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# Polymer solar cells with electrodeposited CuSCN nanowires as new efficient hole transporting layer



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## ABSTRACT

Here, we report for the first time that electrodeposited CuSCN nanowires (NWs) could be successfully used as a new hole transporting layer (HTL) in a conventional polymer solar cell (PSC) with a poly[*N*-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]:[6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PCDTBT:PC<sub>70</sub>BM) blend as an active layer. An efficient PSC with 5.1% power conversion efficiency for 28 mm<sup>2</sup> active surface area is fabricated. The performances of the PSCs prepared with electrodeposited CuSCN thin films and nanowires are compared and the obtained results clearly show that the nanostructuring of the HTL leads to an efficient hole extraction. The influence of the HTL thickness on the device performances was studied and it has been found that the thickness of the CuSCN nanowire array should not exceed the active layer thickness in order to keep high performances. An extraordinary high open circuit voltage (> 900 mV) and a fill factor about 60% were measured. It is shown that the electrodeposited CuSCN thin films and NWs could be directly used in the polymer solar cells without any subsequent annealing process, which is a crucial point for the reduction of the device costs.

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## 1. Introduction

The recent advances on bulk heterojunction (BHJ) polymer–fullerene solar cells led to achieve power conversion efficiencies (PCE) up to 9% for the new generation low-bandgap polymers [1]. The most widely used and investigated configuration is the conventional architecture of the polymer solar cell (PSC) where an organic poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) p-type interfacial layer is used for the efficient extraction of positive carriers at the anode. In this PSC, the PEDOT:PSS plays role not only of a hole transporting layer (HTL) but it also planarizes the ITO surface and increases its work function. Despite the wide utilisation of PEDOT:PSS, its electrical inhomogeneity [2] limits the electron blocking capability and its acidic nature produces chemical instability at the transparent conductive oxide/PEDOT:PSS interface [3]. To circumvent these problems, its replacement by a chemically inert inorganic p-type semiconducting material is actively investigated.

Until now, mainly oxide materials like V<sub>2</sub>O<sub>5</sub>, NiO<sub>x</sub>, WO<sub>3</sub> and MoO<sub>x</sub> have been proposed [4]. Despite the achieved excellent PCEs with NiO<sub>x</sub> [5], WO<sub>3</sub> [6] and MoO<sub>x</sub> [7], it is still challenging to discover and/or develop new inorganic p-type semiconductors as efficient hole transporting layers. One interesting inorganic compound exhibiting p-type conductivity is copper thiocyanate (CuSCN). The unique properties of β-CuSCN are related to its quasi-molecular structure [8]. In addition to its good transparency in the visible and near-infrared light spectrum range and a reasonable hole mobility (between 0.01 and 0.1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) [9,10], CuSCN possesses also a good chemical stability [11]. It is mainly used as solid hole-transporting electrolyte in dye-sensitized and extremely thin absorber solar cells [12–18]. In microelectronics CuSCN have been integrated in nanostructured vertical channelled transistors [19] and transparent thin film transistors [9,10]. In a recent Konarka's patent [20], Cu (I)-containing materials have been assigned as an unexpected discovery for the replacement of the acidic hole transporting PEDOT:PSS. In this patent no example of functional PSC is given. To our knowledge, till now, only once CuSCN was integrated in PSCs and an efficiency of 2.5% was achieved for a very small (4 mm<sup>2</sup>) active surface area [21]. After the discovery of an easy method for room-temperature template-free CuSCN nanowires (NWs) electrochemical

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deposition [22], we decided to integrate them in polymer solar cells. Here, for the first time an efficient conventional PSC (5.1% PCE for 28 mm<sup>2</sup> active surface area) based on electrodeposited copper thiocyanate nanowires HTL is reported. The advantages of the nanostructured CuSCN over a 2D layer (thin films) for the fabrication of PSCs with good performances are clearly demonstrated.

## 2. Experimental

### 2.1. Hole transporting layers preparation

Continuous CuSCN thin films are prepared at room temperature from a stable aqueous electrolyte containing triethanolamine as the copper(II) cations chelating agent [23]. CuSCN NWs are grown from an aqueous solution where the triethanolamine is replaced by ethylenediaminetetraacetic acid (EDTA) [22,24,25]. CuSCN electrodeposition is based on a two-step reaction, where in the first one Cu<sup>2+</sup> is reduced to Cu<sup>+</sup> (Eq. (1)) and in the second one CuSCN is formed by chemical precipitation of Cu<sup>+</sup> with SCN<sup>-</sup> (Eq. (2)) [21–23].



