio frequency (RF) sputtering. As the hydrothermal reaction proceeds, 2D sheet-like CuS nanoflakes form in-situ on the FTO glass. Copper nanoparticles react with excess sulfur powder and finally these intersected flakes form a whole layer of

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