#### 2.1.1. CuSCN electrodeposition

Copper sulfate (CuSO<sub>4</sub>·5H<sub>2</sub>O, purity > 99.9%, Sigma-Aldrich), ethylenediaminetetraacetic acid (EDTA, purity ≥ 99.0%, Fluka), triethanolamine (TEA, purity ≥ 99%, Sigma-Aldrich) and potassium thiocyanate (KSCN, purity ≥ 99%, Sigma-Aldrich) were used for electrolytes preparation as received. For the electrodeposition of CuSCN nanowires, 12 mM CuSO<sub>4</sub>·5H<sub>2</sub>O, 12 mM EDTA and 3 mM KSCN were mixed into deionized water [22]. CuSCN 2D layers were deposited from an aqueous solution containing 12 mM CuSO<sub>4</sub>·5H<sub>2</sub>O, 120 mM triethanolamine and 60 mM KSCN, as described elsewhere [23]. CuSCN electrodeposition was carried out at room temperature in standard three-electrode electrochemical cell on glass substrate covered with ITO layer. The active surface area of the working electrode (glass/ITO, sheet resistance  $R=4 \Omega \text{ sq}^{-1}$ ) was 1.7 cm<sup>2</sup>. A helical platinum wire and a saturated calomel electrode (SCE,  $E=+0.24 \text{ V}$ . vs normal hydrogen electrode (NHE)) were employed as counter and reference electrode, respectively. CuSCN was potentiostatically deposited at fixed potential  $E=-0.4 \text{ V}$  vs SCE. The electrochemical deposition was performed on a potentiostat/galvanostat (Princeton Applied Research PAR-STAT 2273) monitored by the POWERSUITE software. To prepare CuSCN as thin film or nanowires different electrolytes were used (as described above).

#### 2.1.2. PEDOT:PSS preparation

For the reference device, a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) HTL was spin coated from an aqueous dispersion (Heraeus) and subsequently annealed at 140 °C for 10 min in air atmosphere.

### 2.2. Polymer solar cells preparation

Conventional polymeric photovoltaic devices were fabricated by the following steps. A blended solution of poly[*N*-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]:[6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PCDTBT:PC<sub>70</sub>BM, ratio 1:3.6 dissolved in *ortho*-dichlorobenzene) was spin-coated in a glove box at room temperature onto previously deposited HTL. The TiO<sub>x</sub> electron transporting layer (10 nm) was spin-coated and the stack was annealed on a hot plate at 70 °C for

10 min. Finally, aluminium cathodes (200 nm) were evaporated at a pressure of around 10<sup>-6</sup> mbar. The active area of the fabricated PSC was 28 mm<sup>2</sup>.

### 2.3. Characterization

Scanning electron microscopy (SEM, FEI Nova NanoSEM) was used for the surface morphology characterizations. X-ray diffraction (XRD) spectra of the films were recorded using an X-ray diffractometer (Philips PW-1710) and the Co, K $\alpha$ 1 radiation,  $\lambda=1.7889 \text{ \AA}$  wavelength. TEM characterization was done with a FEI Tecnai Osiris microscope at 200 kV, an objective aperture was inserted to select the transmitted beam and reveal the crystalline nature of the specimen. The optical transmission properties of the electrodeposited CuSCN layers were determined in the visible-near-infrared wavelength region using a Perkin Elmer Lambda 35 spectrophotometer. The work function of the electrodeposited CuSCN layers was measured in ambient conditions with a scanning Kelvin probe system (SKP, KP Technology LTD) using a gold surface as a reference. The thickness of the deposits was measured with a stylus-based surface profilometer (KLA-Tencor Alpha Step IQ) by setting the scan rate to 50  $\mu\text{m s}^{-1}$ . All the current density–voltage ( $J$ – $V$ ) measurements were performed in a glove box, under white light simulated illumination AM 1.5, 100 mW cm<sup>-2</sup>. Current–voltage characteristics and power conversion efficiencies were measured via a computer controlled Keithley<sup>®</sup> SMU 2400 unit. The XPS method used for chemical characterization can be found in the Appendix A, Supporting information.

## 3. Results and discussion

In Fig. 1a are shown SEM images of CuSCN thin film and nanowire array grown by electrochemical deposition on ITO-covered glass substrates. The electrodeposited CuSCN NWs exhibit hexagonal shape with a diameter around 80 nm, whereas the morphology of the electrodeposited thin films resembles small crystallites in rhombohedral form. The XRD analyses of these layers (Fig. 1b) reveal that they are crystallized in rhombohedral  $\beta$ -CuSCN phase with preferential growth perpendicular to the plane, which is more pronounced for the NWs. Both thin film and NWs exhibit very good crystalline quality, confirmed by the small full width at half maximum (FWHM) of the belonging diffraction peaks (Appendix A, Table S1). On the low magnification TEM image of a single CuSCN nanowire (Fig. 1c), one can clearly distinguish the lattice fringes. The close-up high resolution TEM (HRTEM) image shown in Fig. 1d indicates that CuSCN nanowires are almost mono-crystalline. This observation confirms that room temperature grown CuSCN NWs are of good crystalline quality. The stoichiometry of the electrodeposited CuSCN thin film and NWs was examined by X-ray photoelectron spectroscopy (XPS) (Appendix A, Fig. S1 and Table S2). The XPS results imply that the chemical composition of both layers is close to the stoichiometric CuSCN. The optical transmission of CuSCN NWs and thin films deposited on glass/ITO substrates is depicted in Fig. 1e. In the visible and near-infrared wavelength range, both layers exhibit the same transmittance (around 80%) as the glass/ITO substrate on which they are electrodeposited. By extrapolation of the  $(ah\nu)^2$  vs  $h\nu$  curve (Appendix A, Fig. S2), a 3.8 eV bandgap value ( $E_g$ ) of the CuSCN was determined, which is in excellent agreement with the literature values [23,26].

The polymer solar cell used in this study has the following architecture (Fig. 2a): glass covered with ITO layer as the transparent electrode, an electrodeposited CuSCN thin film or NWs with various thicknesses as the HTL, a solution-processed BHJ active layer of PCDTBT:PC<sub>70</sub>BM, a spin-coated TiO<sub>x</sub> electron transporting layer,

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